Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems

by

Timothy E. Long

Dissertation submitted to the Faculty of the Virginia
Polytechnic Institute and State University in
partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

Approved:

J. E. McGrath, Chairman

T. C. Ward

L. T. Taylor

H. W. Gibson

D. G. I. Kingston

October, 1987

Blacksburg, Virginia

Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems

by

Timothy E. Long

Committee Chairman: Dr. J. E. McGrath

Department of Chemistry

(ABSTRACT)

The anionic synthesis of alkyl methacrylates has received sparse attention in comparison to the synthesis of nonpolar hydrocarbon monomers such as styrene or the dienes. The two major reasons for the sluggish synthetic development of this class of polar monomers are the protic impurities present in most commercially available grades of monomer and the inherent side reactions associated with the ester functionality during anionic polymerization. However, by very carefully controlling various synthetic parameters and utilizing rigorously purified monomers, one can take advantage of the "living" nature of this polymerization to synthesize a variety of well-defined polymeric materials.

Small variations in polymerization conditions drastically affect the properties of the polymers obtained. However, the effects depend largely upon the size of the ester alkyl group involved. The subtle relationships among such variables as ester alkyl group size, polymerization temperature, polymerization solvent and initiator have been explored and are discussed. Extensive thermal, microstructural and mechanical characterization reveal very interesting effects on the resulting polymer properties.

Styrene-acrylic, acrylic-acrylic and diene-acrylic block copolymers have been synthesized demonstrating predictable molecular weights, narrow molecular weight distributions and controlled composition. These novel block copolymers also serve as excellent precursors for the preparation of acid- and ion- containing polymers. By selective hydrolysis of certain labile poly(alkyl methacrylate) esters and subsequent neutralization, metal carboxylates were introduced into a variety of block copolymers. In addition to the preparation of surfactant-like macromolecules and blend compatibilizers, novel ion-containing block copolymers were synthesized.

Dedication

The many hours of laboratory research and the preparation of this dissertation are dedicated to my father who taught me through his actions the definitions of hard work, perseverance, and courage.

ACKNOWLEDGMENTS

There have been many people who have contributed to my personal and scientific development in the past four years. I have always maintained that a problem is half-solved after discussing it with another colleague and successful research generally involves a group effort. Thus, I want to extend my deepest regards to all the members in the research group who have shared their insight and expertise with me especially Dr. , Dr. , Ms. and Dr. . I owe a particular word of thanks to Dr. for both stimulating technical discussions and helping me to prepare this manuscript. The members of Lab 120A were some of the best people that I have known and I hope our friendships persist in the years to come.

Many technicians have come and gone, but all are remembered for their sincere and concerted efforts. I especially want to thank Mrs. who is an excellent person and scientist. , , and contributed their skills in thermal analysis of various polymeric systems.

I was also quite fortunate to have had the opportunity to interact with and . I'm especially thankful for their patience during my transition period and participating in each "last experiment". I am confident that both these men will make significant contributions to the scientific community in the next three years to come.

I would like to acknowledge the financial support of Exxon ( ), Lithco ( ), Ethyl Corp. ( ) and Dow ( ). In addition, I feel quite fortunate to have received an IBM fellowship and have had the opportunity to visit their facilities for two weeks. Special thanks to who is a good friend and fellow scientist. played an integral role in my first year as a graduate student and I am greatly indebted.

I sincerely thank my advisor, Dr. James McGrath, for extending infinite opportunity to me. His enthusiasm often surpassed mine during research discussions. He is a wealth of knowledge and experience. Thank you Dr. McGrath for your patience, support, guidance and friendship. I also wish to acknowledge my other committee members-Dr. Ward, Dr. Gibson, Dr. Taylor and Dr. Kingston for their patience and advice during my four years.

Finally, there are a few special people that I wish to acknowledge. First, to my good friend and roommate who helped me in countless ways. Second, to and for their secretarial support and patience. Finally, to my family, , and other friends who made the holidays and the weekends at home nice.

TABLE OF CONTENTS

Page

LIST OF SCHEMES

LISTS OF TABLES

LIST OF FIGURES

I. INTRODUCTION

A. Research Objectives

The initial objective of this research project was to investigate the feasibility of incorporating alkyl methacrylate monomers into polymeric materials via anionic techniques. Anionic polymerization studies of polar monomers such as alkyl methacrylates have not received significant attention compared to nonpolar diene and styrene monomers. This fact can be attributed to inherent side reactions associated with the polar functionality during anionic polymerization and protic impurities present in most commercially available grades of monomer. Thus, the primary goals were to develop practical purification methodologies for all reagents and monomers and further define the various synthetic parameters in order to achieve "living" homopolymerizations. Such variables as polymerization temperature, polymerization solvent, monomer structure and initiator basicity were explored. The constraints of these variables were a function of the alkyl methacrylate monomer.

After developing the proper anionic techniques and establishing the polymerizability of various alkyl methacrylate monomers, the goals of the research project were aimed at the synthesis of block copolymers containing alkyl methacrylates. The utilization of a wide variety of comonomers including dienes, styrenes and other alkyl methacrylates was considered both fundamentally and industrially interesting. In most cases, the preparation of the block copolymer had remained previously unexplored or was addressed only briefly in the literature. This is attributed, in a similar fashion, to the reasons stated above for the anionic polymerization of alkyl methacrylate homopolymers. In addition to defining the polymer structure by classical techniques, it was desirable to investigate the thermal, mechanical, stereochemical and morphological characteristics of the various block copolymer systems.

The last important objective of the research project was to take advantage of the polymeric ester functionality in a variety of subsequent polymer modification reactions. Most importantly was the desire to introduce carboxylic acid groups in block-like sequences into a variety of the block copolymers. Thus, an investigation of the ease of hydrolysis of various poly(alkyl methacrylate) esters was necessary. In addition, it was desirable to develop the proper characterization techniques in order to comment on the structure-property relationships that resulted after modification. Metal carboxylates could also be introduced by neutralization of the acid groups with various bases. This reaction allowed for the preparation of novel, block ion-containing polymers. Interesting comparisons could be made to both random and one-unit (telechelic) ionomers described previously in the literature. It should be noted that the acid-containing block copolymer precursors behave very differently than the corresponding random systems.

B. Material Requirements

All homopolymers, block copolymers and derived block copolymers must possess narrow molecular weight distributions (1.05-1.35) and predictable molecular weights. These observations establish if the polymerization proceeded by a "living" or termination-free mechanism. In order to confidently assess structure-property relationships, it is necessary to prepare high molecular weight polymers (>30,000 g/mole). In all cases, molecular weights greater than 80,000 g/mole result in better film-forming properties. All chemical compositions must be uniform and predictable, based on monomer charges.

The homopolymer samples are particularly interesting from a fundamental viewpoint, but lack significant industrial interest and application. The preparation of block copolymers are more interesting in terms of potential material applications due to the contribution of physical properties from each constituent. The ultimate goal is to prepare surfactant-like macromolecules based upon a hydrocarbon block and a hydrophilic poly(methacrylic acid) block. These materials are interesting as oil additives due to their ability to disperse oil contaminants while remaining soluble in the hydrocarbon media. In addition, in either the acid or the neutralized ionic form, these block copolymers can be used as viscosity enhancement reagents in oil. This property increases the useful temperature range of oil and generally allows for higher use temperatures without reduction in viscosity. Consequently, the nature of the hydrocarbon block and the concentration of the acid block are interesting aspects to be studied.

It is also desirable to ascertain the minimum concentration of block carboxylates required to surpass the polymer properties of terminal, one-unit sulfonates. It has been shown by a variety of workers that sulfonate ionomers demonstrate better aggregation behavior than carboxylate ionomers. It is believed that by placing the carboxylates in blocks that phase separation or ionic aggregation will occur easier. Thermomechanical analysis of the block ionomers has shown the development of a rubbery plateau associated with ion clustering.

Finally, elastomeric materials containing ionic functionalities in block-like sequences has remained relatively unexplored. Thus, it was desirable to synthesize elastomers containing 2-20 mole percent of block metal carboxylates. A major portion of this effort was to prepare triblock poly(alkyl methacrylate-b-diene-b-alkyl methacrylate) precursors by employing a difunctional initiator. In addition to classical elastomers such as poly(butadiene) and poly(isoprene), the use of long ester alkyl methacrylates affords materials with glass transition temperatures below -20°C. These all-acrylic, ionomeric elastomers may have many advantages over poly(dienes) due to the absence of residual unsaturation.

The block copolymer precursors and derived acid/ion-containing polymers are also useful as compatibilizers in polymer blend applications. The acrylic-acrylic or diene-acrylic block copolymers can be utilized for eliminating the brittle nature of many acrylic coatings.

II. LITERATURE REVIEW

A. Alkyl Methacrylate Homopolymer Studies

1) Monomer Preparation and Characteristics

A wide variety of alkyl methacrylate monomers can be prepared due to the creative alteration of the ester alkyl group. This has lead to the synthesis of polymeric materials which possess very diverse physical properties. Thermoplastic, elastomeric and semi-crystalline polymers can be synthesized by utilizing this single class of polar monomers. Although alkyl methacrylates cost more than many other common monomers such as the dienes or styrenes, their enhanced stability characteristics, ease of handling, copolymerization ability and ultimate polymer performance justify the elevated cost. In 1982, the total production capacity of methyl methacrylate monomer in the U.S. was estimated at 576,000 tons/year and trends predict a steady increase [1].

In 1880, G. W. A. Kahlbaum prepared poly(methyl acrylate) for the first time and noted that depolymerization did not occur at temperatures exceeding 320°C [2]. The remarkable properties of acrylic polymers were first extensively reported in Otto Rohm's doctoral dissertation in 1901 and this report marks the beginning of the commercialization of acrylics. In 1909, Rohm and Otto Haas formed a German company which began the first limited production of acrylates in 1927 [3]. The subsequent development of methacrylates lagged behind the acrylates and methacrylate applications were limited to merely the hardening of acrylic polymers. The utility of poly(methyl methacrylate) as a glazing material was soon realized and research efforts were aimed at PMMA by the late 1930's. Poly(methyl methacrylate) currently is used in a variety of applications such as dental resins, safety glass, signs, surface coatings, adhesives, fixtures and contact lenses [4,5]. Trade names for poly(methyl methacrylate) include Plexiglass, Lucite and Perspex.

Most commercially available grades of alkyl methacrylate monomers except MMA contain 2-3 % of the esterifying alcohol. Although protic impurities are not deleterious in free radical polymerizations, their presence prohibits successful anionic and group transfer polymerization. All current synthetic routes for the monomers involve either esterification or transesterification with the alcohol which ultimately defines the ester alkyl. Consequently, the use of alkyl methacrylates as anionic monomers has been relatively limited and most commercial products are prepared using free radical initiators. In addition, academic research has been largely confined to free radical polymerization studies for the same reason.

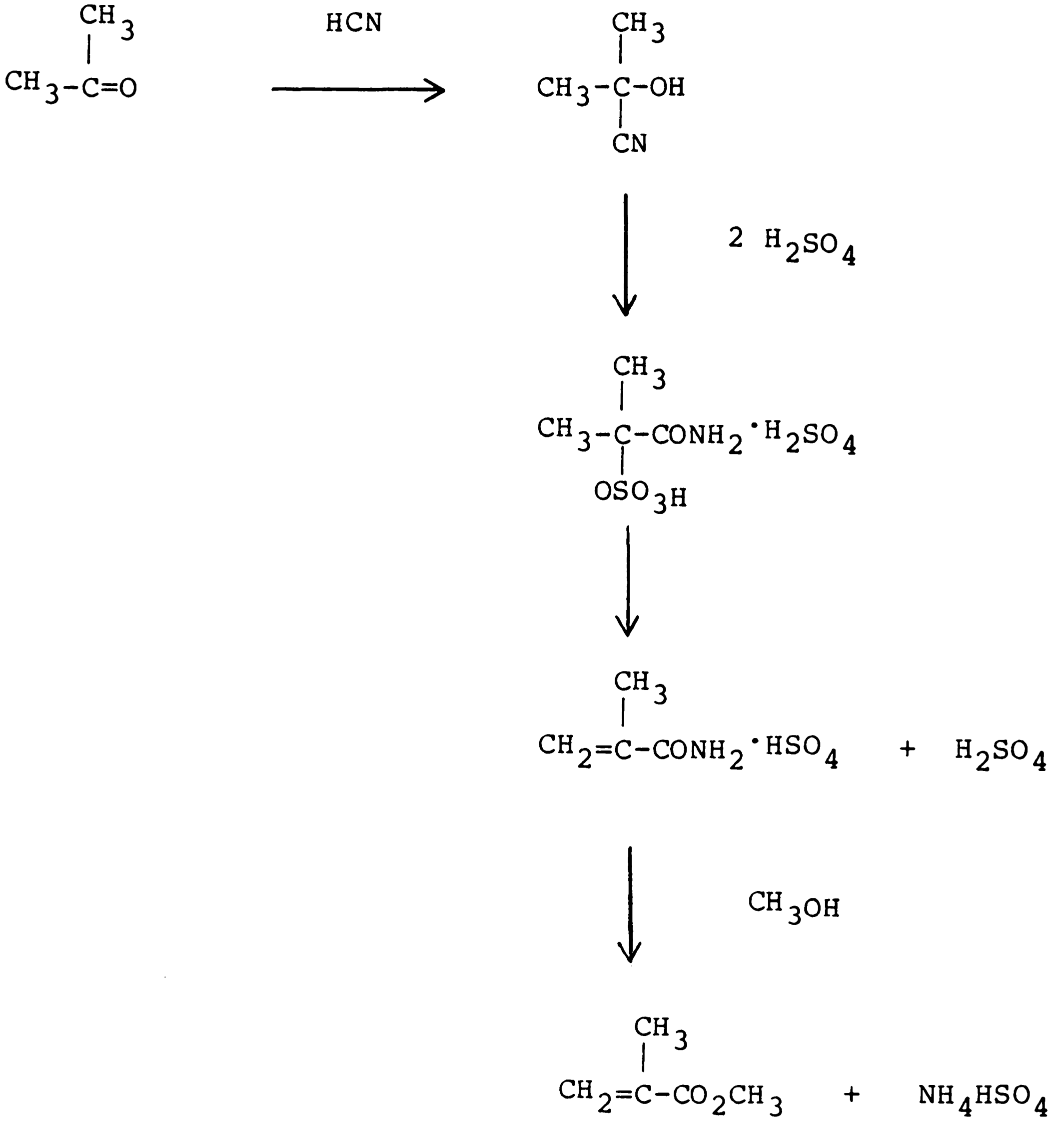
Two major synthetic routes have been employed for the preparation of the monomers. The most common alkyl methacrylate ester currently in production is methyl methacrylate and preparation involves the acetone cyanohydrin (ACN) process [6]. The monomer is prepared from acetone and hydrogen cyanide which forms 2-cyano-2-propanol. After treatment with 98% sulfuric acid, the propene-2-amide and sulfuric acid salt is formed. The salt is reacted with methanol to yield methyl methacrylate and ammonium bisulfate. The chemistry and reagents that are involved in the ACN process are depicted in Scheme I. The availability of inexpensive acetone is excellent; however, the future supply of hydrogen cyanide appears limited. Consequently, alternate routes are currently being considered to overcome the raw material limitations.

It is predicted that by 1990 the production of methyl methacrylate will be based on hydrocarbon oxidation processes [7]. The preparation of methacrylic acid is based on a two stage oxidation of isobutylene or t-butanol according to Scheme II. After isolation of the methacrylic acid product, the ester is formed by esterification with the desired alcohol. The current utilization of t-butanol for the production of methyl t-butyl ether as an octane booster may limit the availability of this feedstock. Thus, novel technologies are currently being developed to replace the necessity of the C_4 chemistry.

Dow Chemical has recently introduced two new acrylate

Scheme I

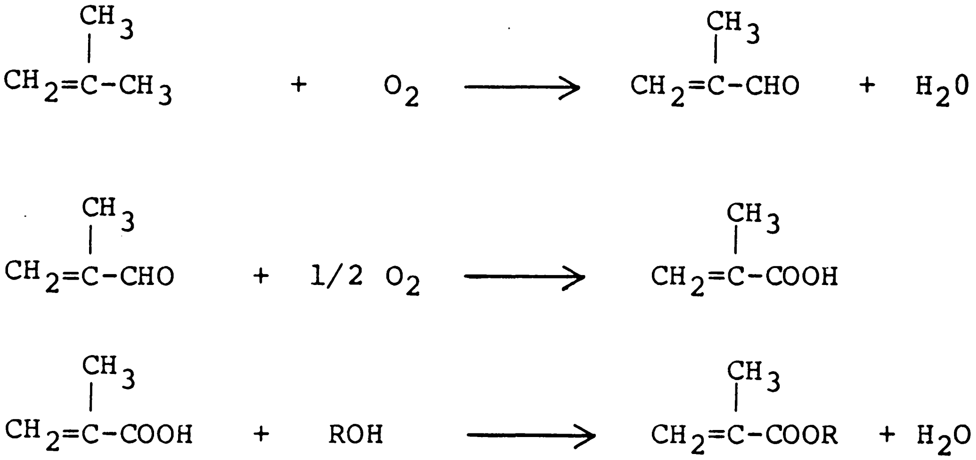
The ACN Process: Commercial Preparation of MMA [6]



* Alcohols are required in the final step

Scheme II

The Oxidation Process: Commercial Preparation of Alkyl Methacrylate Monomers [7]



$$\mathrm{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 \; + \; O_2 \longrightarrow CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CHO \; + \; H_2O}$$

$$\mathrm{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CHO \; + \; 1/2\ O_2 \longrightarrow CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOH}$$

$$\mathrm{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOH \; + \; ROH \longrightarrow CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOR \; + \; H_2O}$$

* Alcohols and carboxylic acids are required in the final step.

and methacrylate ester processes that derive from C_1 chemistry [8]. The first approach involves the use of organic carbonates as esterifying agents in carbonylations and acrylates are produced without the use of an alcohol. The second process yields acrylate esters after the generation of 2-halo-1-alkenes from hydrocarbon streams. The alkene is further treated with carbon monoxide, alcohol and a halogen accepter to form the appropriate methacrylate or acrylate ester. The preliminary results of the reevaluation of petrochemicals and feedstocks by Dow Chemical has been described in detail earlier [9].

Methyl methacrylate monomer can also be recovered from scrap or off-grade poly(methyl methacrylate) by simply heating (thermal cracking) at 300-320°C. The recovered monomer yield is >80%. This behavior is very unique to most poly(alkyl methacrylates). On the other hand, poly(acrylates) give a complex mixture when pyrolyzed at the same conditions [2].

The molecular weight, boiling point, refractive index and specific gravity are listed in Table 1 for a variety of commercially available alkyl methacrylate monomers [1]. The predicted increase in boiling point with molecular weight is evident. This observation is significant when considering purification by vacuum distillation. The longer ester alkyl methacrylate monomers are very difficult to distill and appreciable thermal polymerization can occur prior to

Table 1

Properties of Various Alkyl Methacrylate Monomers [1]

Compound	Mol. wt. g/mole	Bpt. °C (mm Hg)	Ref. Index	Density g/cm^3
Alkyl Methacrylates				
methyl	100.11	100	1.4120	0.939
ethyl	114.14	119	1.4116	0.909
isopropyl	128.17	125	1.4334	0.885
t-butyl	142.19	52(35)	1.4120	-
2-ethylhexyl	197	47(0.1)	1.4380	-
allyl	126	32(10)	1.4328	-
isodecyl	226	120(3)	1.4410	0.878
lauryl	262	272-343	1.444	0.868

distillation. Significant interest has been generated for the incorporation of long ester alkyl groups into multiphase polymeric systems. Thus, it would be desirable to develop a purification technique that did not involve distillation.

Inhibitors such as hydroquinone (HQ), butylated hydroxytoluene (BHT) or the monomethyl ether of hydroquinone (MEHQ) are present in alkyl methacrylates at concentrations less than 100 ppm. This low amount often eliminates the necessity of removal prior to free radical polymerization. Both HQ and MEHQ require the presence of oxygen to be effective inhibitors. Consequently, the monomers should be stored for long periods of time in air rather than in an inert atmosphere. It is recommended that inhibited alkyl methacrylate monomers are not stored for longer than one year. If the inhibitor has been removed, then it is recommended that the monomer be stored below 10°C for no longer than a few weeks. All alkyl methacrylate monomers should be treated as flammable chemicals especially methyl and ethyl methacrylates which have flash points below 27°C.

Liquid methyl and ethyl methacrylate have been shown to be moderately toxic when taken internally, contacted with the eyes or absorbed through the skin. Table 2 lists the toxicity of various common acrylic monomers which were determined in animals under severe conditions [10]. Methacrylic acid is more acutely toxic than the esters which do not contain reactive functional groups. Methyl

Table 2

Toxicity of Methacrylic Monomers [10]

Monomer	Acute oral toxicity in rats LD_{50}, g/kg
methyl methacrylate	7.9
ethyl methacrylate	13.5
n-butyl methacrylate	20.3
isodecyl methacrylate	>5.0

methacrylate is not carcinogenic at inhalation exposures of 400 ppm for two years in rats. Further studies have shown that methyl methacrylate is rapidly and extensively converted to carbon dioxide and methyl malonate in the human body. The longer ester alkyl methacrylate monomers are less volatile and the possibility of inhalation is diminished. However, it is strongly recommended that protective gloves, goggles and adequate ventilation be utilized at all times when handling all monomers.

2) Free Radical Polymerization Studies

Free radical polymerization of alkyl methacrylates involves the three fundamental kinetic steps of chain polymerization: initiation, propagation and termination. Initiators for methacrylates include both peroxides and azo compounds. Table 3 depicts various initiators that were tested as initiators of methyl methacrylate polymerizations [11]. The generation of the initiator radicals and the subsequent addition reaction are depicted in Scheme III. Termination occurs by chain transfer, disproportionation and combination. The termination mechanisms involved in the radical polymerization of methyl methacrylate and their effects on the ultimate polymer performance have been recently studied in detail by a variety of workers [12-14]. The polymerization of alkyl methacrylates can be accomplished by bulk, suspension, solution or emulsion techniques. The bulk and, to a lesser extent, suspension

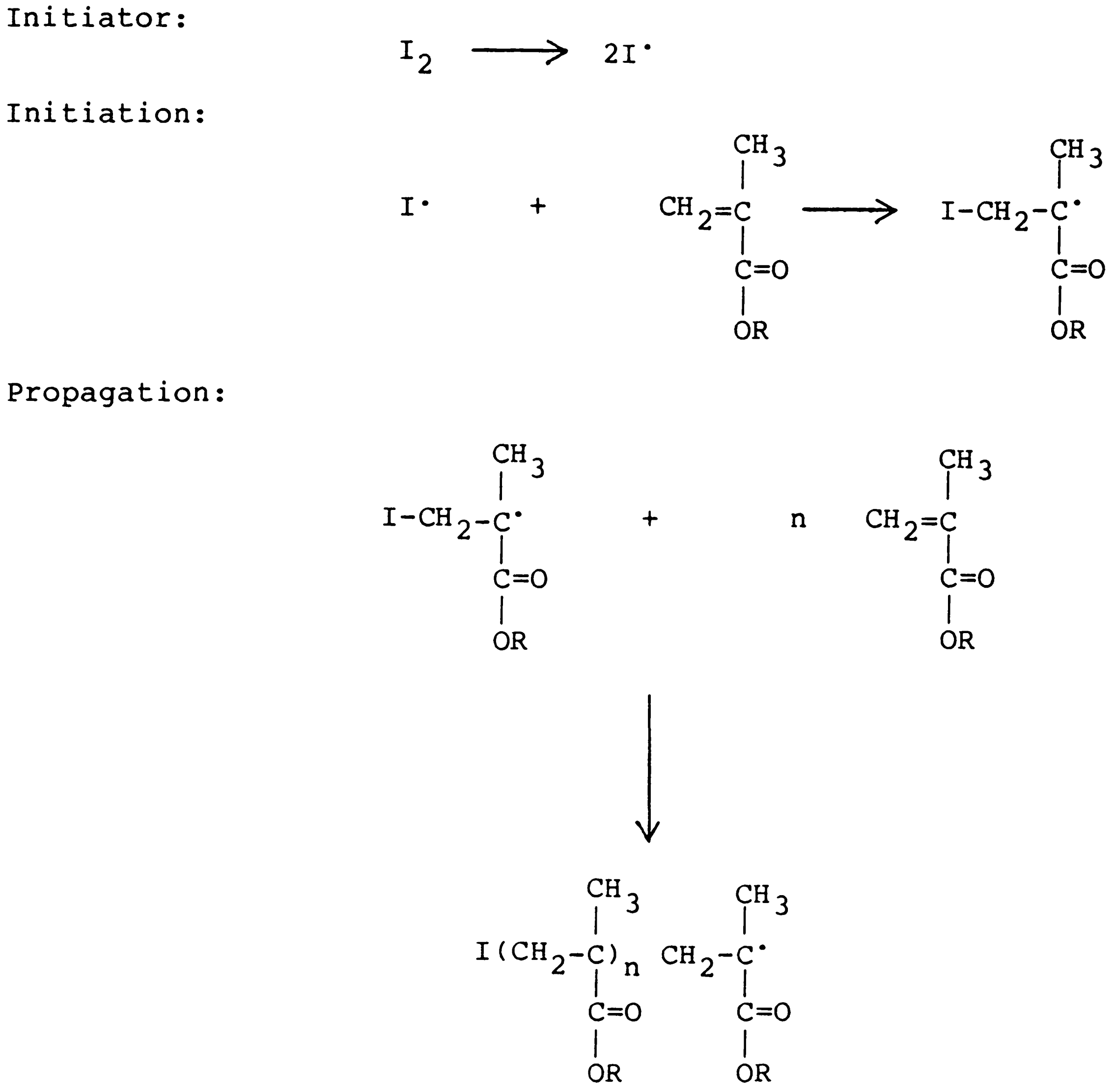
Table 3

Free radical Initiators for Methyl Methacrylate [11]

Initiator	Purity	Trade Name	Molecular Weight	10-hr half-life temp., °C
Lauroyl peroxide	98	LYP-97F	398.6	62
Azo bis-isobutyronitrile	98	Vazo-64	164.0	64
2,2-azo bis(2,4-dimethyl valeronitrile	98	Vazo-52	248.4	52
Cumyl peroxy neodecanoate	75	Esperox 939M	306.4	37.5

Scheme III

Radical Initiation and Propagation of Methyl Methacrylate



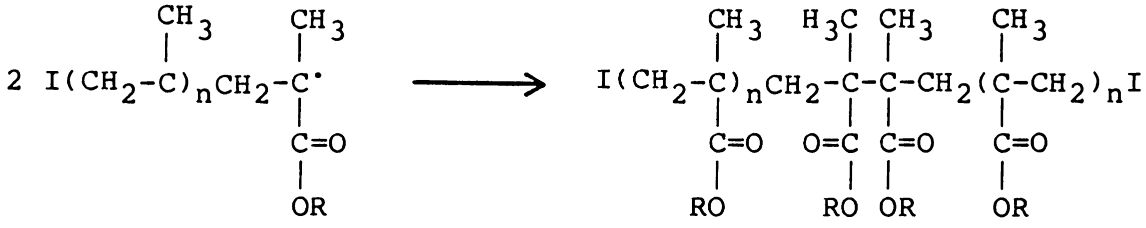
polymerizations are the most commercially important methods for the radical polymerization of alkyl methacrylates.

Free radical polymerizations of alkyl methacrylates generally terminate by a disproportionation mechanism rather than combination. This has been attributed to the steric bulk of the propagating radical due to the α-methyl and ester functionalities. Scheme IV depicts both mechanisms of termination and the nature of the resulting polymer chain end. Disproportionation results in equal amounts of the oxidation and reduction product i.e. the unsaturated chain end and the saturated chain end respectively. Combination of two propagating radicals leads to a head-to-head linkage (H-H) rather than a head-to-tail linkage (H-T). Since degradation of alkyl methacrylates proceeds by an unzipping mechanism which begins at the chain end, the nature of the chain end will define the thermal stability. Recently, Solomon et al. synthesized a series of low molecular weight poly(methyl methacrylate) model compounds which resembled each chain end [15]. Oligomers containing H-H linkages degrade first at temperatures near 190°C. In comparison, oligomers containing the unsaturated chain ends degrade at 255°C and the saturated chain ends are stable until 300°C. Although the unzipping is a three stage process, the critical temperature (Tc) is often quoted as a single value near 165°C. This study helped to define the termination mechanisms involved in the polymerization and illustrate

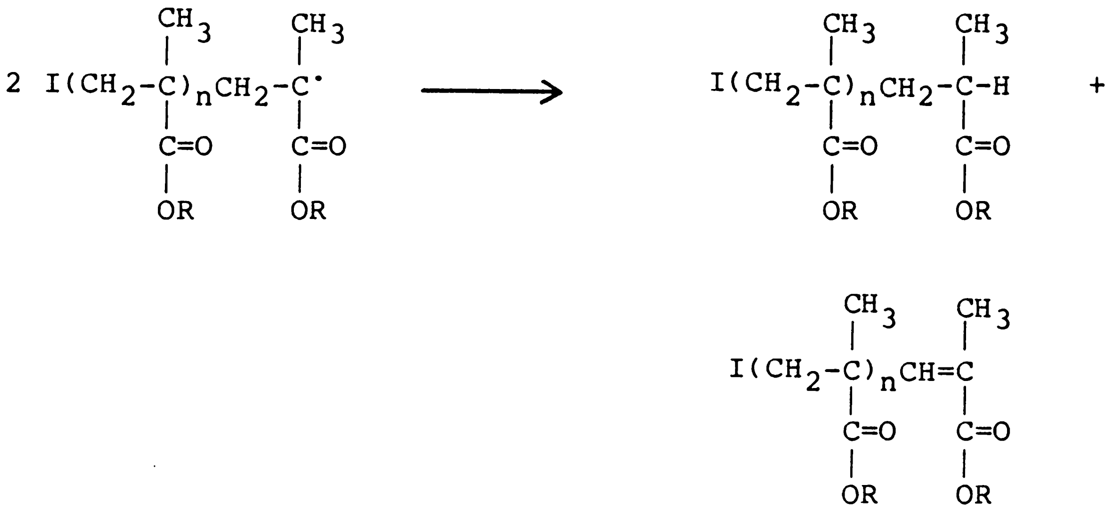
Scheme IV.

Free Radical Termination Mechanisms of Alkyl Methacrylates

Combination:



Disproportionation:



their effects on the polymer thermal stability. In addition, it was demonstrated that thermal analysis could indicate the presence of thermally labile groups in poly(alkyl methacrylates). Thus, this technique could be used to confirm the absence of termination mechanisms in a living polymerization. In fact, a polymer obtained by a living polymerization technique would contain only head-to-tail linkages and should be stable to 300°C. Hatada et al. have recently investigated the role of polymer tacticity, molecular weight, initiator and test atmosphere [16]. Their results substantiated those found by Solomon. Possible mechanisms for end initiation and oxidative termination of radicals initiated from scission at the head-to-head linkages were given. There was also no difference in the thermal or oxidative stability of the polymers that were initiated with either azo or peroxide initiators.

The thermal stability of poly(methyl methacrylate) blends with other polymers has also been studied [17]. This study attempted to investigate the roles of polymer miscibility and chemical interactions on the thermal stability of each constituent. Enhanced PMMA stability when blended with poly(ethylene oxide) was attributed to a certain degree of compatibility. However, the authors were hesitant to use the activation energy for decomposition to determine compatibility. This work further exemplified the utility of thermal analysis for the elucidation of the thermal stability of poly(alkyl methacrylates).

The fact that termination mechanisms are concurrently occurring during polymerization prohibits the opportunity to prepare block copolymers by sequential addition of monomers. Molecular weight versus conversion is not a linear relationship. In fact, high molecular weight is obtained very rapidly. Typical molecular weight distributions of the resulting polymers range from 1.5 to 2.0. The limitations of free radical techniques are well appreciated and the preparation of well defined polymeric systems via free radical polymerization is quite difficult. Creative approaches to prepare block copolymers and functionally terminate polymer chains in order to circumvent these limitations will be described in detail later.

3) Characterization of Free Radically Prepared Polymers

An abundance of literature exists on the various characterization techniques which have been applied to poly(alkyl methacrylates). This class of polymers are widely studied for two reasons. First, the polymers are easily synthesized by free radical techniques. Second, the physical properties can be varied over a wide spectrum while remaining in the same class of monomer.

A pseudochiral carbon is present in poly(alkyl methacrylates) at the quaternary carbon position in the polymer backbone. The prefix "pseudo" is used because two of the four different groups on the carbon are the polymer backbone of different lengths. The other two remaining groups are the α-methyl and the ester functionality. Significant efforts have been directed recently to further define the stereochemical sequences by spectroscopic techniques [18-20]. As NMR frequencies increase, the ability to define longer sequences exists. In fact, heptad sequences are currently being reported by Ovenall and Ferguson [21]. The determination of polymerization statistics based on sequence distribution has been appreciated since the late 1950's [22].

The stereochemistry or tactic composition plays a significant role in determining polymer properties, especially the glass transition temperature. In most cases, higher percentages of random or heterotactic sequences are obtained in free radical polymerizations of acrylic monomers [23-24]. The polymers are generally 55-60% syndiotactic and 35-35% heterotactic. Strictly speaking, the polymers are not truly random since less than 50% of the sequences are heterotactic. The remaining sequences are isotactic. However, very bulky ester alkyl methacrylates such as trityl methacrylate often form highly isotactic polymers when polymerized with azo initiators at 60°C. Since the free radically prepared polymer contains a major percentage of syndiotactic sequences, the glass transition temperature is often similar to the stereoregular, syndiotactic polymer. In 1968, Karasz and MacKnight published an early discussion of the role of stereoregularity on the glass transition temperatures of vinyl polymers [25]. Although this report is comprehensive concerning the role of the substituent, recent synthetic developments in stereoregular synthesis will accent their early findings. Table 4 lists the glass transition temperature for a variety of poly(alkyl methacrylates) that were all prepared by free radical polymerization [26]. It is evident that the size of the ester alkyl group strongly influences the position of the glass transition temperature. This table also illustrates the breadth of thermal properties that are obtainable with poly(alkyl methacrylates).

Table 5 lists the corresponding poly(acrylates) and the glass transition temperatures [27]. The significantly lower Tg for the poly(acrylate) is due to the absence of the pendant methyl group on the polymer backbone. Thus, the backbone requires less thermal energy to undergo segmental motion.

Recent attempts to obtain stereoregular poly(alkyl methacrylates) by free radical techniques have appeared in the literature [28]. These efforts have been focused on polymerizing a monomer in the presence of a preformed stereoregular polymer. Despite earlier reports by Challa et al. [29], insignificant changes in the final tactic

Table 4

Physical Properties of Conventional Poly(alkyl methacrylates)[26]

Homopolymer	Tg (°C)	Density (at 20°C) g/cm^3	Solubility parameter (cal/cm^3)$^{1/2}$	Refractive index n20,D
poly(alkyl methacrylates)				
methyl	105	1.190	9.07	1.490
ethyl	65	1.119	8.93	1.485
isopropyl	81	1.033	-	1.552
t-butyl	107	1.022	8.29	1.4638
2-ethylhexyl	-10	-	-	-
n-decyl	-60	-	-	-

Table 5

Glass Transition Temperatures of Poly(alkyl acrylates) [26]

Homopolymer	Tg (°C)
poly(alkyl acrylate)	
methyl	6
ethyl	-21
butyl	-55
2-ethylhexyl	-85

composition were noted.

In addition to demonstrating the role of the ester alkyl group for determining the Tg, Table 4 also lists the densities, refractive indices and solubility parameters for the same alkyl methacrylate homopolymers. Special attention should be given to the solubility parameters because the values will be useful for predicting phase separation behavior in block copolymers. The solubility parameter is also useful for determining appropriate solvents. The smaller the difference between the solubility parameters of the polymer and the solvent leads to better solubility. Table 6 depicts the solubility of various poly(alkyl methacrylates) in several different solvents [30]. Many recent efforts have been directed toward the understanding of solubility and solution behavior of alkyl methacrylate homopolymers [31-35]. In addition, radii of gyration and characteristic ratios for PMMA of various stereochemistries have been determined by different scattering techniques [36,37].

There has not been significant attention devoted to the effects of polymer structure and tacticity on the mechanical response of poly(alkyl methacrylate) homopolymers [38-40]. This observation is particularly true for homopolymers that have similar molecular weights and narrow molecular weight distributions. Due to the wide range of accessible monomers, one can select the glass transition temperature

Table 6

Solubility of Poly(alkyl methacrylates in Various Solvents [30]

Solvent	CH_3	C_2H_5	iso-C_3H_7	t-C_4H_9
3-Heptanone	I	S	S	S
Methanol	I	I	I	Sw
Ethanol	I	Sw	S	S
Ethyl Acetate	S	S	S	S
Diethyl Ether	I	S	S	S
Hexane	I	I	I	Sw
Acetic Acid	S	S	S	S
Formic Acid	S	Sw	I	I
Dimethylformamide	S	S	S	S

Polymerization Condition: $LiAlH_4$-Et_2O catalyst, -70°C, S, soluble; I, insoluble; Sw, swelling; 0.1g per 10 ml, 24 hours.

and corresponding mechanical properties that are necessary for a particular application. In addition, copolymerization of rubbery and rigid polymers provides the capability to "dial-in" the desired physical properties. Table 7 demonstrates the tensile strength and elongation at break for various homopolymers [41]. As the ester alkyl group is increased, the elongation at break increases and the tensile strength decreases. This is explainable by noting the difference in the glass transition temperature relative to ambient test temperatures. Longer, linear ester alkyl groups will lead to crystallization and the polymers become more brittle. In 1948, this was reported to occur for poly(octyl methacrylate) homopolymers [42]. Consequently, many branched, long ester alkyl methacrylate homopolymers such as poly(2-ethylhexyl methacrylate) are quite interesting as rubbery, noncrystalline materials.

In addition to the monomer being quite hydrophilic, most poly(alkyl methacrylates) can absorb 2-3 mass percent of water [43,44]. This phenomenon drastically affects both the dynamic and mechanical response and a water-induced transition can be observed between -100 and -80°C [45,46]. The sorption of various gases such as carbon dioxide and ethylene in poly(methyl methacrylate) has also been recently investigated [47]. However, a systematic study of the effects of ester alkyl group and polymer tacticity on gas permeability has not been found in the literature.

Table 7

Mechanical Properties of Various Poly(alkyl methacrylates) [41]

Homopolymer	Tensile strength (MPa)[b]	Elongation at break (%)
Poly(alkyl methacrylate)		
methyl	62	4
ethyl	34	7
n-butyl	6.9	230

[b] To convert MPa to psi, multiply by 145.

Poly(methyl methacrylate) is used in a variety of applications due to the many desirable physical properties. In addition to the chemical inertness of the polymeric ester to hydrolysis, the polymer is quite stable in outdoor environments for long times. Table 8 compares the outdoor stability of PMMA to other widely used polymeric materials such as polycarbonates [48]. As one can observe, neither the haze or the percent light transmittance change after 3 years of outdoor exposure. Long-chain methacrylates are also used as additives to improve the performance of lubricating oils and hydraulic fluids. The long ester alkyl group is required to impart hydrocarbon solubility. The homopolymers or copolymers add insignificant viscosity to oil at lower temperatures, but at higher temperatures the viscosity is increased. Oils that have constant and controlled properties are obtainable by controlling both the composition and the molecular weight of the polymeric additive [49].

4) Living Polymerization Studies of Alkyl Methacrylates

The anionic synthesis of poly(alkyl methacrylates) has received less attention compared to free radical polymerization studies. This has been attributed mainly to the inherent side reactions associated with the carbonyl during anionic polymerization. In addition, the presence of protic impurities in most commercially available grades of monomer prohibits termination-free polymerization. This

Table 8

Relative Outdoor Stability of PMMA [48]

Material	Initial light transm. %	Light transmittence after 3 yr. outdoor exposure %	Initial haze %	Haze after 3 yr outdoor exposure %
Poly(methyl methacrylate)	92	92	1	2
Bis-A Polycarbonate	85	82	3	19
Cellulose acetate butyrate	89	68	3	70

latter factor has been less appreciated, but is certainly an important consideration. However, in the absence of termination mechanisms, the polymerization is termed "living" and the molecular weight of the propagating polymer increases linearly with conversion. This behavior is contrasted to the nonlinear behavior described earlier for radical chain polymerizations. The advantages of anionic polymerization include: predictable molecular weight, narrow molecular weight distribution, controlled stereochemistry, functional termination capability and block copolymer synthesis. In order to take advantage of these capabilities, the reaction conditions must be properly defined. However, the synthetic conditions are largely a function of the nature of the ester alkyl group in the alkyl methacrylate monomer.

A wide variety of basic initiators have been utilized for the anionic polymerization of alkyl methacrylates. The initiator must be sufficiently basic to form the enolate-like propagating species and nonnucleophilic in order to avoid reaction with the carbonyl of the monomer. The use of alkyllithium initiators such as n-butyllithium or sec-butyllithium leads to significant attack on the carbonyl of the monomer [50-52]. Consequently, a major percentage of the initiator is consumed and the resulting molecular weight is low. This realization has lead to the development of sterically hindered bases as more efficient initiators for anionic polymerization. Initiators such as diphenylmethyl sodium (or potassium) [53], diphenylhexyl lithium [54] and cumyl cesium [55] are routinely seen in the recent literature. In many instances, these initiators are prepared by reacting the unsaturated compound with the appropriate metal and the initiator solution is decanted. The selection of the cation is dictated by the selection of the metal. However, diphenylhexyl lithium can be prepared insitu in the polymerization vessel by reacting 1,1-diphenylethylene with alkyllithiums. Wenger had shown in 1959 that PMMA-Li remained living for 40 hours in tetrahydrofuran at -78°C [56]. Goode's assessment was based on the observation that monomer could be added after 40 hours and polymerization continued. These two observations have made the use of diphenylhexyl lithium very wide spread.

Group II metal initiators such as Grignard reagents have also received much attention, but, in most cases, the mechanisms are complex and not well understood. In addition, the preparation of the reagent is often quite tedious, irreproducible, and in limited yield. Many papers have been reported on the polymerization of alkyl methacrylates by organomagnesium compounds. Goode [57] and Nishioka [58] both utilized Grignard reagents to polymerize methyl methacrylate in 1960. These attempts represent some of the first efforts to polymerize methyl methacrylate by an anionic mechanism. Recent review articles have described the organomagnesium compounds in detail and the postulated mechanisms were discussed [59,60,24]. Hatada et al. have published many papers recently describing living polymerizations of methyl methacrylate using t-butylmagnesium bromide [61,62]. Purely (100%) isotactic polymers could be prepared with narrow molecular weight distributions. In addition, Hatada describes the use of a totally deuterated monomer technique in order to define the polymerization mechanisms [63].

Alkali metal alkoxide can initiate only the oligomerization of methyl methacrylate in the presence of methanol [64]. However, the anionic initiation can be enhanced by increasing the solvent polarity and high molecular weight can be obtained. Methanol will lead to the broadening of the molecular weight distribution and decreased yields. Müller et al. have more recently shown that methoxide is able to initiate polymerization of MMA in THF [65]. This was not the case when initiation was attempted in nonpolar solvents. Lithium t-butoxide or 1,1-dimethylbutoxide have been shown to yield high molecular weight PMMA in both polar and nonpolar solvents. The polymers prepared in toluene were highly isotactic [66]. Alkali metal alkyl initiators have been demonstrated to be superior to alkali metal alkoxides because the rate of initiation of the latter is significantly lower. Thus, if both alkoxide and alkyl are present in a polymerization, the alkyllithium will initiate the alkyl methacrylate first. The only time the alkoxide will initiate in this situation is when all the alkyl lithium initiated anions are terminated and residual monomer is still present. This observation is significant if one is concerned if the alkyl lithium initiator contains alkoxide impurities. As will be discussed later, alkoxide can be generated during polymerization due to side reactions at the ester carbonyl. The final criterion for an anionic initiator for all monomers is that the rates of initiation must be faster than the rate of propagation. This situation leads to narrow molecular weight distributions.

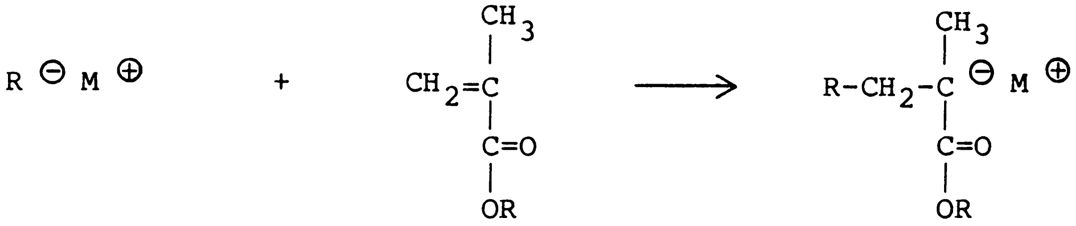
Scheme V depicts the initiation and propagation of alkyl methacrylates in the absence of termination mechanisms. Intentional termination is accomplished by adding a protonic source such as an alcohol to the reaction. The propagation is far more complex in the case of a polar monomer because the polar substituent in the polymer can intramolecularly complex with the propagating anion. One interpretation is that the ion pair can be intramolecularly complexed with the ester carbonyl of either the penultimate or antepenultimate as depicted in Figure 1 [67,68].

A major limitation of the anionic polymerization of polar monomers is that the propagating anion can undergo side reactions with the monomeric and/or polymeric ester carbonyl. There are three main termination mechanisms that

Scheme V

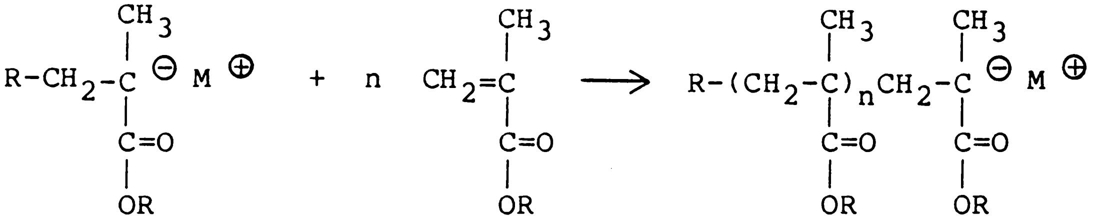
Anionic Initiation and Propagation of Alkyl Methacrylates

Initiation:

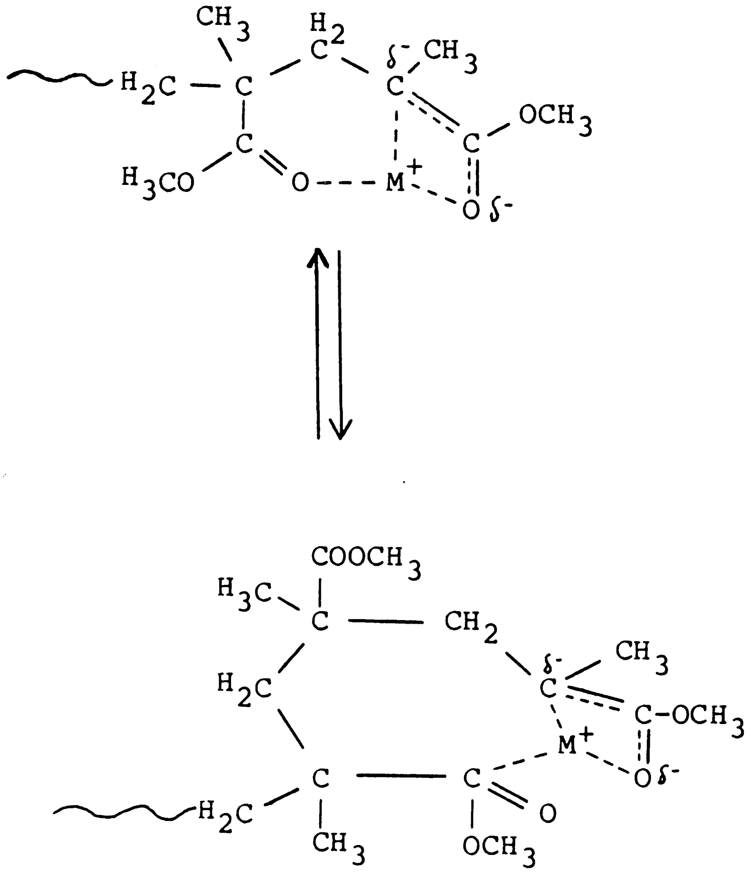


$$R^{\ominus}M^{\oplus} + CH_2{=}C(CH_3)(C{=}O)(OR) \longrightarrow R{-}CH_2{-}C(CH_3)(C{=}O)(OR)^{\ominus}M^{\oplus}$$

Propagation:



$$R{-}CH_2{-}C(CH_3)(C{=}O)(OR)^{\ominus}M^{\oplus} + n\ CH_2{=}C(CH_3)(C{=}O)(OR) \longrightarrow R{-}(CH_2{-}C(CH_3)(C{=}O)(OR))_nCH_2{-}C(CH_3)(C{=}O)(OR)^{\ominus}M^{\oplus}$$



$M^{\oplus}$: $Na^{\oplus}$ or $Cs^{\oplus}$

Figure 1: Intramolecular Complexation During Anionic Polymerization of Alkyl Methacrylates [67,68]

can occur during polymerization assuming that the initiator has not attacked the monomer first to form a vinyl ketone monomer. Figure 2 illustrates the three mechanisms i.e. monomer termination, intermolecular polymer termination and intramolecular termination (backbiting) [69,70]. In each case, alkoxide is the reaction product. Hatada et al. [70] has also investigated the reaction of an unhindered initiator such as n-butyl lithium with monomer to form the vinyl ketone. The vinyl ketone can subsequently add to the propagating ester enolate; however, addition of more alkyl methacrylate to the ketone anion chain end is slow. Consequently, many chain ends are terminated with the ketone linkage. Despite the increased occurrence of these termination reactions as the temperature is increased, many workers continue to polymerize methyl methacrylate at >-50°C.

Alkyl acrylates cannot be polymerized in a controlled fashion by the anionic techniques described above for alkyl methacrylates. This has been attributed to both the acidic α-hydrogen on the polymer backbone and the side reactions associated with the ester carbonyl. Many unsuccessful attempts have been made to circumvent these problems [71]. Recently Teyssie et al. have described the successful anionic polymerization of t-butyl acrylate [72]. The t-butyl ester was chosen in an attempt to minimize reactions at the ester carbonyl. The polymerizations were modified by

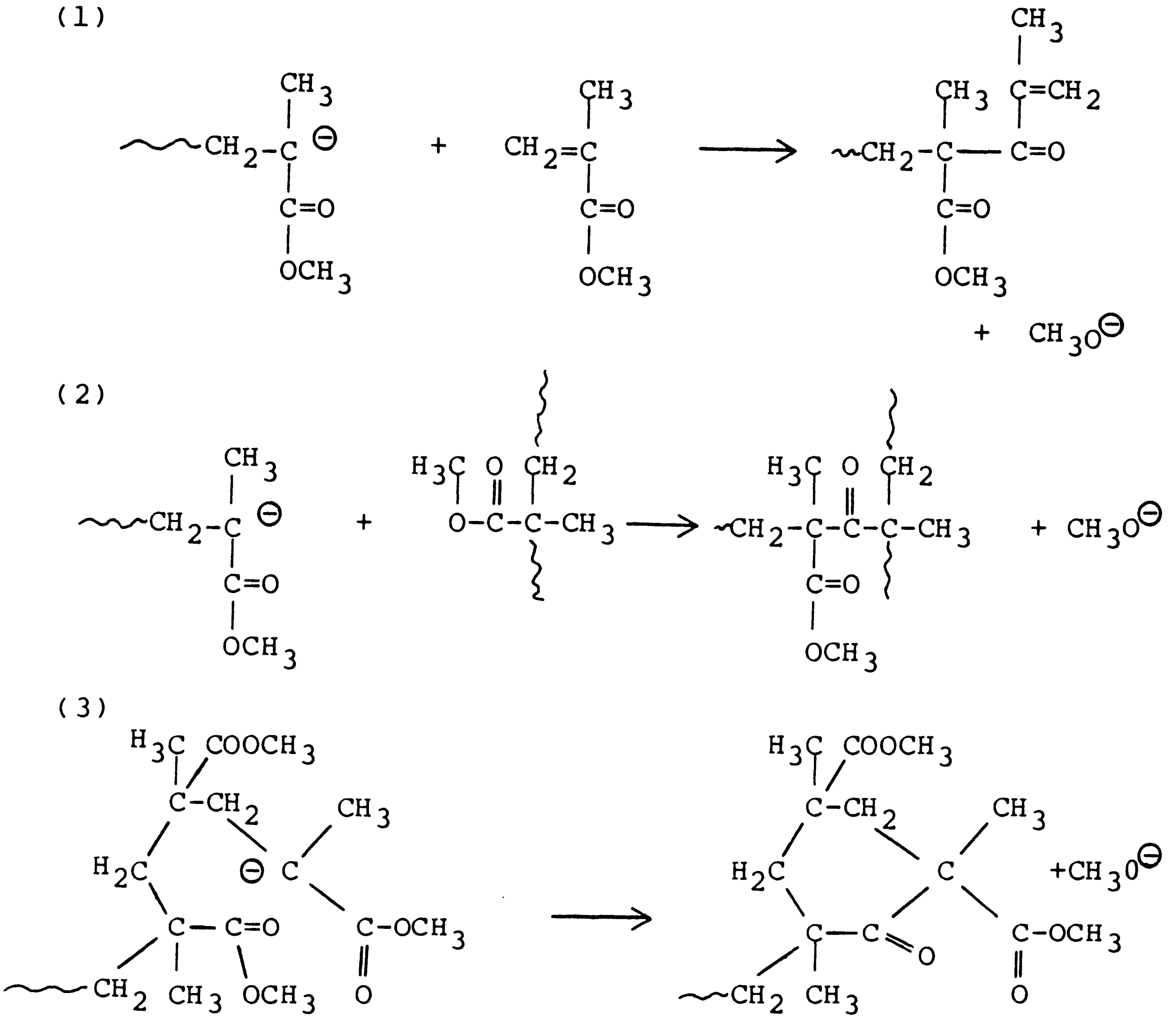


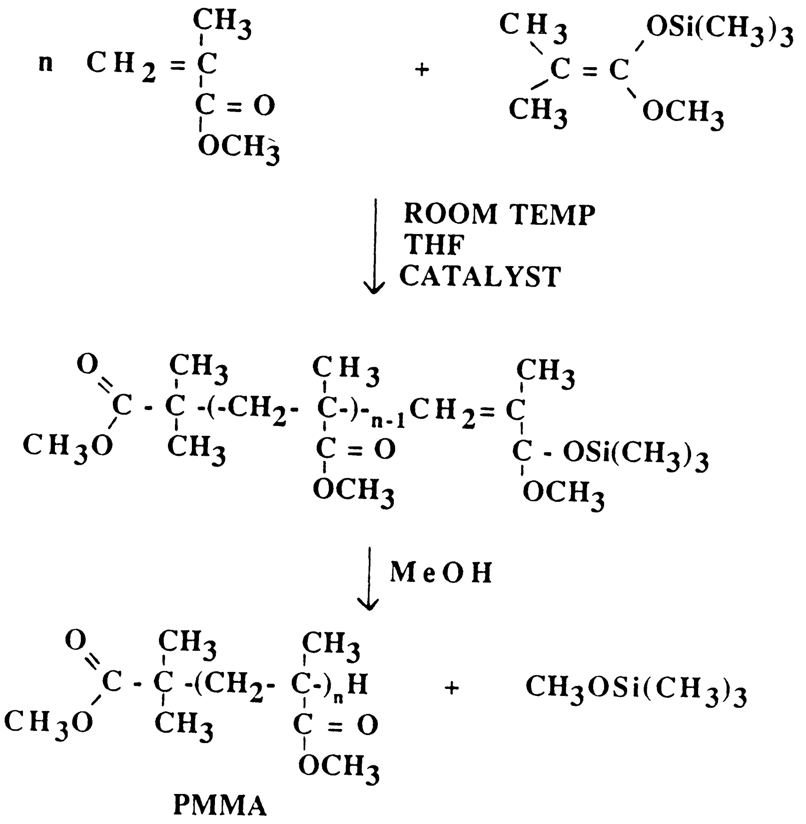
Figure 2: Termination Mechanisms in the Anionic Polymerization of Alkyl Methacrylates [69,70]

the addition of lithium chloride salt ([LiCl]/[RLi] ranged from 0.59 to 2.00) to the reaction at -78°C. A broadening of the distribution was noted for polymerizations conducted at -30°C and 0°C. Both tetrahydrofuran and THF/toluene mixtures as the polymerization solvents were investigated and in both cases narrow molecular distributions were obtained. This observation will definitely enhance the utility of acrylates as viable anionic monomers and permit the synthesis of many novel acrylic block copolymers.

Group Transfer Polymerization (GTP) has been introduced by Dupont as a synthetic route for the "living" polymerization of acrylates and methacrylates at ambient temperatures [73,74]. Controlled polymerizations are achieved over a broad range of polymerization temperatures by using silyl ketene acetals as initiators in the presence of anionic or Lewis acid catalysts. The reagents and the chemistry of the process are depicted in Scheme VI. The process was termed "group transfer" because the trimethyl silyl group is transferred to the incoming monomer and becomes a part of the propagating chain end. Sogah et al. have recently published a detailed account of the procedures, various monomers, polymerization temperatures and catalysts that have been successfully utilized [75]. In addition, the preparation of high molecular weight materials with narrow molecular weight distributions and novel block copolymers are discussed. Despite the early complexities of

Scheme VI.

Group Transfer Polymerization [75]



GTP, this advancement will facilitate the commercialization of "living" polymerizations of acrylic and methacrylic monomers.

A second mode of "living" polymerization that has been extended to acrylates and methacrylates has been introduced by Otsu et al. and is termed Iniferter Polymerization [76-78]. The concept of iniferter (Initiator-Transfer Agent-Terminator) has been utilized to design the polymer chain end by free radical polymerization. The iniferter is a free radical initiator that thermally dissociates into two free radicals. However, only one of the radicals initiates polymerization and the other can recombine with the propagating chain end. For the phenylazotriphenylmethane (PAT) iniferter, the phenyl radical initiates and the unreactive trityl radical reacts only with the propagating radical. A complete understanding of the exact mechanism has not been achieved and the polymerization cannot be truly living since molecular weight distributions can broaden significantly after long reaction times [78]. However, block copolymers can be obtained which indicates that the polymeric iniferter is formed to some extent. Many investigations are in progress to elucidate the exact polymerization mechanism.

One distinct advantage of anionic polymerization over Group Transfer or Iniferter Polymerization is the ability to control stereochemistry by variation in solvent polarity and counterion. Fox et al. discovered in 1958 that the experimental conditions had a drastic effect on the tacticity of anionically prepared PMMA [79]. Many workers have subsequently devoted significant attention to the determination of the nature of the propagating chain end in order to predict tacticity. However, a complete understanding will not be achieved until many different systems have been investigated. Table 9 depicts the effects of solvent polarity and counterion [80]. The more polar dimethoxyethane (DME) leads to increased levels of syndiotacticity and as the solvent polarity is decreased, the amount of isotacticity increases. In fact, high levels of isotacticity (80-85%) are obtained when polymerizations are conducted in toluene at -78°C. It can also be seen in Table 9 that the larger counterions lead to decreased levels of syndiotacticity. This can also be attributed to the tighter ion pair due to decreased external solvation. Consequently, when considering the Group IA metals, lithium leads to the highest level of stereochemical control i.e. the highest level of syndiotacticity in polar solvents. Increased size of the ester alkyl and increased polymerization temperature generally decrease the amount of syndiotacticity in polar solvents [81]. These latter two effects have not been extensively investigated in nonpolar solvents due to the psuedo "living" nature of the polymerization.

Table 9

Effects of Solvent and Counterion on Poly(methyl methacrylate Tacticity [80]

Counterion/ solvent	T (°C)	Iso (%)	Hetero (%)	Syndio (%)
Na / DME	-55	1	22	78
Cs / DME	-65	2	37	60
Na / THF	-61	4	36	58
Cs / THF	-66	5	53	42
Na / THF (difunctional)	-75	39	41	20

DME = Dimethoxyethane
THF = Tetrahydrofuran
Iso = Isotactic (mm)
Hetero = Heterotactic (mr)
Syndio = Syndiotactic (rr)

Many physical properties including the glass transition temperature depend on the tacticity of the poly(alkyl methacrylate). Conversely, the glass transition temperature is not a function of the tacticity for poly(acrylates). The ability to control the tacticity in alkyl methacrylate polymerizations allows for a large range of thermal properties. For example, Table 10 lists the glass transition temperatures for isotactic, atactic and syndiotactic poly(methyl methacrylate) [82]. For all poly(alkyl methacrylate) homopolymers, the isotactic polymer has a lower Tg than the corresponding syndiotactic material. The atactic polymer which contains high levels of syndiotacticity has an intermediate Tg, but is closer to the syndiotactic polymer. It can be seen that the glass transition temperature can be controlled over a 70°C range by only varying the tacticity. In the poly(alkyl methacrylate) family, the difference in Tg between the isotactic and syndiotactic forms is larger as the ester alkyl group becomes smaller. Thus, PMMA exhibits the largest difference. Although these polymers are termed "tactic", the percentage of tacticity is generally less than 100 percent and this fact often complicates interpretations of structure-property relationships. If the stereoregular polymer has not been synthesized, the Tg of the 100% syndiotactic or isotactic homopolymer can be obtained by extrapolation of a Tg versus triad tacticity plot. The

Table 10

Glass Transition Temperatures of Poly(methyl methacrylate) of Different Tacticities [82]

Tacticity[a]	Tg(°C)
Isotactic	42-45
Atactic	104-108
Syndiotactic	105-120

[a] Percentages are not specified, but assumed >50%

extrapolated Tg for purely syndiotactic PMMA is 160°C [83]. Variation in the Tg arises due to the difference in the polar interaction between the pendant ester groups. It has been argued that the Tg syndiotactic is higher than the isotactic because of higher rotational barriers [84]. The difference has been quantified by using the Gibbs-DiMargio theory and is summarized in the following equation

$$Tg(\text{syndiotactic}) - Tg(\text{isotactic}) = 0.59(\Delta E/k)$$

where ΔE is the difference in the Gibbs-DiMargio flex energy between the syndiotactic and isotactic polymer and k is the Boltzmann's constant [26].

One can imagine that other physical properties such as modulus, tensile strength, mechanical properties and solubility may also be a function of the polymer configuration. Jenkins et al. have reported that the dimensions of the isotactic coiled chain are more extended in solution and in the amorphous solid state than the corresponding syndiotactic polymer [85]. Atactic PMMA is also known to exhibit poor resistance to environmental stress cracking (ESC) and poor fracture toughness. However, both of these limitations can be overcome by blending in small amounts of isotactic PMMA [86]. Thus, one can see that PMMA has very diverse physical properties by virtue of the polymer stereochemistry.

The blending of poly(alkyl methacrylates) has been somewhat limited to various tactic poly(methyl methacrylate) homopolymers. It is well known that blends of syndiotactic and isotactic poly(methyl methacrylate) lead to the formation of a stereocomplex by the intermolecular association of the two tactic polymers [87,88]. Although many studies in the past two decades have attempted to elucidate the exact nature of the complex, the stereoassociation phenomenon remains a mystery. Challa et al. have shown that the methyl ester groups of the isotactic chain and the α-methyl groups of the syndiotactic chain are responsible for stereocomplex formation [89]. It has also been suggested that the complex results from the formation of an inner helix of isotactic PMMA surrounded by an outer helix of syndiotactic PMMA [90]. Recent endeavors have been directed toward the preparation of block copolymers whose constituent blocks form the stereocomplex [91]. The novel preparation of all-acrylic block copolymers will permit the study of many miscible acrylic polymer blends. For example, the blend of a poly(methyl methacrylate)-b-poly(2-ethylhexyl methacrylate)-b-poly(methyl methacrylate) copolymer where the PMMA blocks are syndiotactic with the corresponding triblock where the blocks are isotactic would yield a material with crystalline hard phases.

B. Alkyl Methacrylates in Multicomponent Systems

1) Random Copolymers

A vast majority of the commercially available acrylate and methacrylate polymers are copolymers. Copolymerization allows for precise engineering of physical properties by controlling chemical composition (monomer feed). An unlimited number of products can be prepared by the judicious choice of monomers and the relative amounts of each unit in the copolymer. For example, acrylate polymers tend to be soft and tacky. On the other hand, methacrylates are often hard and brittle. Thus, one can vary the appropriate composition in the copolymer to achieve the desired hardness for a specific application.

Free radical rather than ionic initiators are typically employed due to the less stringent demands on monomer purity. As described earlier for radical homopolymerizations, the same three kinetic steps are involved for chain copolymerization i.e. initiation, propagation and termination. However, the ability of a propagating radical of monomer 1 (M1) to initiate the second monomer (M2) and visa-versa must be defined. The propensity for homopolymerization of M1 versus crossover to the radical of M2 is defined by a reactivity ratio (r_1)

$$r_1 = k_{11}/k_{12}$$

where k_{11} is the rate constant for homopolymerization of M1 and k_{22} is the rate constant for crossover from M1 to M2. An analogous equation can be written for M2. For a more detailed discussion, Professor Odian has written an excellent chapter which reviews the derivation of the reactivity ratio and its function in copolymerization kinetics [92].

In general, acrylic and methacrylic monomers copolymerize readily with each other or most other vinyl monomers by free radical processes. Table 11 describes the copolymerizability of several alkyl methacrylate monomers with other common comonomers in 1:1 mixtures [93]. The "relative ease of copolymer formation" is defined by (r smaller/r larger)100 and values that exceed 25 indicate that copolymerization is feasible. If the reactivity ratios are equal, then the equation approaches 100. However, as (r smaller/r larger) approaches zero (which dictates that k_{11} or k_{22} be large), significant homopolymerization of the more reactive monomer will occur.

Less attention has been focused on the determination of reactivity ratios for anionic copolymerization. Table 12 lists the reactivity ratios determined for methyl methacrylate with other alkyl methacrylate monomers at -78°C [94]. In most cases, the relative reactivity of the monomer was not greatly affected by the choice of solvent. It is interesting to note that t-butyl methacrylate polymerizes slowly relative to MMA in both THF and toluene.

Table 11

Relative Ease of Copolymer Formation for 1:1 Ratios of Alkyl Methacrylate and Other Monomers [93]

Monomer 2	Monomer 1		
	Methyl	Ethyl	n-Butyl
acrylonitrile	13	24	19
butadiene	33	8.6	8.1
styrene	88	60	90
vinyl chloride	0.1	0.6	0.5
vinylidene chloride	9.5	14	16
vinyl acetate	0.1	0.9	0.2

"copolymerizability" = 100 x r smaller / r larger

Table 12

Monomer Reactivity Ratios in the Copolymerization of MMA (M_1) with Various Methacrylates by n-BuLi at -78°C [94]

	In toluene		In THF	
M_2	r_1	r2	r_1	r_2
Alkyl Methacrylate				
Ethyl	1.10 ± 0.10	0.38 ± 0.22	1.13 ± 0.07	0.52 ± 0.18
Iso-Propyl	2.75 ± 0.45	0.20 ± 0.37	2.29 ± 0.18	0.42 ± 0.20
t-Butyl	4.41 + 2.55	0.02 + 0.05	36 ± 27	0.43 ± 0.75
Diphenyl methyl	0.57 ± 0.15	0.55 ± 0.61	1.11 ± 0.22	1.57 ± 0.61
Trityl	6.28 ± 0.30	0.13 ± 0.07	0.62 ± 0.08	0.62 ± 0.32

$r_1 = k_{11}/k_{12}$; $r_2 = k_{22}/k_{21}$

r values 0-1: monomers will copolymerize
$r_1 > 1$: prefers homopolymerization
$r_1 = 0$: prefers to alternate
$r_1 = r_2 = 1$: perfectly random
(r1)(r2) = 1: Termed "ideal" system

There is an increasing amount of literature concerning the determination of monomer sequence distribution in copolymers [95]. The determination of the sequence distribution in copolymers is valuable for establishing structure-property relationships. C-13 NMR has been routinely utilized for the quantification of triad compositional distributions. These values are often compared with calculated values that were determined by actual reactivity ratios for the synthetic process.

2) Block Copolymers

The many advantages of block copolymers have been extensively exploited over the past two decades [96-98]. Block copolymers are comprised of extended sequences of different types of monomer units as depicted in Figure 3. A diblock is represented as AB and a triblock is represented as either ABA or ABC. Due to the formation of extended sequences, the blocks can phase separate depending on the molecular weight and solubility parameter of each block. However, the presence of the covalent bond between the different blocks prohibits macrophase incompatibility at the interface. In most cases, if the respective homopolymers are mixed at similar compositions, the blend will be immiscible due to the lack of interfacial adhesion. Consequently, block copolymers are often used as compatibilizers for polymer blends in order to enhance interfacial adhesion. Significant attention has also been

(1) Diblock Copolymer:

AAAAAAAAAAAAA-BBBBBBBBBBBBB

(2) Triblock Copolymer:

AAAAAAAAAAAAA-BBBBBBBBBBBBB-AAAAAAAAAAAAA

AAAAAAAAAAAAA-BBBBBBBBBBBBB-CCCCCCCCCCCCC

(3) Multiblock Copolymer:

AAAAAAAAA-BBBBBBBB-AAAAAAA-BBBBBBBB-AAAAAA

Figure 3: Linear Block Copolymer Architecture

directed toward determining the solution properties of block copolymers in solvents which are selective for one block [99,100].

Living anionic polymerization provides for the most elegant mechanism for the sequential addition of monomers to form block copolymers [101]. Two major limitations have impeded the development of block copolymer synthesis by anionic techniques. First, the propagating anion of the first block must be able to initiate the second block. If an ABA triblock structure is desired, then the propagating anion of the second monomer must be able to reinitiate the first monomer. Consequently, the relative basicity is important. For example poly(styryl) lithium can initiate methyl methacrylate, but not vice versa. This consideration limits the potential number of block copolymers. The second limitation is monomer impurities which will terminate the propagating first block or diblock. Consequently, homopolymer impurities will be present in diblock products and both homopolymer and diblock impurities can be present in triblock products. These polymeric impurities will alter the physical properties of the desired block copolymer. Despite these two limitations, an abundance of di- and triblock copolymers which possess well defined chemical architecture have been prepared by anionic techniques [97,102].

The preparation of a triblock ABA copolymer can be accomplished in three ways by anionic techniques. First, the monomers can be added in a sequential fashion as described above. Second, a two stage process can be utilized with a difunctional initiator. Third, a two stage process can be used in conjunction with a coupling agent. Each technique has inherent advantages and limitations. Most of the systems in the literature that have employed these three techniques have been based on styrenes and dienes [103]. Alkyl methacrylate containing block copolymers have received significantly less attention presumably due to the impurities present in most monomers.

In 1964, Rempp et al. investigated the synthesis of poly(styrene)-b-poly(methyl methacrylate) copolymers and reported that the first block must be capped with diphenylethylene in order to avoid attack on the carbonyl of the monomer [104]. This work represents the first attempt to prepare well defined block copolymers containing alkyl methacrylates and styrene. In addition, the discovery that a hindered initiator was necessary for alkyl methacrylate polymerizations revived the interest to anionically polymerize alkyl methacrylates. Subsequent investigations by Rempp involved the comparison of the conformations of the block copolymers with the random copolymers in dilute solutions [105]. The necessity to cap the poly(styrene) block has gone unappreciated in the literature and many subsequent investigations of poly(styrene)-b-poly(methyl methacrylate) do not include the capping step. The utility of poly(styrene)-b-poly(alkyl methacrylates) continues to receive attention [106]. However, these systems receive only sparse attention compared to styrene and diene based copolymers.

The synthesis of all-methacrylate block copolymers has not been addressed in detail in the literature. In fact, most investigations in the literature involve extensive extraction procedures in order to remove homopolymer impurities and decrease the molecular weight distributions [107]. In 1970, Gallot et al. demonstrated that the copolymerization was independent of the order of monomer introduction in the reaction media. The significance of this realization in relation to triblock synthesis is still unappreciated today. Despite these early efforts, the synthesis of these block copolymers has received only sporadic attention [108-111]. The lack of interest is attributed to the presence of protic impurities in most commercially available acrylic monomers and the inherent side reactions that can occur during anionic polymerization. In addition, the propensity for styrene-diene based block copolymers to phase separate is well appreciated and yields materials with advantageous properties. This fact has also helped to diminish interest in acrylic block copolymers. The excellent properties of Shell's Kraton, poly(styrene)-b-poly(isoprene)-b-poly(styrene), thermoplastic elastomer is an excellent example of the result of phase separation. However, the large breadth of solubility parameters within the alkyl methacrylate family of monomers has not been appreciated for the preparation of novel microphase separated block copolymers.

Diene monomers such as butadiene and isoprene are readily available in very pure grades for the preparation of block copolymers by anionic techniques. In addition, dienes polymerize in a controlled fashion without many of the problems of side reactions that lead to termination. Consequently, poly(dienes) are frequent components in block copolymers with styrenes [97,101]. However, the preparation of diene-methacrylate block copolymers has only received limited attention. The major reason for this sluggish synthetic development is the fact that elastomeric poly(dienes) require nonpolar polymerization solvents and alkyl methacrylates generally require polar solvents. Consequently, the polarity of the reaction media must be altered without termination of the first block. Also, the addition of usually impure alkyl methacrylate monomers leads to homopolymer contamination.

In 1973, a German patent was issued for the preparation of poly(isoprene-co-styrene)-b-poly(methyl methacrylate) star copolymers [112]. The synthesis involved the addition of divinylbenzene during the formation of the first block to form the star. In addition, it was stressed that the use of diphenylethylene to cap the first block was required. Tetrahydrofuran (approximately 20% by volume) and cooling to -40°C facilitated the polymerization of the methyl methacrylate block. The authors were primarily concerned with increasing the melt index and improving solubility. However, the verification of composition and the molecular weight distributions were not given. These latter two observations are required to ensure living polymerization conditions and the formation of well defined block copolymers.

French workers in 1976 described the construction of a medium-size anionic polymerization plant and its operation for the preparation of block copolymers [113]. In addition to the preparation of poly(styrene) homopolymers and isoprene-styrene block copolymers, the utility of the plant for the preparation of isoprene-b-methyl methacrylate block copolymers is mentioned. But, controlled polymerization conditions for their preparation were not described in detail. Finally, in the same year, a published account of the preparation of poly(isoprene)-b-poly(methyl methacrylate) copolymers appeared in the open literature [114]. The preparation of the copolymers was conducted exclusively in polar solvents. Consequently, high levels of vinyl addition were present in the poly(isoprene) and the Tg of the block was near 0°C. The work did show that the addition of diphenylethylene was not necessary due to the decreased reactivity of polyisoprenyl potassium at -70°C. The authors also state that the low temperature also eliminates the possibility of isomerization of the living diene chain end. The block copolymer samples demonstrated controlled molecular weight and narrow molecular weight distribution (<1.15). The morphology was determined by microscopy to be characteristic of a hexagonal bidimensional network of long cylinders. The cylinders were composed of the poly(isoprene) blocks and poly(methyl methacrylate) filled the cylindrical spaces.

More recently, the synthesis, characterization and morphology of a cis-1,4 poly(isoprene)-b-poly(n-butyl methacrylate) diblock copolymer have been described [115]. A microphase separated morphology was demonstrated and the glass transition temperature of the poly(isoprene) block was -70°C. The Tg of the poly(n-butyl methacrylate) block was 20°C, but the transition was very broad (>70°C) in viscoelastic experiments. The abstract describing this work did not include compositional verification, molecular weight control, or molecular weight distribution of the resulting block copolymers. A detailed description of the synthetic procedure and the characterization of the polymers has not been found in the available literature.

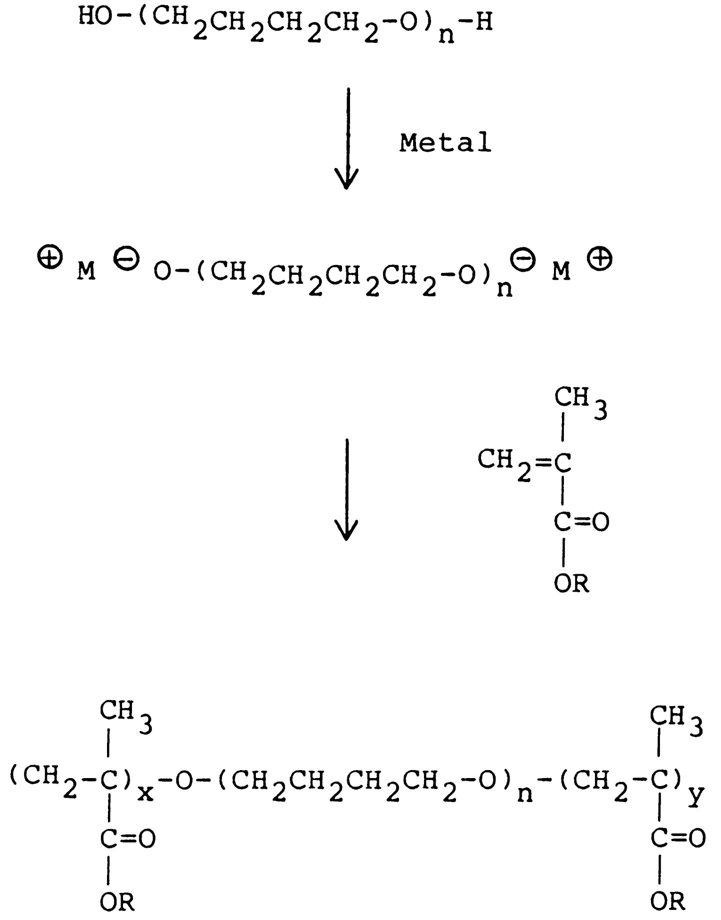
In conclusion, only sporadic attention has been directed toward the synthesis of diene-methacrylate block copolymers. Neither systematic variations in the ester alkyl group nor the preparation of triblock copolymers have been described. Despite the many system variables and potential synthetic complications, only a few aspects have been noted in the literature.

In addition to the sequential anionic techniques for block copolymers containing alkyl methacrylates, coupling reagents have also been recently demonstrated to produce well defined block copolymers [111]. Another area of recent interest is the preparation of macromolecular dialkoxide initiators for alkyl methacrylates. Both the disodium salt of poly(tetrahydrofuran) [116] and poly(ethylene oxide) [117] were utilized as initiators for MMA and narrow molecular weight distribution triblock copolymers were obtained in both cases. The chemistry of this process is represented in Scheme VII. The synthesis of poly(ethylene oxide)-b-poly(methyl methacrylate) via sequential anionic techniques has been described, but is limited to the preparation of diblocks [118]. The anionic synthesis of other alkyl methacrylate containing block copolymers with more unusual monomers such as hexamethyltrisiloxane (D3) [119], 2-vinylpyridine and 9-vinylphenanthrene have also been described [120,121].

Although ionic techniques have been shown to be very feasible for the preparation of well defined block copolymers, other "living" mechanisms such as Group Transfer Polymerization [75] and Iniferter techniques [76] can be

Scheme VII.

Poly(ether) Based Triblock Synthesis [116]



used in a controlled manner. Transformation reactions which involve different mechanisms of polymerization for each block have also been described. For example, Tung et al. have prepared macromolecular chain transfer (CT) agents using anionic techniques [122]. Free radical polymerization of a second monomer in the presence of the polymeric chain transfer agent yields a block copolymer. If a difunctional, polymeric CT agent is utilized, then triblock structures are obtained. Due to the attractive physical properties and potential applications of block copolymers, their preparation continues to receive significant attention.

3) Graft Copolymers

Graft copolymers are comprised of polymeric branches (B) which are dispersed along a polymer backbone (A). This type of chemical architecture is depicted in Figure 4. The techniques to construct macromolecules in this fashion have been described in detail [123,124]. Free radical techniques have received the most attention in the literature and are used to prepare many commercial products such as impact poly(styrene). The reactive site such as a radical can be generated on a preformed polymer backbone and polymerization of the grafts can occur from the backbone. On the other hand, one can perform the polymerization of the graft in the presence of a preformed polymer backbone which contains labile hydrogen. Abstraction of the hydrogen by the propagating radical or the free radical initiator affords a

```
AAAAAAAAAAAAAAAAAAAAAAAAAAAAA
    B         B    B
    B         B    B
    B         B    B
    B         B    B
    B         B
    B         B
              B
```

Figure 4: Graft Copolymer Structure

site for polymerization. In addition, a propagating radical can combine with the radical on the polymer backbone to form a graft. The formation of graft homopolymer during the copolymerization is the major disadvantage of this process. Consequently, many recent techniques have been introduced to circumvent this problem. This section will highlight some recent advances in alkyl methacrylate containing graft copolymer preparation. Special attention will also be directed toward defining the reactivity of the propagating alkyl methacrylate enolate with various reagents. The capability to functionalize the polymer allows for controlled graft copolymer synthesis.

One method of controlling the molecular weight and molecular weight distribution of the graft is to utilize "living" polymerization techniques. Hatada et al. have described the anionic copolymerization of 1,1-diphenylethylene and m-and p-divinylbenzenes [125]. If an excess of diphenylethylene was used, the resulting polymers were soluble and contained pendant vinyl groups. Reactive polymer anions were formed by adding sec-butyl lithium in THF at -78°C. The resulting hindered anions were suitable initiating sites for various alkyl methacrylates and graft copolymers with a predetermined concentration of branches resulted. This procedure exemplifies an alternative ionic approach to conventional free radical techniques. One should note that this system is unique because the polymer backbone also possesses predictable molecular weight and a narrow molecular weight distribution.

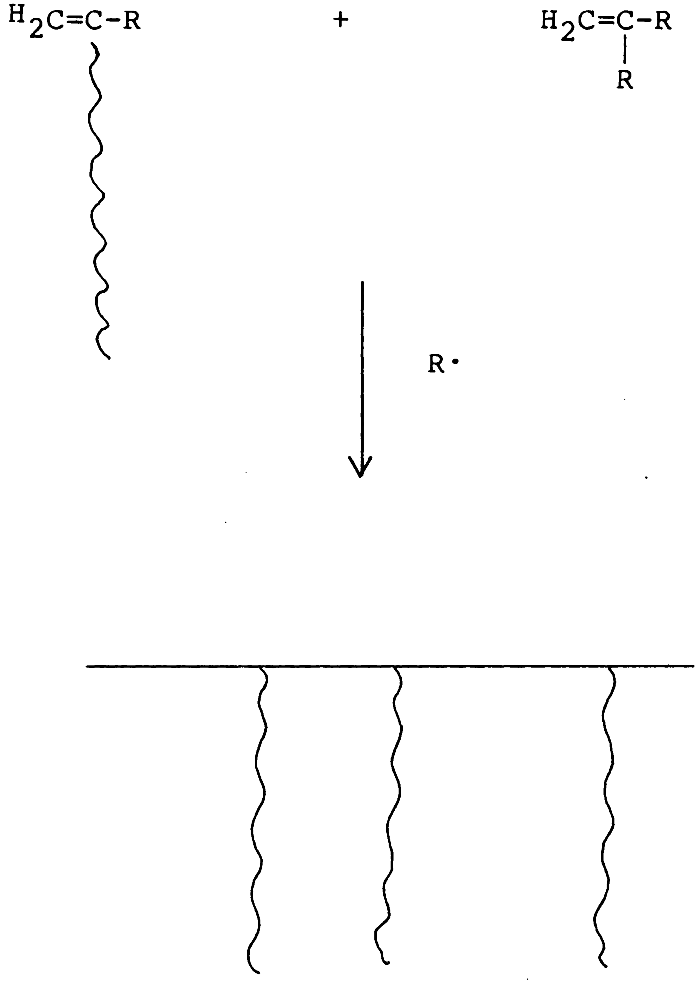
Step-growth polymerization techniques have also been utilized to prepare alkyl methacrylate containing graft copolymers. Poly(methyl methacrylate-co-hydroxyethyl methacrylate) random copolymers can be prepared by free radical polymerization techniques [126]. The resulting hydroxyl groups can be reacted with isocyanate terminated prepolymers. Poly(urethane) grafts are placed at the position of the pendant hydroxyl group and the composition can be controlled by controlling the amount of hydroxyethyl methacrylate in the copolymer backbone. Since the backbone was prepared by free radical techniques, the molecular weight distribution is broad. One method to circumvent this situation would be to utilize anionic techniques with protected functional alkyl methacrylate monomers e.g. trialkylsilyl protected hydroxyethyl methacrylate [127]. Narrow molecular weight distribution backbones would result and the exact placement of the graft would be controlled by the order of monomer addition.

Milkovich and coworkers have described the preparation of graft copolymers that exhibit thermoplastic elastomer properties [128-130]. The controlled synthesis of the the graft copolymers is accomplished by the macromonomer technique which involves the copolymerization of a macromonomer with a vinyl monomer. This approach is depicted in Scheme VIII. A macromonomer is a polymeric molecule which contains a polymerizable functional group generally at one chain end. The "polymeric monomers" are generally prepared by "living" techniques that involve the functional termination of the propagating species. Rempp and coworkers have recently reviewed this new class of polymeric intermediates [131] and many specific examples of macromonomer synthesis can be found in the recent literature [132-136].

Several recent publications describe the free radical polymerization and functionalization of poly(alkyl methacrylates) to form macromonomers [137,138]. The synthesis is generally achieved in a two stage process. The first step involves the free radical polymerization of the alkyl methacrylate monomer in the presence of an efficient functional (-OH or -COOH) chain transfer agent. The terminal functional group is subsequently converted to a vinyl containing end group. The graft copolymer is formed by the free radical polymerization of the macromonomer with another monomer. Both the copolymers and the macromonomers that have been prepared by this technique have not been characterized adequately in the past. The free radical approach has two distinct disadvantages. First, the molecular weight of the macromonomer is difficult to control by free radical mechanisms. Second, the subsequent reaction to generate the unsaturated chain end often occurs in

Scheme VIII.

The Macromomer Tachnique for Graft Copolymer Synthesis
[128]



limited yields.

The use of anionic techniques to prepare poly(alkyl methacrylate) macromonomers has received very little attention [139,140]. The synthesis involves two problems. First, the preparation of low molecular weight poly(alkyl methacrylates) with narrow molecular weight distributions is difficult. This has been attributed to either slow initiation or side reactions with the ester carbonyl. Second, the nucleophilicity of the poly(alkyl methacrylate) enolate is believed to be poor. Despite these limitations, Rempp has reported the controlled synthesis of poly(alkyl methacrylate) macromonomers by direct deactivation of the living enolate with p-vinyl or p-isopropenylbenzyl bromide [140]. Diphenylhexyl lithium and the dimer of Na/diphenylethylene were utilized as initiators in THF at-60 to -80°C. It was stressed that slow addition of a monomer solution in THF was desirable. The functionalization of the polymeric enolate with the organohalide was quantitative and the resulting macromonomers possessed both predictable molecular weights and narrow molecular weight distributions. Quirk, Young and Fetters have written an excellent review of various functionalization reactions and highlighted the many considerations and complications that may arise [141].

Group Transfer Polymerization has also demonstrated incredible capabilities for the functionalization of poly(alkyl methacrylates). Asami and coworkers have devised two procedures for the preparation of macromonomers [142]. The first procedure involves functional termination of the living silylenolated chain end with vinyl benzyl halides. This is quite similar to the methodology described above by Rempp for anionic deactivation. The second approach utilizes a functional initiator such as a silyl ketene acetal having a vinylbenzyl functionality. Both methods result in the preparation of well defined macromonomers that can be utilized in subsequent graft copolymer preparations.

C. Anionic Polymerization of Nonpolar Monomers

In contrast to the polar alkyl methacrylates, the anionic polymerization of nonpolar monomers such as the styrenes and the dienes have received a vast amount of attention in the literature. These monomers are generally available in commercial grades which are sufficiently pure to permit "living" polymerization. In addition, the anionic polymerization of styrenes and dienes proceeds in the absence of termination reactions at a variety of reaction conditions. This section will not attempt to completely review the anionic polymerization of nonpolar monomers, but highlight the well appreciated and pertinent capabilities relative to this research endeavor.

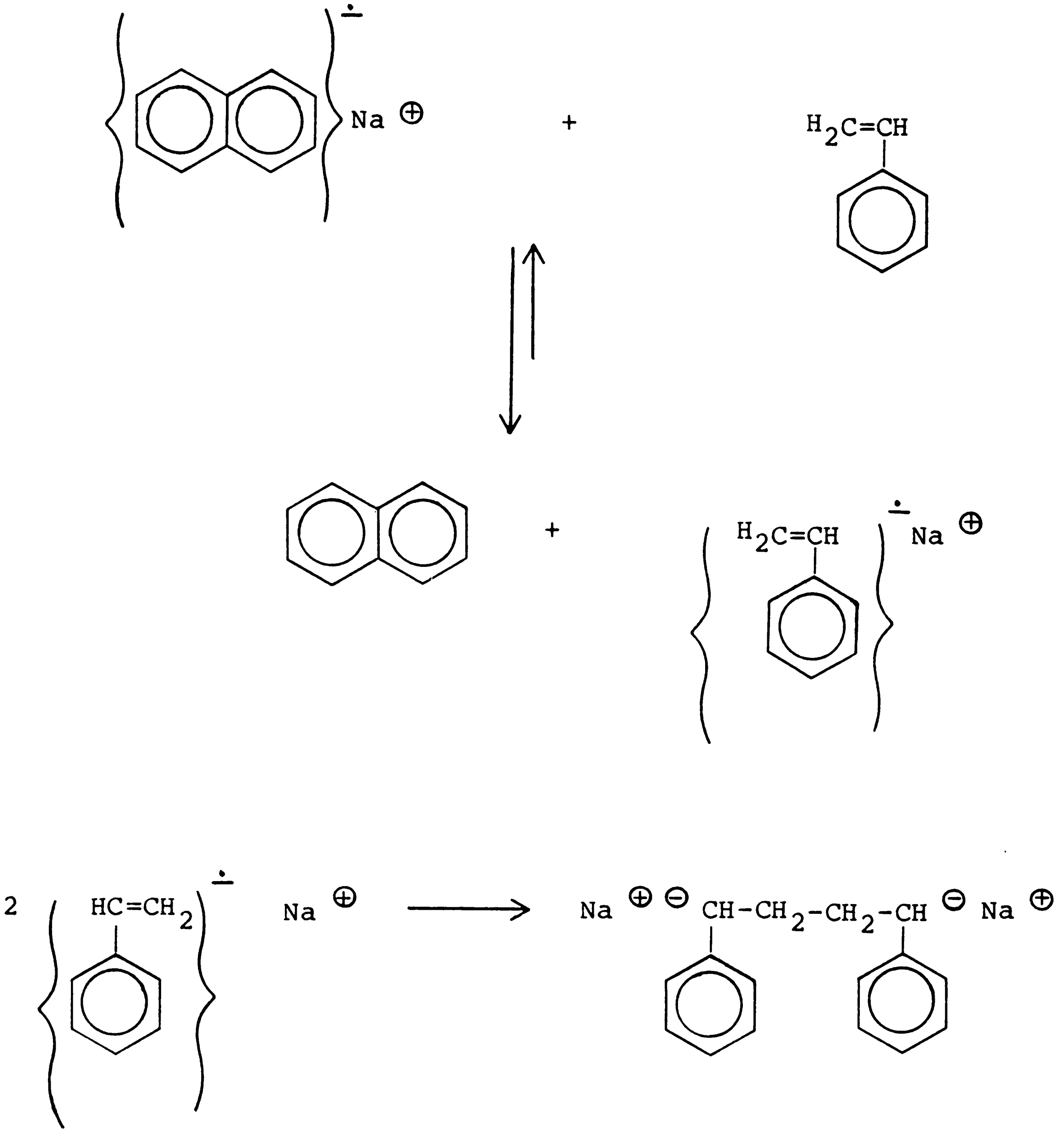
1) Styrene and Substituted Analogues

In 1956, Szwarc, Levy and Milkovich first realized the termination-free nature of a styrene polymerization which was initiated by the radical anion of sodium/naphthalene [143]. The reaction was described as a "living" polymerization because subsequent monomer additions increased the molecular weight. The utility of this difunctional initiator is still appreciated today and has been extended to other systems. The formation of the radical anion and the subsequent propagation is depicted in Scheme IX. Since this realization, styrene has been utilized routinely in the literature as an anionic monomer and many commercial products which are prepared by anionic techniques contain poly(styrene) [144,145]. Morton has compiled an extensive list of various initiator systems and polymerization solvents that have been investigated for the anionic polymerization of styrene and styrenic derivatives [146]. The monomers which have received the most attention include: styrene; α-methyl- and substituted α-methylstyrenes; halogenated styrene; o- and p-methylstyrenes, and methoxy styrenes.

Many kinetic investigations have pursued the initiation and propagation behavior of styrene. For example, it has been determined that the rates of chain initiation depend on the solvent type and the nature of the alkyl group attached to the lithium [147,148]. In most systems, it is important to have fast initiation and generally secondary and tertiarybutyl lithiums are superior to n-butyllithium or

Scheme IX.

Sodium/Naphthalene Initiation of Styrene [143]



ethyllithium. This has been explained by the fact that branched alkyllithium reagents are less associated than linear analogues. The order of decreasing reactivity of various alkyllithium initiators for styrene are as follows [146]:

menthyl > s-butyl > i-propyl > n-butyl and ethyl > t-butyl

The slow initiation of t-butyllithium can be attributed to steric clashes of the t-butyl group and the phenyl ring in the monomer. However, other workers have shown that a small amount of the initiator is active initially and rapidly initiates polymerization [149]. The remaining inactive initiator has been speculated to be cross-associated with the poly(styryl) lithium chain ends. Studies of this nature have further defined anionic polymerization kinetics for poly(styrene) and the information can be extended to other systems such as alkyl methacrylates. In addition, it is clear that initiation and propagation kinetics are very complex due to association of anionic species in hydrocarbon solvents.

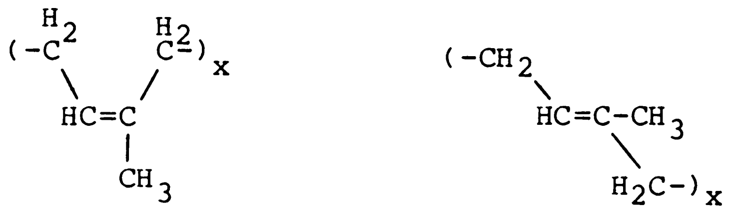
The effect of the polymerization solvent on the propagation kinetics has also been investigated to a large extent [150,151]. A more polar solvent leads to faster rates of propagation and a nonpolar solvent decreases the rate significantly. This is attributed to the nature of the ion pair i.e the more solvated ion pair reacts faster. From a practical viewpoint, the polymerization of styrene using sodium/naphthalene in tetrahydrofuran at -78°C is complete instantaneously. In fact, the monomer must be added to the initiator solution at -78°C dropwise in order to avoid an uncontrollable exotherm. On the other hand, polymerization of styrene in cyclohexane with alkyllithium initiators requires several hours. The fact that the polarity of the reaction media controls the rate of an anionic polymerization can be extended to other monomer systems.

Recent endeavors related to the anionic polymerization of styrene have been focused on multiphase materials and spectroscopic studies of the polymer stereochemistry. Anionically prepared poly(styrene) is atactic and the preparation of tactic polymers can only be accomplished with transition metal catalysts. This is in sharp contrast to the anionic polymerization of alkyl methacrylates. In 1986, the preparation of crystalline syndiotactic poly(styrene) was described and the polymer was characterized by NMR [152]. Structure-property relationships of the syndiotactic polymer versus the atactic sample were described.

2) 1,3 Dienes

Ziegler and coworkers conducted the first systematic studies of alkyllithium initiated polymerizations of dienes in the mid-thirties [153]. The concept of a nonterminating polymerization was observed, but the polymerization was not described as anionic or "living". Although early scientists realized the myriad of poly(diene) properties that were available by varying polymerization conditions, it was difficult to define the reasons for these observations.

The advent of infrared spectroscopy in the 1950's attributed the diverse physical properties to polymer microstructure (geometric isomerization) [154,155]. Figure 5 illustrates the various geometric isomers that are present for poly(isoprene). The desire to control the polymer microstructure by altering various synthetic parameters served as the impetus for further investigations. It was soon realized that lithium was capable of producing high levels of cis-1,4 units during the polymerization of isoprene in hydrocarbon solvents. This was approaching the microstructure that was present in natural rubber. In addition, poly(isoprene) that was prepared in ethers resulted in stereochemistry which was rich in 3,4-, 1,2-, and trans-1,4-microstructures [155,156]. Similar results were later reported for the alkyllithium initiated polymerization of butadiene in n-heptane [157]. Nuclear (^1H) magnetic resonance (NMR) soon became the method of choice for the precise quantification of geometric isomerization in poly(dienes) [158-161]. A vast amount of literature exists on the determination of geometric isomerization in poly(dienes) and this area continues to receive attention in the current literature [162].



CIS-1,4 TRANS-1,4

3,4 1,2

Figure 5: Geometric Isomerism in Poly(isoprene)

In addition to the interest in stereochemical determination techniques, many investigators have realized the ease of anionic polymerization of diene monomers. The monomer is readily available in very pure grades and the subsequent polymerization proceeds without termination reactions. Consequently, an abundance of kinetic investigations have been reported in the literature [163]. The role of the polymerization solvent has been investigated in detail by a variety of workers. Table 13 summarizes the effect of solvent polarity on the resulting polymer microstructure for butadiene and isoprene monomers [164]. As previously mentioned, nonpolar solvents result in higher levels of 1,4- addition and the polar solvents yield predominantly 1,2 products. The effects of initiator counterion are summarized in Table 14 [165]. Immediately one can see the impetus for the use of lithium based initiators due to resulting high levels of cis-1,4 poly(isoprene). Alkyllithium initiators are also widely used due to their solubility in hydrocarbons and their controllable initiation kinetics. Kuntz and Gerber reported that the initiator and monomer concentration did not affect the structure of poly(butadiene) [157]. However, the structure of the alkyllithium initiator does influence the kinetics and final molecular weight distribution. This aspect was described above for the polymerization of styrene. The microstructure was also independent of

Table 13

Effects of Solvents on Chain Microstructure in Alkyllithium-Initiated Polymerizations of Isoprene and Butadiene [164][a]

Polymer	Solvent System		$[S]/[I]$[b]	Microstructure (mole%)[c]			
	Nonpolar	Polar		cis 1,4	trans 1,4	3,4	1,2
Poly(isoprene)							
	Benzene	-	-	69	25	6	-
	Cyclohexane	-	-	80	15	5	-
	n-hexane	-	-	81	15	4	-
	n-hexane	THF	2	68	19	13	-
	n-hexane	THF	15	-	69	31	-
	n-hexane	THF	d	-	26	66	9
Poly(butadiene)							
	n-hexane	-	-	35	57	-	8
	n-hexane	diethyl ether	6.3	29	50	-	21
	n-hexane	THF	1.0	25	40	-	35
	n-hexane	THF	8.2	21	31	-	45
	n-hexane	THF	17	14	28	-	58
	n-hexane	THF	53	7	10	-	85

[a] 0.5M Monomer, 20-30°C

[b] $[S]/[I]$ = molar ratio of polar solvent to initiator

[c] Precision of ^1H NMR data: cis-1,4 or trans-1,4 = ±2%, 3,4 or 1,2 = ±1%

[d] 10 volume % THF

Table 14

Chain Structure in Alkali Metal Initiated Polymerization of Butadiene and Isoprene (by IR Spectroscopy) [165]

Initiator	Solvent	Chain Microstructure (mole%)			
		cis-1,4	trans-1,4	1,2	3,4
Poly(isoprene)					
n-butyl Li	n-heptane	93	0	0	0
n-butyl Li	THF	0	30	16	54
phenyl Na	n-heptane	0	47	8	45
phenyl Na	THF	0	38	13	49
benzyl K	n-heptane	0	52	10	38
benzyl K	THF	0	43	17	40
Rb	None	5	47	10	38
Cs	None	4	51	8	37
Poly(butadiene)					
Ethyl Li	n-hexane	43	50	7	
Ethyl Li	THF	0	9	91	
Na	None	10	25	65	
K	None	15	40	45	
Rb	None	7	31	62	
Rb	THF	0	25	75	
Cs	None	6	35	59	

Polymerization Temp. = 25-50°C

polymerization temperature over a wide range. The effect of polymerization temperature on the stability of polymeric lithium systems such as polybutadienyllithium has been reported in detail [166,167].

The primary conclusions that can be drawn from these extensive investigations are as follows:

(1) The percentage of 1,4-addition is highest for lithium based initiators and decreases with decreasing electronegativity of the alkali metal.

(2) As the polarity of the polymerization media is increased, the amount of resultant vinyl groups increases.

(3) Reaction temperature does not significantly influence the ultimate microstructure, but high temperatures can degrade anionic chain ends.

Investigations continue to further define the kinetics and mechanisms of diene polymerizations. Morton has compiled an extensive list of various substituted dienes that have been investigated as potential anionic monomers [168]. Some recent research efforts have been directed toward the modification of living polydienyl chain ends with complexing reagents such as 1,2-dipiperiodinoethane [168] and the further investigations of metallic lithium as an initiator for anionic polymerizations [169].

D. Ion-Containing Polymeric Systems

(1) Introduction

The introduction of ions into polymers has resulted in the emergence of a new classification of polymers which possess very interesting and advantageous properties. These novel materials which typically contain a maximum of 10 mole percent ionic moieties pendant on a hydrocarbon backbone have been classified as ionomers [170]. This term was first introduced by Rees and Vaughan in 1965 when referring to the Surlyns^{R} (Dupont materials based on copolymers of ethylene and methacrylic acid) and has been generally accepted in the polymer field [171].

Due to the intense interest in ion-containing polymers, many review articles and books have been devoted solely to this class of polymers [172-177]. Despite the generous academic and industrial attention devoted to the study of ionomers over the past decade, many questions related to synthesis, structure and morphology remain unanswered. It has been generally accepted that the ions aggregate to form ion-rich domains in the presence of a nonpolar polymer matrix as depicted in Figure 6 [176]. The ionic domains or aggregates are unique to these systems and cannot be found in polymers consisting of nonionic backbones. The ability of the ions to aggregate or phase separate is surprising because the ionic groups are generally dispersed in a random fashion along the polymer backbone. The resulting bulk

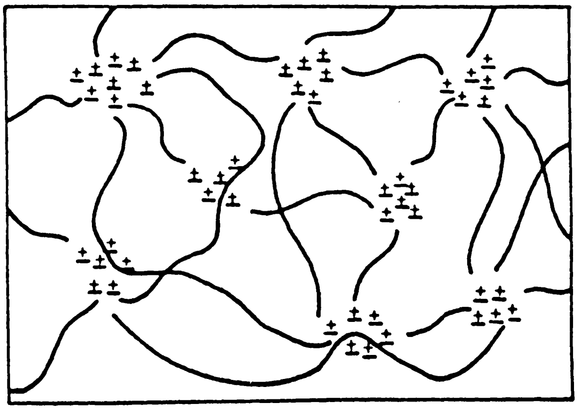


Figure 6: Aggregate Morphology in Ionomers [176]

polymer properties are unique and continue to gain industrial importance.

The versatility of ionomers can be demonstrated by considering the molecular parameters which may alter the properties of the polymer. The six molecular parameters which have received the most attention are as follows:

(1) The type of backbone
(2) Ionic content (0-10 mole %)
(3) The type of pendant ionic group
(4) The extent neutralization
(5) The nature of the cation
(6) Ion Location/Polymer Architecture

The polymer architecture and the location of the ionic groups on a polymer backbone have received far less attention. Investigations of these six parameters have provided for an abundance of insight into ionomers [178]. In addition to the development of novel synthetic routes, a better understanding of ionomeric morphology has been accomplished.

This section will focus on the most popular synthetic methodologies that have been developed for the preparation of various ionomeric systems. The models that have been outlined to define the aggregate morphology will only briefly be described. Special attention will be dedicated to investigations of the six molecular parameters and the ultimate structure-property relationships that have been realized.

(2) Synthesis of Ion-Containing Polymeric Systems

Two general approaches have been developed over the past two decades for the introduction of ionic moieties onto a polymeric backbone. The first approach involves the free radical copolymerization of a low level of a functional monomer such as methacrylic acid with a nonfunctional comonomer such as styrene or a diene. The metal carboxylate is generated by subsequent neutralization with an appropriate metal hydroxide or metal acetate. The final ionic content is controlled by the initial functional monomer charge. The second method involves the direct functionalization of a preformed polymer (post reactions). For example, functionalization could involve the sulfonation of aromatic structures or addition reactions across unsaturated sites in the polymer backbone. In fact, most sulfonated polymers are obtained by a subsequent polymer modification reaction. Since polymer modification reactions typically result in limited yields, the ionic content can only be somewhat controlled by the concentration of reactive sites on the polymer chain. Most attention has been directed toward introducing metal carboxylates and sulfonates via either of these two approaches. The inherent advantages and disadvantages of each methodology will be described in detail for a variety of ion-containing polymeric systems.

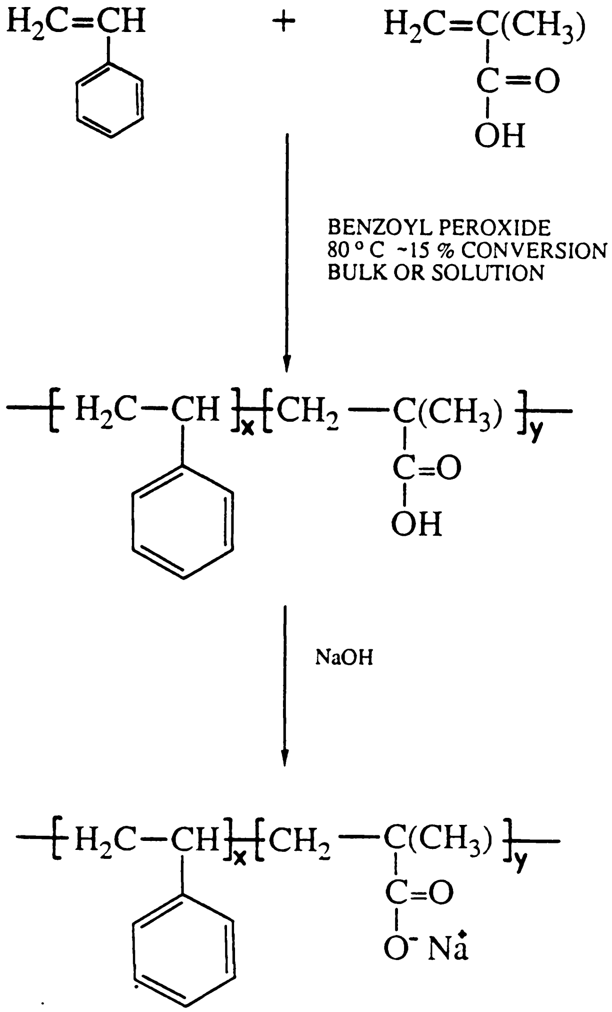
a) Functionalized Comonomer Approach

Typical carboxylate ionomers are synthesized by direct copolymerization of a low level of acrylic or methacrylic acid with ethylene, styrene, alkyl acrylates, alkyl methacrylates, dienes and similar comonomers employing free radical initiators [178-184]. The ethylene based systems (Surlyns^{R}) are commercially prepared by Dupont and are utilized in a variety of applications [185,186]. Scheme X depicts the solution or bulk free radical copolymerization of styrene and methacrylic acid. The carboxylate is generated by simple titration (neutralization) of the acid groups with various bases. Other examples include styrene-butadiene-acrylic acid, butadiene-acrylonitrile-acrylic acid and butadiene-acrylic acid (Hycar, Goodrich) copolymers. In each case, less than 6 mole% of the carboxylic monomer is generally utilized in order to preserve the elastomeric properties of the major component. In 1982, the butadiene based systems reached a worldwide production estimated to be in excess of 0.5 million tons per year [182].

A majority of these systems are prepared by emulsion polymerization [182]. It is assumed that the free radical mechanisms lead to random incorporation of the carboxyl groups. Since the free acid copolymerizes much easier than the salt, the copolymerizations are performed in acidic

Scheme X

Synthesis of Styrene-Carboxylate Ionomers by Free Radical Copolymerization [179-184]



emulsion formulations. The salt form has limited solubility in the hydrocarbon phase and this fact prevents significant monomer incorporation. A typical procedure for the preparation of carboxylate containing copolymers via emulsion techniques has been defined in detail [187]. The direct copolymerization approach is often preferred due to its simplicity, ease of product control and economics.

Recently, several workers have investigated the polymerizability of sodium styrene sulfonate with styrene [188], dienes [189,190] and acrylates [191]. Consequently, in an emulsion polymerization, the sodium styrene sulfonate serves as both comonomer and surfactant. Thermal analyses for the acrylate and styrene based systems indicated that the glass transition temperature was independent of the concentration of styrene sulfonate. This is in sharp contrast to observations for sulfonated poly(styrene) which was prepared by subsequent sulfonation of poly(styrene). These observations indicated that the copolymerization involving a charged monomer results in a different structure than materials prepared from subsequent sulfonation reactions.

Cationic pendant functionalities can also be introduced by free radical copolymerization of a functionalized comonomer. Eisenberg has devoted significant attention to the incorporation of vinylpyridine into copolymer systems [192]. The ionic charge is introduced by quaternization with methyl iodide. In contrast to the anionic ionomers, the cationic ionomers do not microphase separate, but remain dispersed in the polymer matrix. The authors also observe that dequaternization occurs over time at elevated temperatures under vacuum. This inherent attribute may complicate drying procedures of the hydrophilic ionomers.

A new class of ionomer has recently been disclosed by Salamone et al. which contain both cationic and anionic pendant groups [193,194]. These ampholytic ionomers are obtained by copolymerization of anionic-cationic monomer pairs with a neutral monomer such as styrene. For both the styrene and n-butyl acrylate based systems, a linear relationship was observed for Tg and mole % ionic groups. However, this was not true when methyl methacrylate was utilized as the neutral comonomer. This further exemplifies the complexities that can arise when copolymerizing charged monomers.

b) Reactions on Polymers

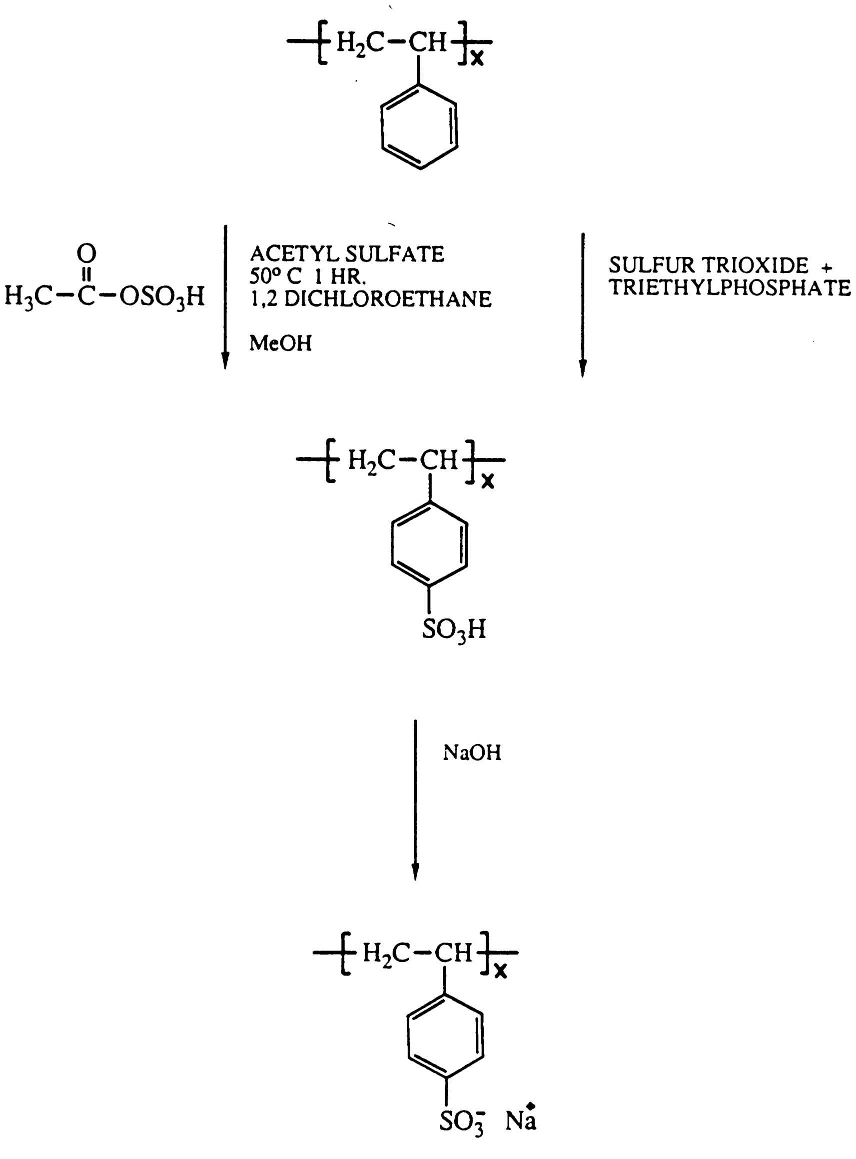
The alternate approach to introducing ionic functionalities into polymeric systems involves subsequent polymer modification reactions. This approach is especially suited for the introduction of sulfonate groups via sulfonation of aromatic or unsaturated sites [195,196]. The simplest example is the sulfonation of poly(styrene) with either acetyl sulfate or sulfur trioxide-triethylphosphate as depicted in Scheme XI. Acetyl sulfate is the reaction product of acetic anhydride and sulfuric acid. In addition, aromatic rings which are in the polymer backbone rather than pendant can also be sulfonated readily [197].

The sulfonation of ethylene-propylene-diene monomer (EPDM) systems has received significant commercial attention [195,198]. By employing Ziegler-Natta catalysts, a random copolymerization of these three monomers is achieved [199]. One of the preferred dienes is 5-ethylidene-2-norborene which contains an endo- and exocyclic double bond. Polymerization occurs through the endocyclic double bond and the exocyclic unsaturated site is available for subsequent sulfonation. The structures and chemistry involved in the transformation are shown in Scheme XII. The sulfonation reactions generally proceed at 95% conversion of sulfuric acid to polymer-sulfonic acid based on titration of the final product. MacKnight and Lundberg have described in detail the reaction conditions that are necessary for quantitative and controlled sulfonation of EPDM [200].

In a similar fashion, poly(pentenamers) (PP) can be sulfonated as illustrated in Scheme XIII. The starting PP contains 82% trans and 17% cis double bonds with fewer than 1% vinyl side groups (Goodyear Tire and Rubber Company) [201]. The PP ionomers have also been subsequently hydrogenated and the effect of backbone crystallinity on the ability of the ions to phase separate has been investigated

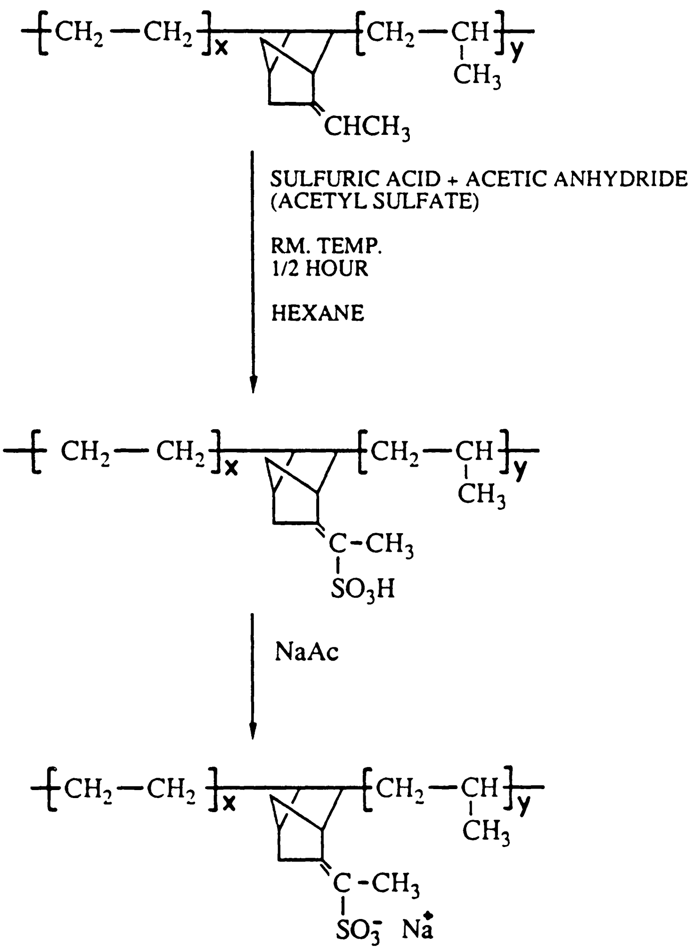
Scheme XI

Sulfonation of Poly(styrene) [195,196]



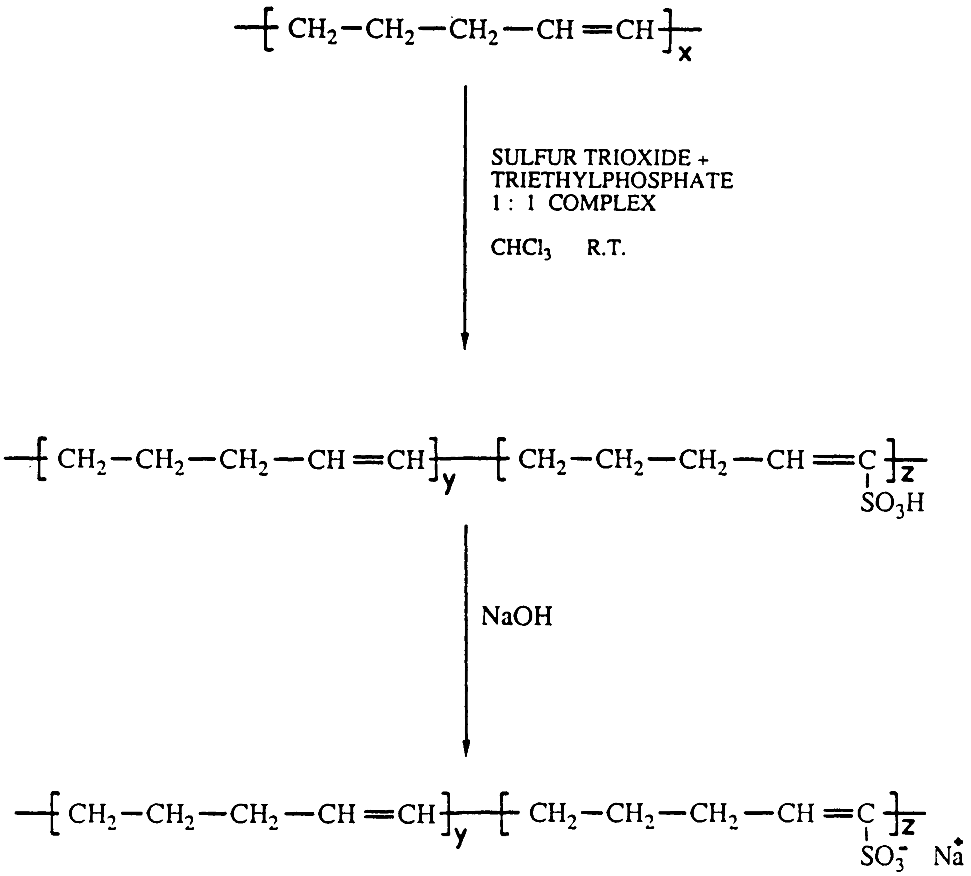
Scheme XII

Sulfonation of EPDM [200]



Scheme XIII

Sulfonation of Poly(pentenamers) [201]



[202]. This unique polymer provides for a model system which can contribute to the understanding of the effects of ionic domains on polymer morphology.

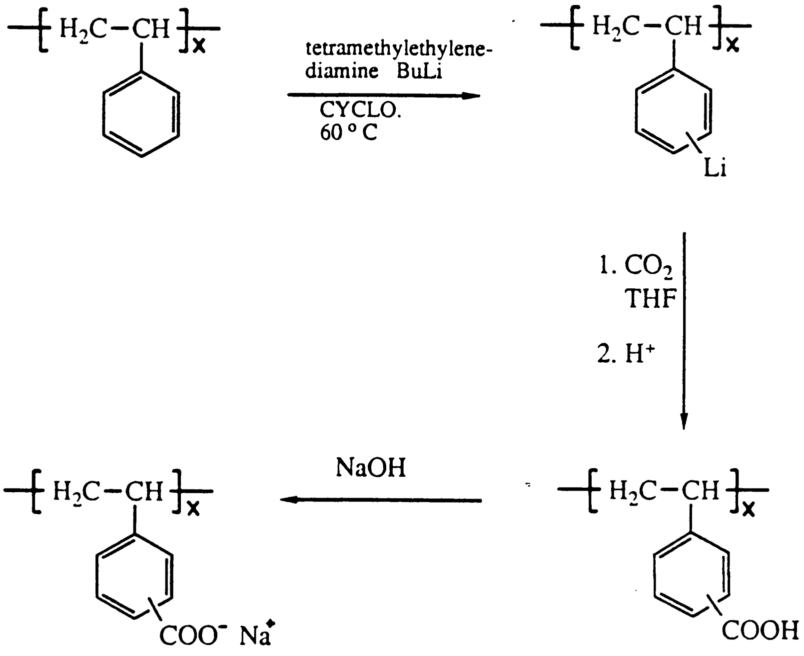
The sulfonation of poly(isoprene) using acetyl sulfate is accompanied by extensive cyclization [203]. It was found that cyclization is the primary reason for the increase in the glass transition temperature. However, the melt viscosity and shear moduli are affected in a similar manner to other ionomers.

Subsequent carboxylation reactions on polymer substrates have also received significant attention. Examples of carboxylation of pendant aromatic rings such as in poly(styrene) [204] and backbone benzene rings, e.g. poly(phenylene oxide) [205], can be found in the literature. Scheme XIV illustrates the carboxylation of poly(styrene) using butyllithium in cyclohexane at 60°C. The presence of a polar modifier such as tetramethylenediamine is required in order to promote lithiation [206]. The phenyllithium is reacted with a solution of carbon dioxide in tetrahydrofuran.

The homogeneous lithiation and subsequent carboxylation of poly(styrene) containing a maximum of 14 mole% p-bromostyrene has also been reported [206]. The synthetic approach is shown in Scheme XV. By this technique, poly(styrene) in which a 100% of the original bromine groups had been replaced by carboxyl functionalities was obtained.

Scheme XIV

Carboxylation of Poly(styrene) [206]



The carboxylation of poly(pentenamers) has also been accomplished and described in detail [176].

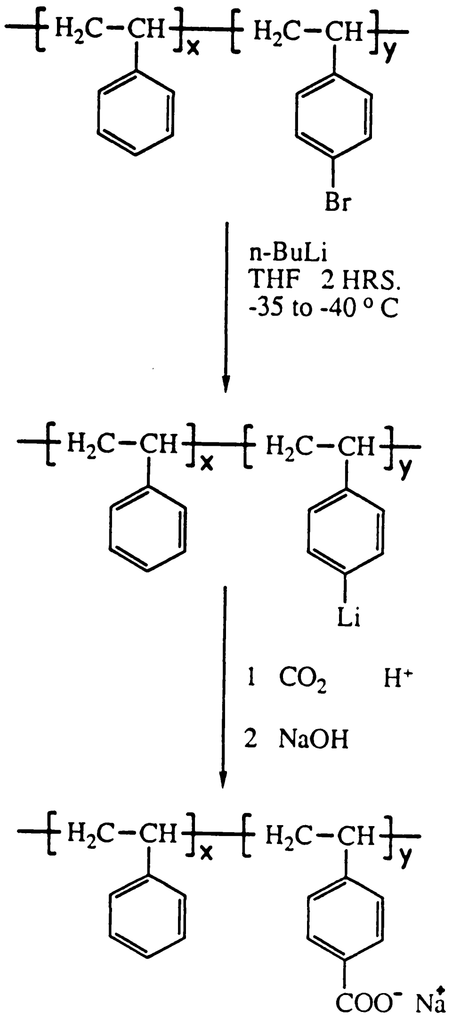
A final approach involving post reactions on polymers is the deprotection of functional groups after copolymerization. A recent example by Eisenberg et al. reports the preparation of poly(styrene-co-4-hydroxy styrene) ionomers (3.0-22 mole%) via the neutralization of demethylated poly(styrene-co-4-methoxystyrene) [207]. The synthetic procedure is represented in Scheme XVI. Scattering and torsion pendulum studies indicate that these materials phase separate in a similar manner as other ion-containing systems. Eisenberg and Clas have demonstrated an alternate route involving the chloromethylation of poly(styrene), followed by esterification, hydrolysis and neutralization [208]. However, no evidence of extensive ion clustering is observed in this latter case.

c) Synthesis of Telechelic Ionomers

All of the ion-containing polymers that have been described above contained ionic groups randomly placed along the polymer backbone. Telechelic ionomers are a special class of materials which contain ionic groups only at the chain end(s). Goodrich has commercialized telechelic poly(butadiene) under the trade name of Hycar for specialty applications [187]. Hycar is a difunctional, carboxylic acid terminated polymer which can be neutralized with a base to generate the terminal metal carboxylates. Two approaches

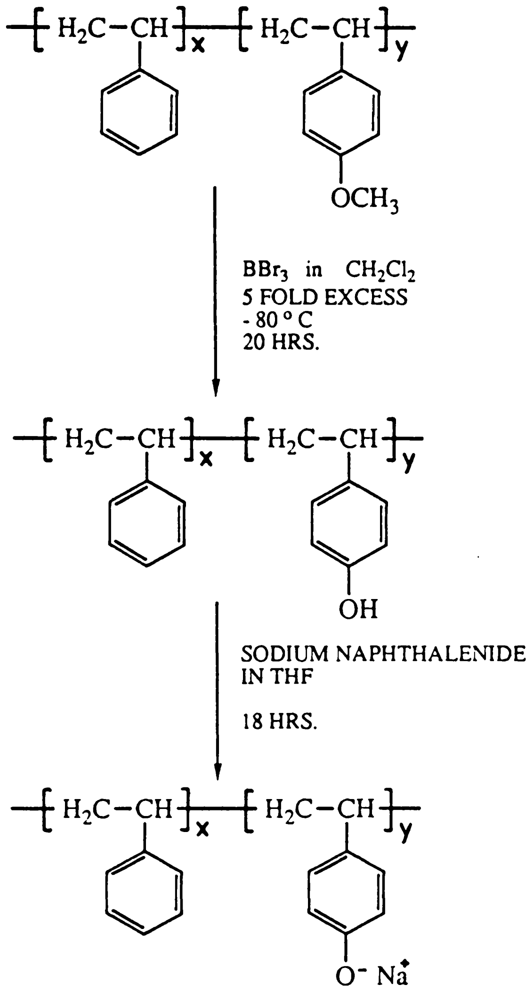
Scheme XV

Carboxylation of p-Bromostyrene Containing Poly(styrene) [212]



Scheme XVI

Demethylation and Neutralization of p-methoxy Containing Poly(styrene) [207]



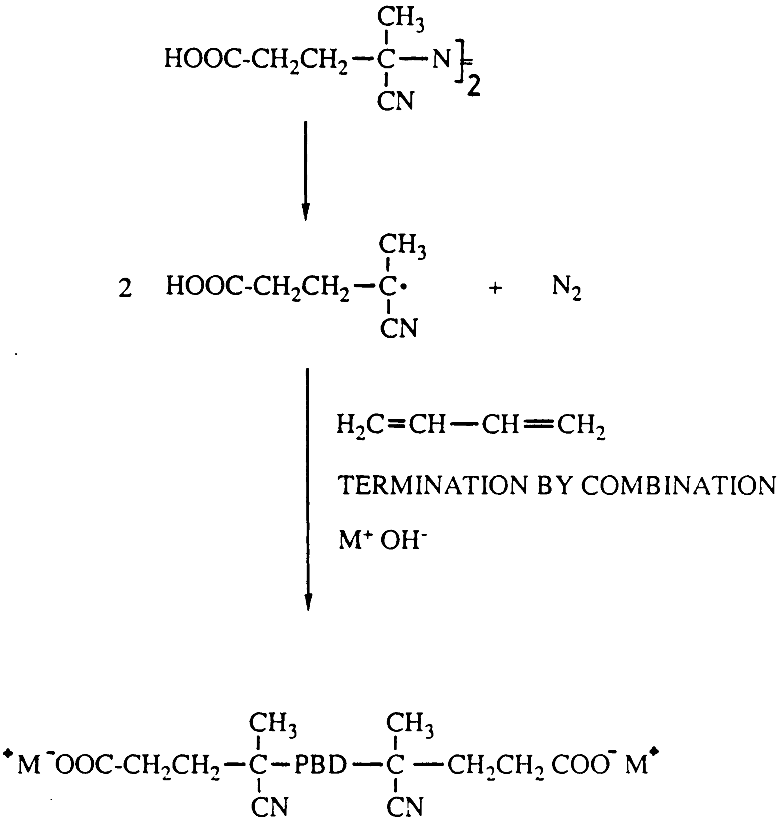
have been developed for the preparation of telechelic poly(butadiene). In principle, the two techniques can be utilized to synthesize many different difunctional telechelic systems. It should be noted that monofunctional telechelic ionomers are not as interesting because one end would be allowed to dangle free and the physical properties would not be as attractive.

A free radical initiator which contains carboxylic acid groups can be utilized to generate telechelic poly(butadiene) and poly(butadiene-co-acrylonitrile) elastomers [200]. These initiators are generally employed at reaction temperatures ranging from 70°C to 130°C. The formation of the functional initiator radicals, propagation and termination by combination are illustrated in Scheme XVII. The selection of the solvent is critical because any chain transfer will destroy the functionality of the polymer. Thus, t-butanol, acetone and tetrahydrofuran are typically employed. The neutralization process with a variety of bases and the ultimate physical properties have been described by Teyssie et al. in detail [209,210].

Anionic polymerization can also be utilized to prepare difunctional carboxylate or sulfonate telechelic ionomers [211]. This approach allows for polymers with narrower molecular weight distributions than the corresponding free radically prepared systems. However, in order to generate materials with molecular weights ranging from 1500 g/mole to

Scheme XVII

Synthesis of Telechelic Carboxylate) Poly(butadiene) via Free Radical Initiation [200]



CAN BE PREPARED BY ANIONIC POLYMERIZATION ALSO

5000 g/mole, large quantities of initiator are required. α-Methylstyrene sodium tetramer can be used as the difunctional initiator and deactivation of the macroanions with carbon dioxide generates terminal carboxylic acid groups. In addition, the macroanions can be terminated with propane sultone or 1-chloro-3-(dimethylamino)propane to generate telechelic sulfonic acid or tertiary amino end groups respectively. Carboxy terminated polymers that have been neutralized have good adhesion and are useful as hot-melt adhesives, thickeners for oils and lubricants, and impact modifiers for poly(vinylchloride) [212]. Teyssie et al. have also introduced the notion of preparing block copolymers of poly(styrene) and poly(butadiene) via ionic interactions [213]. Blending two immiscible telechelic polymers capped with acid and tertiary amine functions is also expected to promote coulombic interactions between the end groups. This phenomenon would promote the formation of multiblock copolymer behavior.

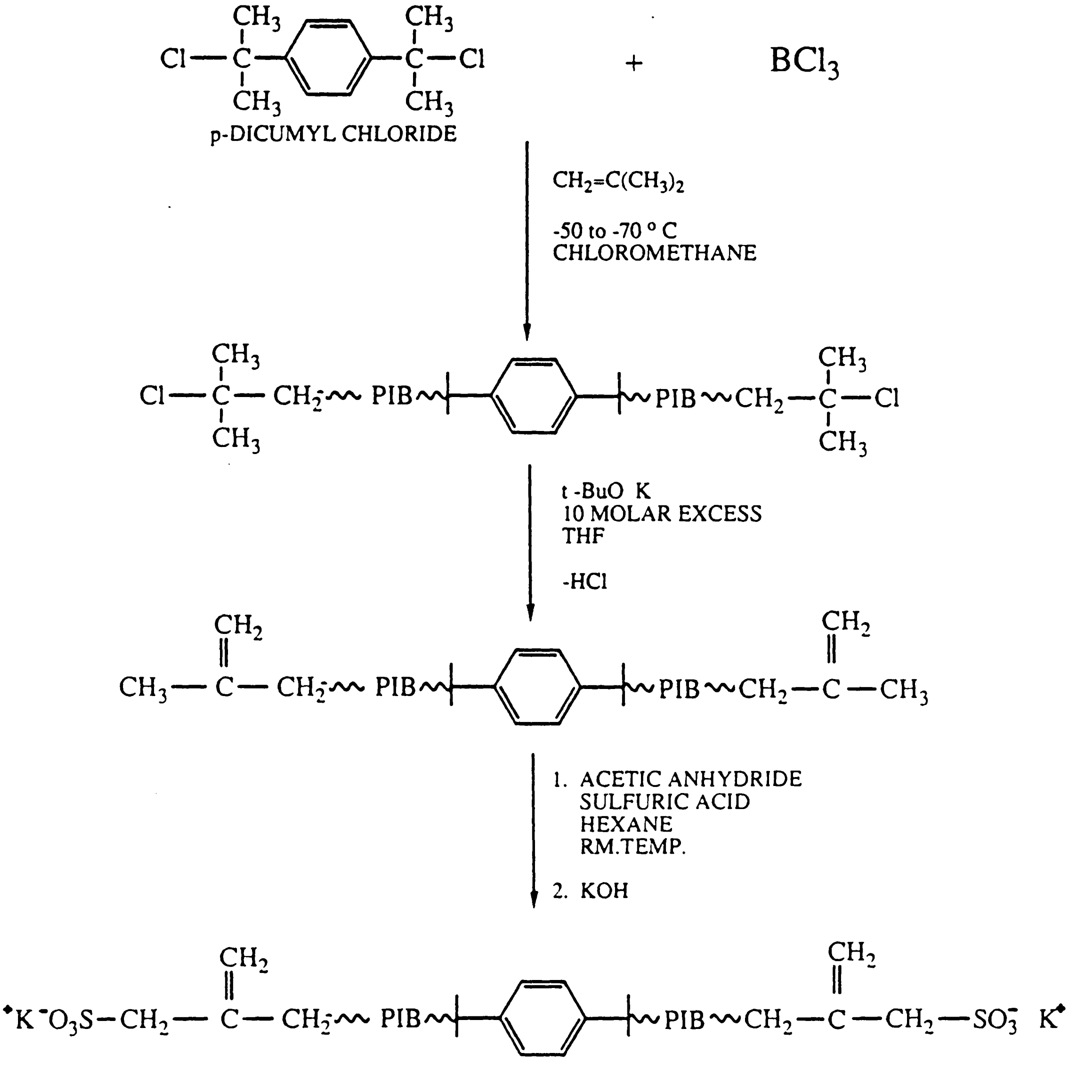
Kennedy has devoted significant attention to the preparation of difunctional telechelic poly(isobutylene) via a cationic mechanism which has been termed the inifer method [214]. Inifer is an acronym for initiator-transfer since the dicumyl chloride initiator also serves as an efficient chain transfer agent. Thus, each poly(isobutylene) chain contains the dicumyl residue in the center of the chain and a chlorine at each terminus. The polymerization is depicted in Scheme XVIII. Subsequent reactions on the chlorine containing end groups has lead to the preparation of olefin or primary alcohol groups [215]. In addition, a tricumyl chloride initiator (trinifer) leads to a 3-arm star telechelic polymer. Subsequent sulfonation (Scheme XVIII) of the olefin terminated difunctional and trifunctional telechelic polymers leads to the preparation of model telechelic ionomers. Wilkes and coworkers have investigated the mechanical properties of the telechelic sulfonate ionomers in detail [216].

d) Synthesis of Block Ion-Containing Polymers

This area of ionomer synthesis has received only sparse attention in the available literature. In fact, detailed studies of the effect of ion placement on ionomer morphology and mechanical properties have not been found. McGrath et al. have introduced the concept of ion-containing block copolymers where the ionomer block was prepared by hydrolysis of poly(alkyl methacrylates) [217,218]. The synthetic approaches will be described in detail later. However, due to limited yields of the hydrolysis reaction, the ionomer blocks actually contained residual alkyl methacrylate units. Eisenberg and Gauthier have recently demonstrated the preparation of poly(styrene)-b-poly(4-vinylpyridinium) ABA block ionomers [219]. Both McGrath and Eisenberg observed only one glass transition temperature by DSC for the neutral blocks. This thermal behavior is

Scheme XVIII

Synthesis of Telechelic Poly(isobutylene) [214]



MONO AND TRIFUNCTIONAL MATERIALS PREPARED ALSO reminiscent of the poly(styrene-co-styrene sulfonates) that were prepared by emulsion polymerization of styrene and sodium styrene sulfonate. Eisenberg also demonstrates that these cationic block ionomers do form well defined ionic domains unlike the corresponding random systems. The extreme difficulty in drying these materials has been attributed to the poly(styrene) surrounded ionic domains which should contain a large number of ions.

3) Characterization of Ionomers

In 1970, A. Eisenberg formulated a very comprehensive theoretical treatment of the spatial arrangement of salt groups in ionomers [220]. This work has been frequently referenced and represents an excellent first approximation to the structural nature of ionomers. It was this publication that many of the terms associated with ionomers were established. Eisenberg's theory attempts to unify the many divergent conclusions that existed prior to 1970. Eisenberg concluded that the size of the domains depended on the concentration of ionic functionality in the polymer matrix. It was further concluded that at a high enough concentration of ions, clustering of ions would take place. This concentration was termed the critical ion concentration (CIC) and it represents the concentration at which ion clustering is energetically favorable. Thus, a multiplet is a group of ion pairs with no intervening hydrocarbon backbone and a cluster which contains backbone is the result of further aggregation of multiplets.

The first idea of ionic clusters was conceived by Bonotto and Bonner in 1965. In 1968, a model depicting small clusters was presented, but it was unclear whether these domains were clusters or multiplets in the terminology defined later by Eisenberg [221]. Since these initial postulations, a countless number of studies have appeared in the literature in an attempt to model the ionomer morphology [222-226]. In most cases, an electrostatic and elastic component are considered to play important roles in defining the nature of the ionic domains. Many of the proposed morphological models are based on the analysis of scattering data. The most convincing evidence for the existence of clusters comes from Small Angle Xray Scattering (SAXS) data [227]. Despite the abundance of academic and industrial attention, the postulation of models for the clustering of multiplets continues [228,229]. Recently, a variety of workers have studied the aggregation in a series of telechelic butadiene and isoprene polymers [230]. It was observed that the characteristic SAXS intensity profile was governed by the configuration of the polymer between the ionic groups and the nature of the cation played only a secondary role. Most interestingly, there is nearly complete microphase separation between the ionic groups and the hydrocarbon chain if there is a narrow molecular weight distribution. The domains were described as multiplets and no evidence of ionic clustering was found.

Due to the vast amount of literature describing the characterization of ionomer properties, an attempt will not be made to present a comprehensive literature review. Instead, each molecular parameter as outlined above for ion-containing systems will be addressed and examples of their primary effects on physical properties will be given.

a) The Backbone

It has been demonstrated that the efficiency of the increase in Tg with ion concentration depends on the host material [231]. As the Tg of the backbone polymer decreases, backbone motion and thus cluster formation are greatly facilitated. The work required to stretch the chains between ionic groups relates to the formation of clusters. Table 15 depicts several host polymers and their respective critical ion concentrations (CIC) [231]. When comparing polyethylene, polystyrene and poly(ethyl acrylate), an increase in the dielectric constant parallels an increase in CIC.

The presence of ions also has been shown to decrease the rate of polymer chain relaxation in stress relaxation experiments. Time-temperature superposition is possible only at certain critical ion concentrations where only one relaxation mechanism is present [232]. Upon the generation of a secondary relaxation mechanism, superposition is not possible. In particular, above a critical ion concentration

Table 15

Critical Ion Concentrations (CIC) for Various Carboxylated Polymer Backbones [231]

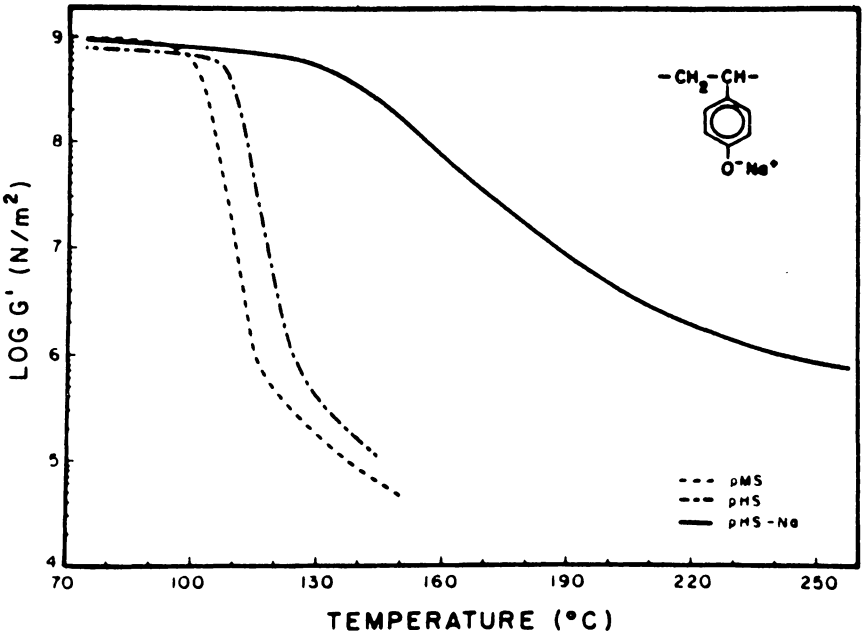
Material	Critical Ion Concentration (mole %)
Polyethylene	1
Poly(styrene)	4-6
Poly(ethyl acrylate)	10-15

(5-6 mole%), a secondary relaxation develops which many workers claim to be due to the formation of clusters.

The incorporation of ions into a polymer results in the modification of the mechanical properties of the polymer matrix [208]. As the ion concentration increases, the loss tangent and storage modulus (G') have been shown to shift toward higher temperatures. Figure 7 shows the modulus versus temperature behavior for the sodium salt of poly(styrene-co-4-hydroxystyrene) and its precursors. The shift is the result of the increase of the glass transition temperature of the nonionic matrix. The formation of ionic aggregates or "crosslinks" tends to restrict the main chain backbone motion. The existence of a second peak at higher temperatures in the tan delta curve and a decrease in the slope of the storage modulus curves with increasing ion concentration have been related to phase separation [233].

b) Ion Concentration

The concentration of ions incorporated into a polymer has been shown to have a drastic effect on the bulk properties of the resulting polymer [234]. Much evidence does exist for a difference in morphology below 6 mole% (the typical CIC value) where multiplets dominate and above 6 mole% where cluster formation is preferred. Many experiments suggest that multiplets and clusters coexist over a large concentration range and at 6 mole% clusters begin to dominate a wide range of properties. It is



The storage modulus (*G'*) as a function of temperature of polystyrene-co-15.3%-4-methoxystyrene (pMS), -4-hydroxystyrene (pHS), and its sodium salt (pHS-Na).

Figure 7: Modulus Versus Temperature Behavior For Poly(styrene-co-4-hydroxystyrene) Sodium Salt [208]

important to realize that a cluster is a very dynamic phase and its structure is continuously changing as ions leave and enter [235].

The most concrete evidence for a change in morphology due to ion concentration is provided by SAXS. For example, in styrene based systems, a low angle peak appears for the sample containing more than 6 mole% of ionic functionality [236]. The "ionic peak" is due to cluster formation or domination over multiplets.

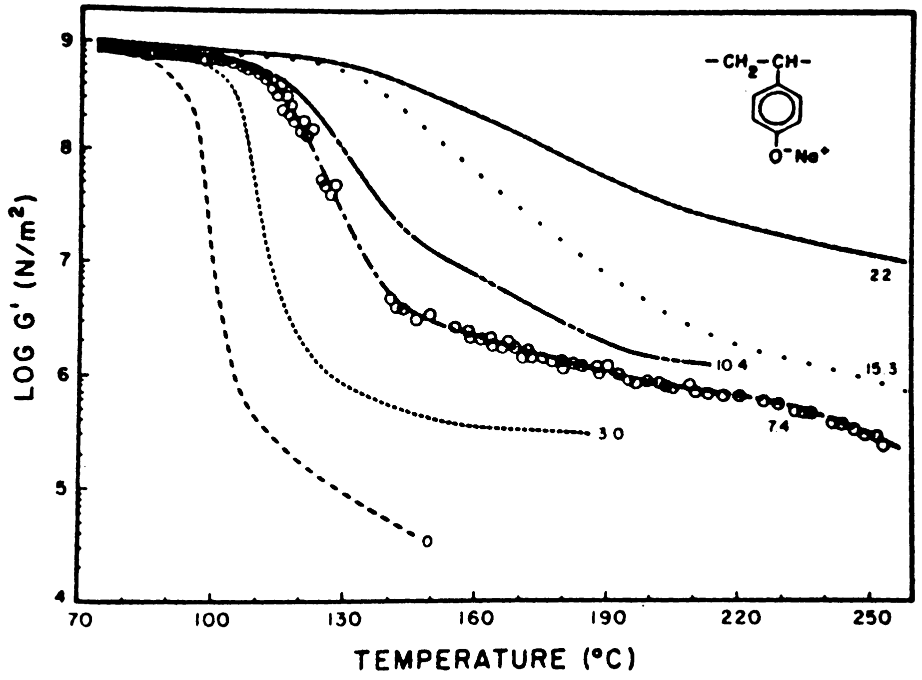
The concentration of ionic groups has a large effect on such properties as the melt viscosity and the tensile strength [204]. Both viscosity and tensile strength increase with small concentrations of ions. But, substantially different tensile properties exist for different base polymers. For example, in polyethylene based polymers, crystallinity may impart extra strength and complicate the analysis. Despite this phenomenon, the tensile results closely parallel the viscosity measurements by demonstrating in increase in cohesive nature.

Eisenberg has shown a linear increase in Tg with ion content (10 mole% maximum) in styrene-methacrylic acid systems [237]. Recently, the effect of ion concentration was investigated for the sodium salts of poly(styrene)-co-poly(4-hydroxystyrene) systems [208]. Figure 8 depicts the corresponding modulus versus temperature behavior for these polymers. Typically, a discontinuity does not exist in the values of Tg at 6 mole%, but a gradual development of clusters would prevent this observation. A large energy dissipation region above the Tg is noted and this feature has been postulated to be the Tg of the clustered ionic regions.

c) Type of Pendant Ionic Group

Lundberg and Makowski have recently published a report which compared metal sulfonates (S) with metal carboxylates (C) [204]. All materials consisted of poly(styrene) (PS) backbones of nearly identical molecular weight and molecular weight distribution. The determined melt viscosity for S-PS was 2-3 orders of magnitude greater than C-PS analogues. Both materials contain the same extent of ionic functionality. This study demonstrates that stronger ionic interactions exist for S-PS compared to C-PS over a range of concentrations studied. A very dramatic effect can also be seen by noting the softening behavior by thermomechanical analysis (TMA) for these two compression molded systems (Figure 9). In both cases, an increase in the glass transition temperature is evident compared to the PS control. For C-PS, the Tg is followed by a plateau which persists to temperatures greater than 150°C. On the other hand, the S-PS plateau extends to temperatures near 225°C indicating that the ionic interactions are much stronger for S-PS than for C-PS.

Similar results were obtained from dilute solution



The storage modulus (G') as a function of temperature of the sodium salts of polystyrene-co-4-hydroxystyrene, for different ion contents (3.0–22 mol%; 0 is for pure polystyrene[13]).

Figure 8: Effect of Ion Concentration on the Modulus Versus Temperature Behavior for Poly(styrene-co-4-hydroxystyrene) Sodium Salt [208]

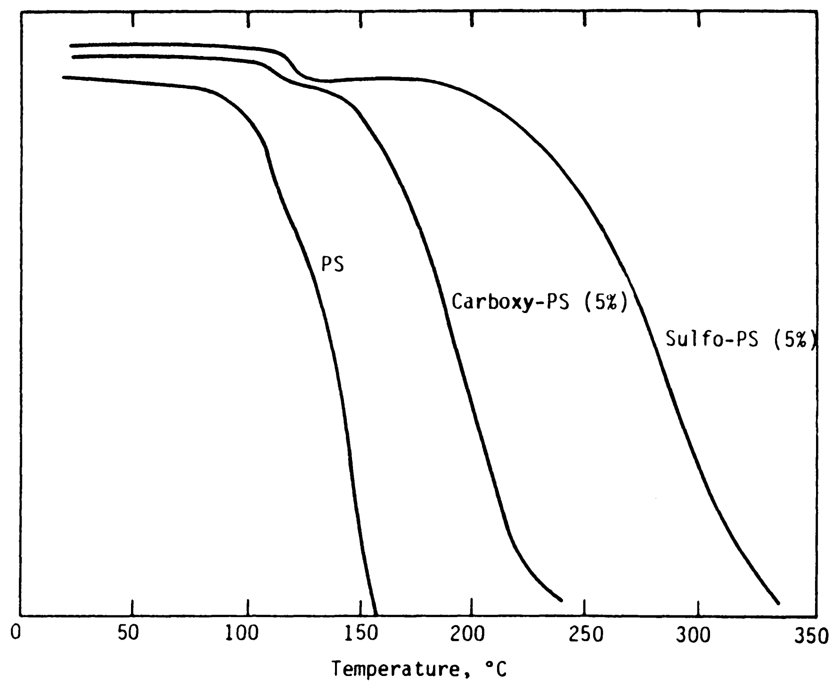


Figure 9: Thermomechanical Behavior for Sulfonated (S)
and Carboxylated (c) Poly(styrene) (PS) [204]

viscosity studies. The interactions are stronger and persist to higher temperatures in all situations studied. The greater degree of interactions for the metal sulfonates has been attributed to the greater polarization in the sulfonate ionomer compared to the carboxylate analogues.

d) <u>Extent of Neutralization (0-100%)</u>

When dealing with this parameter, one is essentially analyzing the effect of acid groups on ionic interactions. For example, if neutralization is complete only to 60%, then 40% of the original acid groups remain.

Eisenberg has investigated partially neutralized poly(styrene-co-methacrylic acid) samples [170]. In stress-relaxation master curves of samples containing 4.6% MAA neutralized to various extents with sodium, the upper inflection disappears when neutralization is less than 50%. The authors attribute this to the failing of the ionic domains to serve as crosslink points below 50% neutralization. Also, calculations of apparent crosslink density for 60% neutralized samples indicate values comparable to densities of only 25% of totally neutralized samples. For very low degrees of neutralization that still represent a significant ionic content, the inflection points are poorly developed. This seems to present a very negative effect of residual acid groups. Eisenberg proposes that the unneutralized COOH groups participate in the multiplets and clusters and effectively weaken the interactions. This is analogous to a polar solvent plasticizing an ionic domain. It is proposed that an exchange mechanism is taking place between the acidic hydrogens and the counterions associated with the carboxyl groups.

e) Nature of the Cation

The type of cation can be important in the determination of rheological and mechanical properties [195]. Typically, the Tg remains constant for various counterions implying the matrix is unaffected by the ionic phase. Although an abundance of work has been done regarding this parameter, it is very difficult to make generalizations [238]. Some workers have postulated that a bulkier cation, e.g. ammonium, results in a much looser network [239]. However, many contradictions can be found in the literature. In most cases, other parameters such as the ion concentration or degree of neutralization are overwhelming factors.

Wilkes has recently commented on the role of the cation type on ionomer properties [240]. Earlier investigations had demonstrated that the ionic potential (q/a, charge to ion size ratio) is an important parameter and is capable of rationalizing many early observations [241,242]. However, Wilkes has postulated that an additional parameter which is termed the ionic/covalent ratio deserves attention. Thus, the electronic configuration , which defines the covalent nature of the atom, can be used as a predictive tool. As electrons are introduced into the $3d^{10}$ level, e.g. zinc, the nucleus is less shielded and hence the atom is more polarized. An easy method for predicting covalent nature is to note the melting point of corresponding salts. The higher melting points are more typical of ionic crystals. These concepts have helped to further rationalize physical and rheological properties of both the solid and melt states.

Figure 10 demonstrates an interesting effect of cation type on the water sensitivity of ionic polymers [243]. The order of water sensitivity was predicted by the authors with the exception of the barium cation. In addition to the effect of cation type on the mechanical and rheological properties of the polymer, the hydrophilicity of the system is also affected.

f) Polymer Architecture

The investigation of the role of ion location has not been extensively explored, but is certainly a variable that will contribute to the ultimate physical properties. As mentioned earlier, the synthesis of telechelic ionomers allows for the correlation of ion location with physical properties. In addition to the work of Eisenberg and McGrath, Kennedy and Wilkes have performed detailed analyses of the effect telechelic functionality on the mechanical properties of poly(isobutylenes) [216,244,245]. Figure 11 depicts the thermomechanical analysis curves for various

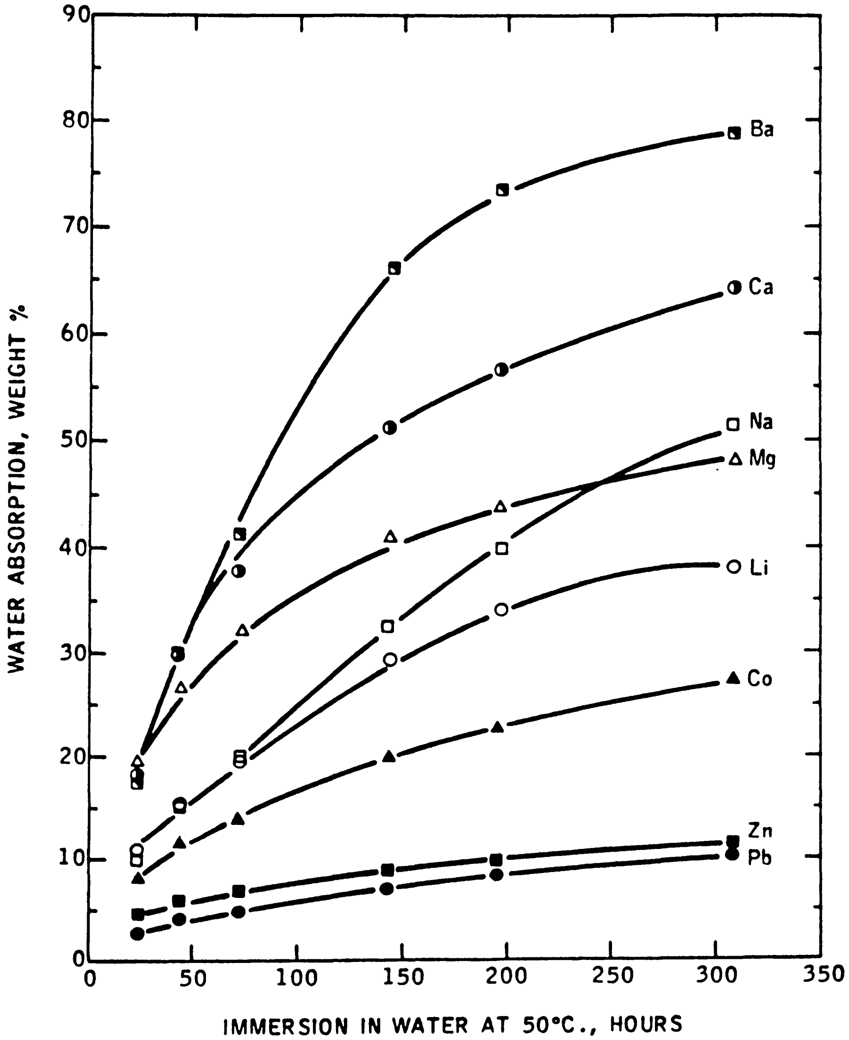


Figure 10: Effect of Cation on Water Sensitivity of Ion-Containing Polymers [243]

sulfonated poly(isobutylene) ionomers. In this figure, the difunctional (D) and the trifunctional (T) potassium (K) sulfonates demonstrate the development of an extended plateau. On the other hand, the monofunctional (M) polymers readily flow above their Tg. Investigations of the mechanical properties of carboxylato-telechelic poly(isoprene) have also been recently reported [246].

The rheological behavior of the poly(isobutylene)-based model elastomeric ionomers has been investigated [245]. Despite the placement of ionic groups only at the chain ends, significant ionic interactions exist in the melt even at 180°C. The triarm based systems are more viscous than the monofunctional polymers. These preliminary mechanical and rheological studies demonstrate the role of ion location on the physical properties of ion-containing polymers.

4) Miscellaneous Systems

This review has focused on polymer backbones which have received the most attention i.e. styrene, dienes, acrylics and other polyolefins. Ions have been introduced into many different polymer backbones. An abundance of work has been recently focused on poly(urethanes) [247,248] and poly(alkylene oxides) [249,250]. The reader is directed to the many review papers and books for a better appreciation of the vast number of ion-containing polymeric systems.

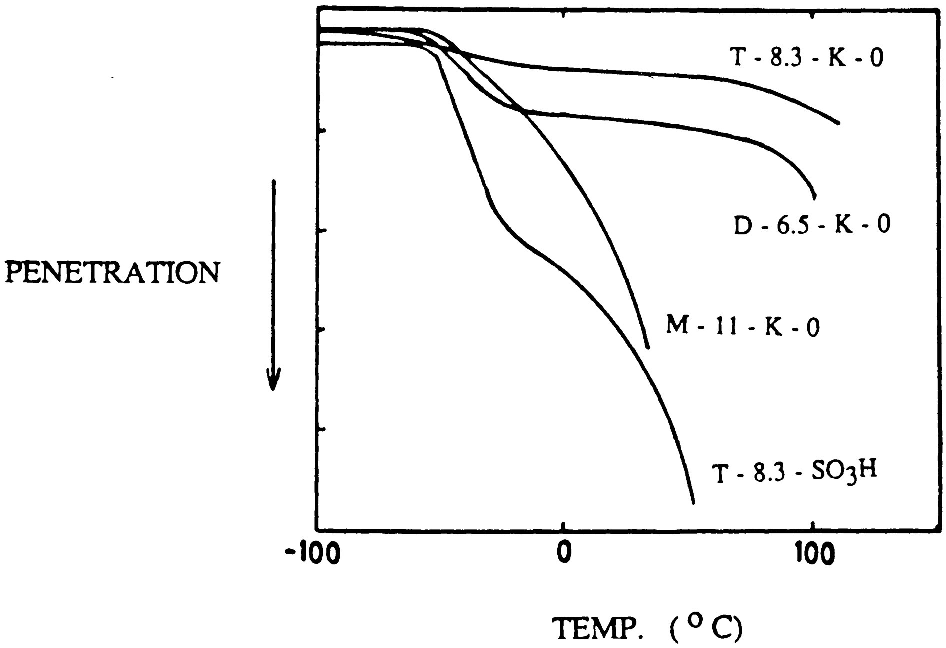


Figure 11: Thermomechanical Behavior for Various Sulfonated Telechelic Poly(isobutylene) Ionomers [259,260]

III. EXPERIMENTAL

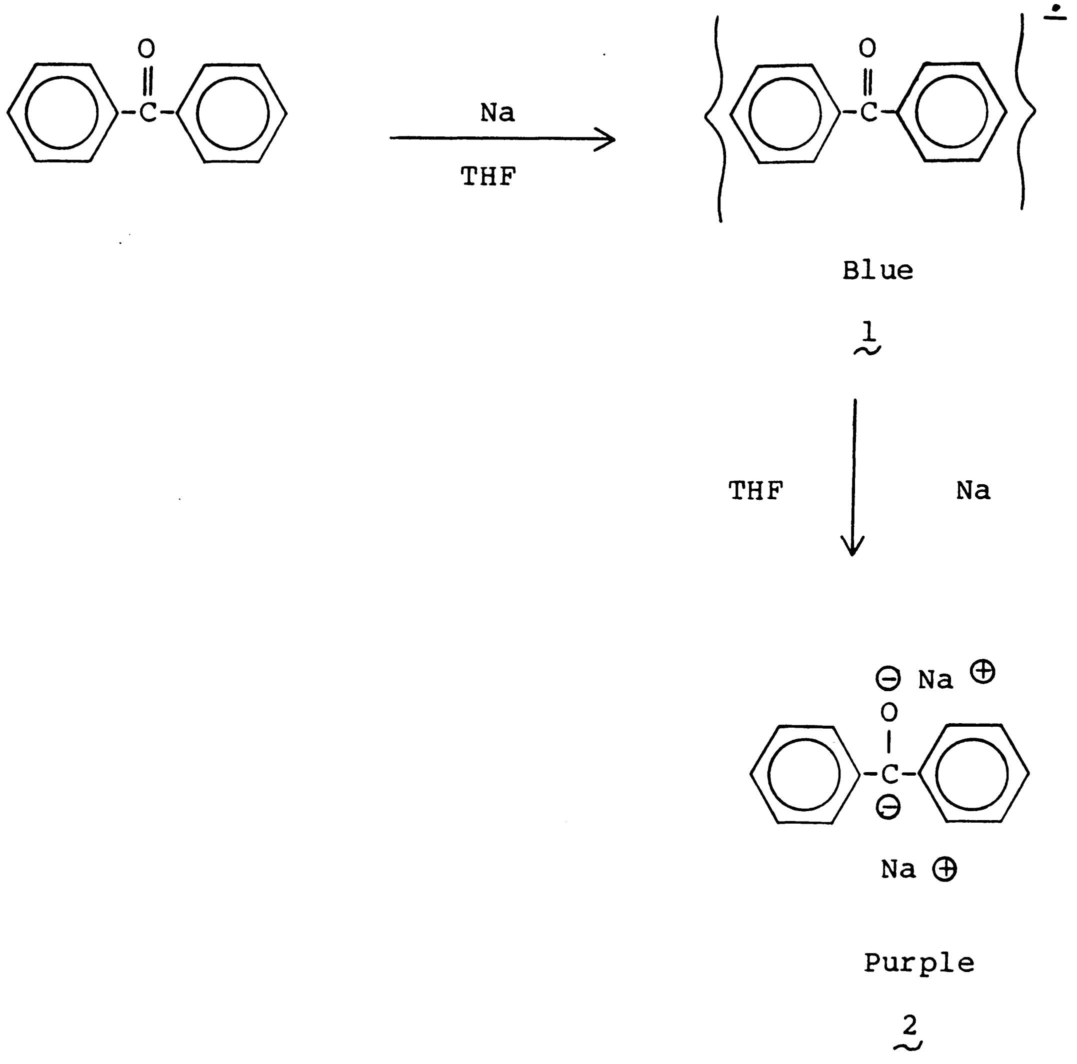
A. Reagents and Purification

1) Polymerization Solvents

a) Tetrahydrofuran (THF) (Fisher, Certified Grade) was placed in a 1000 mL, 1 neck, round bottom flask equipped with a teflon-coated stir bar and allowed to reflux under a nitrogen atmosphere for 2-3 hours in order to remove dissolved oxygen. After cooling under nitrogen, the distillation flask was removed from the distillation column and several grams of sodium metal dispersed in paraffin wax (Aldrich) were added via a powder funnel to the degassed THF. The sodium metal dispersed in the paraffin wax was preferred due to the high surface area of the sodium after complete dissolution of the paraffin wax. Thus, drying was accomplished more efficiently compared to using sodium metal balls. Approximately 0.1-0.3g of benzophenone (Aldrich) were added to the mixture of THF and dispersed sodium and allowed to stir under nitrogen. It is important to use an excess of sodium in order to prevent distillation of the benzophenone. The function of the benzophenone is not for purification, but is needed only for indication of purity. Immediately one could see the formation of a deep purple color associated with the formation of the sodium/benzophenone ketyl. The chemistry of the ketyl formation is depicted in Scheme XIX.

Scheme XIX

Sodium/Benzophenone Ketyl Formation [251]



The formation of the ketyl (2) is accomplished via the initial formation of the radical anion (1) which is blue colored. It is well known that Group IA metals react with benzophenone in this manner [251]. Thus, unless the deep purple color appeared ensuring complete conversion to the dianion, the THF was not completely dry and degassed. If the ketyl at anytime was exposed to the air or moisture, then the color changed to green and after extensive exposure, the contents turned yellow. Revitalization of the ketyl was easily accomplished by degassing as described above and subsequent addition of a small amount of benzophenone (0.1g). It was not necessary to add additional sodium because an excess was used in the initial addition.

The ketyl in THF was allowed to reflux under nitrogen for 2-3 hours prior to collection of the distillate. Approximately 50-100 mls were removed as a first fraction followed by collection into a clean, oven-dried 1000 ml round bottom flask. In most cases, the receiver containing the pure THF after distillation could be quickly fitted with a rubber septum under a positive flow of nitrogen. The septum was secured in place with copper wire in order that a positive pressure of nitrogen could be maintained.

Despite this rigorous purification technique and successful formation of the purple ketyl, polymerization attempts in the pure THF indicated approximately 0.5-1.0 mmoles of impurities/1000 mls THF. Unless the synthesis allowed for titration of impurities prior to polymerization, these small quantities of impurities lead to premature termination of the subsequent "living" polymerization. The impurities were most deleterious when THF was used as a polar modifier and added directly to an anion [252]. Thus, an additional vacuum distillation of the once distilled THF was required in this situation.

Sodium and benzophenone were added to the receiver flask in the ratio described earlier and the THF was allowed to distill onto the heterogeneous mixture. Upon collection of the distillate, the paraffin dissolved and the ketyl was readily reformed. After complete distillation, the receiver was fitted onto the apparatus shown in Figure 12. Degassing was again accomplished by cooling side A with a dry ice/isopropanol mixture and applying vacuum through the 3-way stopcock slowly in order to avoid bumping. If vacuum was applied too quickly, then a "skin" developed on the THF surface and proper degassing was not achieved. After good vacuum was obtained (500 millitorr), the apparatus was flamed while applying vacuum. Once the apparatus had cooled, the system was closed under vacuum and the cooling bath on the left side was replaced with a water bath. First, the contents of the distilling flask were allowed to reach room temperature. Then the receiver was cooled with a dry ice/isopropanol bath slowly in order to avoid bumping. After complete vacuum distillation of the THF, the system

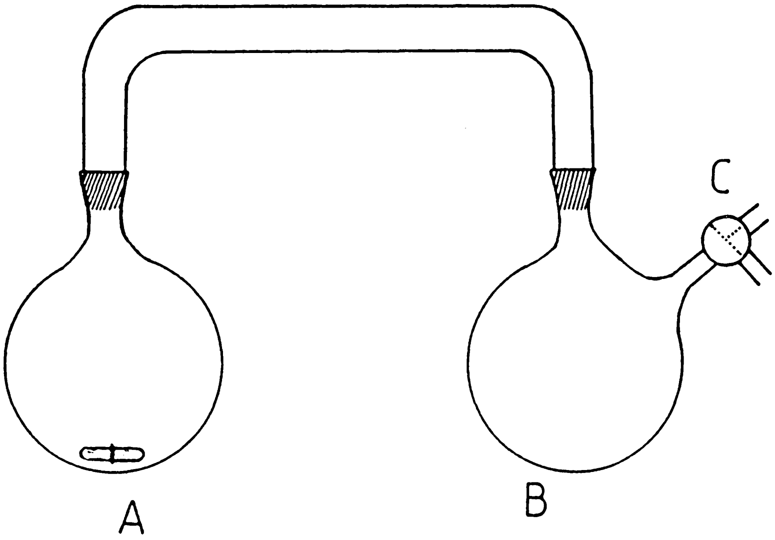


Figure 12: Vacuum Distillation Apparatus for THF

was filled with prepurified nitrogen and used immediately. By observing the purple color of the residue in the distillation flask, one could be confident that the system had remained moisture-free.

b) Toluene (Fisher, Certified Grade) was first distilled under nitrogen from finely dispersed sodium in paraffin wax according to the same procedure as described above for THF. Although benzophenone can be added to form the indicating ketyl, this was generally not done due to the less distinct purple color in toluene. After distillation, the receiver was removed from the distillation apparatus under a positive flow of nitrogen. The receiver flask could be fitted with a rubber septum and secured in place with copper wire. In most cases, polymerization attempts with sodium-pure toluene lead to slow termination of the "living" anion presumably due to the inefficient removal of certain protonic impurities. Thus, further purification was necessary in order to obtain anionically pure toluene.

Styrene monomer (Aldrich) was passed through a column of alumina and silica and degassed under vacuum. A small amount of the column-pure styrene (2-3g) was syringed into the flask containing toluene. The appropriate charge, e.g. approximately 1.0 mmole for 2g styrene, of sec-butyl lithium to generate a polystyrene oligomer with a molecular weight of 2000 g/mole was syringed into the toluene containing styrene. Immediately one could witness the formation of the orange poly(styryl) lithium anion. The toluene was typically allowed to stir in the presence of the anion for 2-3 days. One could be confident that the toluene was anionically pure if the intensity of the orange anion persisted during the stirring period. The toluene flask was placed on an apparatus similar to that was used for the vacuum distillation of THF and distilled under vacuum according to the same procedure. However, due to the higher boiling point of toluene (110°C), bumping was not a concern and higher water bath temperatures were generally required (25-30°C). The anionically pure toluene was used immediately; however, one could be assured of proper storage by observing the persistent, orange color in the distillation flask.

c) Cyclohexane (Fisher, Reagent Grade) was stirred in the presence of concentrated sulfuric acid at room temperature for 5-7 days to remove unsaturated impurities [253]. Cyclohexene is the major impurity in most commercially available grades of cyclohexane and the allylic protons are exceptionally labile to abstraction by strong bases. Thus, one can render the unsaturated impurity water soluble by sulfonation. After stirring, the two layers were allowed to settle out and the cyclohexane layer was decanted. Special caution was taken to avoid accidental decanting of the acidic layer. The decanted cyclohexane was placed in a 1000 ml, round bottom, one-neck flask and 2-3g of sodium dispersed in paraffin were slowly added. The cyclohexane was distilled under a nitrogen purge into a clean, oven-dry flask. After distillation was complete, the receiver was removed under a positive pressure of nitrogen and fitted with a rubber septum. The septum was secured in place with copper wire and the solvent could be stored under nitrogen pressure until use. However, immediate use is recommended in order to avoid possible contamination by the atmosphere due to leaky septa.

2) Initiators and Catalysts

a) Azobisisobutyronitrile (AIBN) (Dupont, VAZO 64) was used as received. The initiator (3) could either be stored as a solid or as a solution in benzene. The concentration of the solution was maintained in a constant range which was desirable for subsequent polymerizations. Typical polymerizations required 0.1 weight percent compared to total monomer charge. Since the half-life of AIBN is 10.0 hours at 64°C and 4.8 hours at 70°C, the initiator was commonly used in most polymerizations at 65-70°C [254]. This results in a fairly convenient decomposition time and corresponding reaction time.

b) 1,1-Diphenylethylene (DPE) (Eastman Kodak Company) was typically vacuum distilled from sec-butyl lithium. This purification approach was possible due to the inability of diphenylhexyl lithium (the reaction product of 1.0 mole of sec-butyl lithium with 1.0 mole of DPE) to initiate the polymerization of DPE. The crude, viscous liquid (bp.= 270 °C) was characterized by a yellow color. The difficulty in obtaining very pure diphenylethylene has been addressed in detail by a variety of workers [255]. In addition, DPE is a relatively expensive reagent to be used industrially as an initiator. Thus, significant efforts have been directed toward developing methods to circumvent the use of this reagent.

The apparatus for the distillation of diphenylethylene is shown in Figure 13. The diphenylethylene (50-100g) was transferred to the previously flamed apparatus via a double-ended needle (cannula). While cooling the distillation flask with a dry ice/isopropanol bath, the DPE was degassed by applying vacuum on the right side of the apparatus. Once the crude DPE froze (mp. = 4°C), the system was refilled with nitrogen and the frozen DPE was allowed to thaw. This approach is commonly referred to as the "freeze-thaw" technique and is used routinely for degassing reagents prior to purification. The "freeze-thaw" technique was performed several times to ensure that the DPE was properly degassed. sec-Butyl lithium (1.35 M in cyclohexane) was added dropwise to the degassed DPE while stirring at room temperature. Immediately, the crude DPE turned an olive green color. After further addition of sec-butyl lithium, the color changed to a dark brown. Finally, the contents of the flask turned to a deep, cherry red color which was indicative of

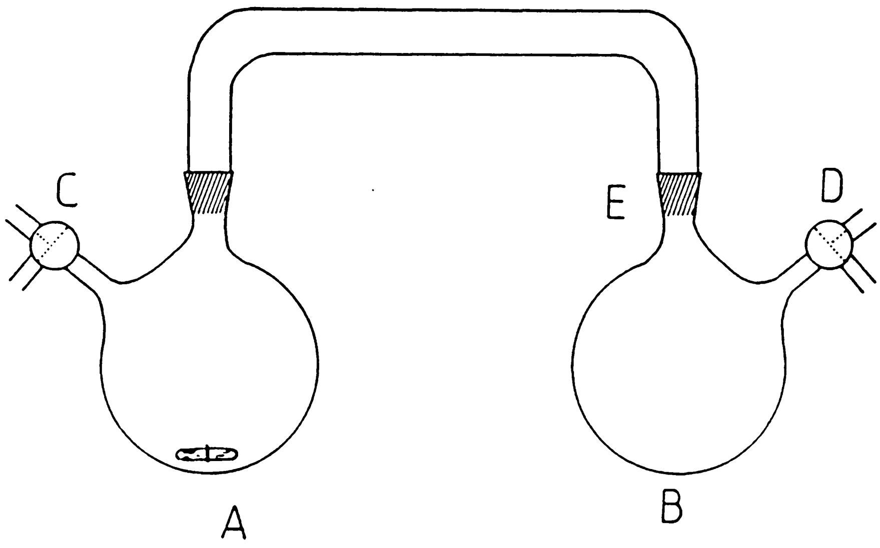


Figure 13: Vacuum Distillation Apparatus for DPE

the successful formation of diphenylhexyl lithium (DPHL). The color changes during titration have been attributed to the trace quantities of biphenyl and benzophenone impurities that are present in most commercially available grades of DPE [256]. When 50 grams of DPE were purified, 6.0-8.0 mls of sec-butyl lithium were typically required to arrive at the red endpoint. The titrated DPE was allowed to stir for approximately 30 minutes prior to freezing and evacuation. Due to the high boiling point of diphenylethylene, the vacuum stopcock was allowed to remain open for the duration of the distillation and liquid nitrogen was used to cool the receiver. In addition, the crosspath was covered with a heating strap and maintained at a high enough temperature to avoid premature condensation of the DPE. The distillation was complete after 2-3 hours at a water bath temperature of 55-65°C. The distillate was colorless and was transferred via a cannula to a dark bottle equipped with a septum. The pure DPE could be stored under nitrogen for relatively long periods of time (2-3 months) in the refrigerator without degradation. It was imperative to maintain a nitrogen pressure due to the facile oxidation of DPE to benzophenone. For this reason, it was desirable to purify only small quantities (<50 g) of DPE more frequently rather than allow larger stocks to stand for longer periods of time.

c) sec-Butyl lithium (Lithco Division of FMC) was available as a 1.35 M solution in cyclohexane and used as received. The solutions were typically stored in the refrigerator while not being used in order to avoid lithium hydride formation at room temperature. The molarity of the solution could easily be indirectly verified by polymerizing styrene via controlled anionic techniques and comparing the obtained molecular weight to the calculated molecular weight. In fact, if one plots the obtained molecular weight versus the calculated molecular weight, the plot should be linear. If the obtained molecular weight was different than the calculated molecular weight, then the active concentration of sec-butyl lithium could be determined. The polymerization could be repeated using the new molarity and closer molecular weights were obtained. In addition to this indirect method of determination, the sec-butyl lithium solution could be directly analyzed using the Gilman "double titration" method [257]. The "double titration" involves one titration for total base and another for alkoxide using 1,2-dibromoethane to selectively couple the alkyl lithium. Alkoxide is generally present in alkyl lithium reagents due to oxidation of the alkyl lithium [258]. Typically, the solution had a concentration ± 0.05 M compared to the nominal value. It should be noted that the molarity did change after long times presumably due to repeated contamination during syringe insertion. Thus, it was desirable to split the stock solution into smaller vessels in order to avoid contamination of the entire stock.

Handling of Pyrophoric Chemicals: Extreme caution was taken when handling alkyl lithium reagents due to their highly reactive nature. All syringes (equipped with 18 gauge needles) were scrupulously cleaned and allowed to dry in a convection oven (110°C) for 24-48 hours. The syringes were allowed to cool in a desiccator until immediate use. Before inserting a syringe into a air/moisture sensitive reagent, the syringe was purged with prepurified nitrogen. The vessel containing the reagent was pressurized with 6-8 psi of nitrogen in order to facilitate removal and avoid air leaking in between the barrel and the plunger. Due to the high pressure in the vessel, caution was taken to avoid having the plunger and the reagent eject. It was also desirable to wear protective gloves during syringe techniques. All syringes were cleaned and returned to the convection oven immediately after use in order to avoid clogging of the barrel and needle.

d) Lithium diisopropyl amide (LDA) (Lithco Division of FMC) was available as a 2.0 molar solution in cyclohexane and used as received. Polymerization results indicated that the concentration agreed well with the given value. Thus, verification of the solution molarity was not performed. Similar storing and handling procedures to sec-butyl lithium were employed.

The presence of the diisopropyl amine chain end in the resulting polymer was confirmed using elemental analysis for nitrogen. The upper molecular weight that could be analyzed was approximately 20,000 g/mole and agreement within 5% of the theoretical and GPC molecular weights was possible.

e) 1,3-Bis(phenylethenyl)benzene (DDPE) was obtained from Dow Chemical Co. as a yellow liquid which crystallizes slowly upon standing. The acronym, DDPE, originates from the expression double(D) diphenylethylene(DPE) and has been used routinely in the literature [259]. DDPE was distilled from n-butyllithium under vacuum in a similar manner as described for diphenylethylene. However, due to the very high boiling point of DDPE (actually decomposes prior to boiling at atmospheric conditions), purification was more facile using high vacuum techniques as described by Broske and McGrath [260]. The distilled product was colorless and could be stored as a cyclohexane solution in the freezer until later use.

f) p-Toluenesulfonic acid monohydrate (PTSA) (Aldrich) was used as received. The hygroscopic solid was stored in a desiccator in order to minimize moisture uptake. Early drying attempts in vacuo at 60°C overnight led to a decoloration of the acid. Consequently, later attempts were not performed since small amounts of moisture would not influence the catalytic performance during polymeric ester hydrolysis.

3) Purification Reagents

a) n-Butyllithium and sec-butyllithium were both obtained from the Lithco Division of FMC as 1.35 M ca. solutions in cyclohexane. These reagents were typically used in order to prepare anionic species for distillation purifications. For instance, diphenylethylene was routinely distilled from sec-butyllithium and 1,3 bis(phenylethenyl)benzene from n-butyllithium. In both cases, the alkyl lithium reacted with the crude reagent e.g. diphenylhexyllithium was formed during the purification of DPE. Consequently, there was no distillation of the base. The cyclohexane had to be vacuum stripped prior to distillation in order to avoid dilution of the purified product. In situations when the possibility of base distillation existed, n-butyllithium was preferred due to a higher boiling point. The difference in boiling point of the alkyllithium reagents can be explained by the fact that n-butyllithium is associated into hexamers whereas sec-butyllithium is associated into tetramers [261]. This observation also explains the enhanced reactivity of sec-butyllithium presumably due to a steric consideration.

b) <u>Trialkyl aluminums</u> (Ethyl Corporation) were obtained as 25 weight % solutions in hexane and used without further purification. The solutions could be carefully transferred into smaller aliquots in order to avoid contamination of the stock due to frequent syringe insertions. This was most easily accomplished using a cannula and pressurizing the solution into flame-dried serum bottles. The serum bottles must be scrupulously dry and allowed to cool under a nitrogen purge. The solutions were quite pyrophoric and must be handled with extreme care. Similar precautions as in the use of alkyl lithium reagents were taken except that air tight syringes were routinely used.

It should be noted that most trialkyl aluminum reagents are pyrophoric unless obtained as solutions less than 15 weight percent. In addition, the size of the alkyl group defines the reactivity of the reagent as well as the pyrophoricity. Both trioctyl and triethyl aluminum have been extensively studied and utilized. The octyl group due to steric contributions drastically decreases the reactivity of the aluminum reagent. Thus, trioctyl aluminum is not highly pyrophoric as a 25 weight percent solution in hexane. However, triethyl aluminum is significantly more reactive and pyrophoric.

The trialkyl aluminum reagents were stored in a flame retardant cabinet for relatively long periods of time (4-6 months). Contamination of the reagents was characterized by the formation of a white precipitate on the bottom of the serum bottle. It was presumed that this was an aluminum hydroxide that formed from the reaction of water or air with the reagent [262]. Due to the enhanced reactivity of trialkyl aluminums with protonic species such as water or alcohols and their ability to complex with α,β-unsaturated esters, they were used extensively for the purification of alkyl methacrylate monomers [263].

c) Dialkyl aluminum hydrides (Ethyl Corporation) were also available as 25 weight percent solutions in hexane. These materials were handled and stored in a similar manner as the trialkyl aluminums. However, the aluminum hydride is significantly more labile toward nucleophilic substitution by protic species than the aluminum alkyl [264]. This attribute was desirable when attempting to remove less reactive or hindered impurities. In addition, the dialkyl aluminums were mixed with the trialkyl aluminums in order to modify the reactivity of the trialkyl aluminum. Mixing of the solutions was accomplished by using a cannula under a nitrogen atmosphere. The mixed reagents were also stable for long periods of time without formation of an aluminum hydroxide precipitate.

d) Dibutyl magnesium (DBM) (Lithco Division of FMC) was available as a 15 weight percent solution in ISOPAR E (hydrocarbon mixture). The solution was used as received and handled according to the procedures described for air sensitive reagents. The primary use for DBM was the purification of hydrocarbon monomers such as styrene or the dienes. This reagent has been shown by Fetters et al. to remove water and air from various hydrocarbon monomers [265].

e) Calcium hydride (Aldrich) was used as received and proved to be an adequate heterogeneous, preliminary drying agent for a variety of monomers and solvents. The solid was finely ground prior to adding to the "wet" reagent in order to increase surface area of the solid and optimize drying.

f) Alumina and Silica (Aldrich) were typically dried in vacuo at 100°C for 24-48 hours in order to "activate" the reagents. After transferring the desired amount of material to a vessel, the top was covered with a tissue in order to avoid bumping while drying under vacuum. The solids were used immediately after activation. Both silica and alumina were used for drying purposes and to remove inhibitors from unsaturated monomers.

g) Sodium and benzophenone (Aldrich) were both used as received for the purification of tetrahydrofuran. The sodium was available as a dispersed metal in a paraffin wax and was generally sliced prior to use. Caution was taken to avoid contacting the sodium with the skin. Both reagents could be stored for relatively long periods of time (6 months) without noticeable effects in efficiency.

4) Monomers

a) Styrene (Aldrich) was purified by vacuum distillation from dibutyl magnesium. A similar apparatus was used as shown in Figure 13 for the distillation of diphenylethylene. However, the sizes of the distilling and receiving flasks were generally larger since more purified monomer was desired.

The dibutyl magnesium solution was added dropwise via a syringe to the distilling flask that contained the impure monomer. A pale yellow color developed due to complexation of the DBM with the unsaturated site in the monomer [266]. The color formation was indicative that all the impurities had been scavenged. The complex was allowed to stir for 20-30 minutes to ensure successful purification. The complex was degassed by the "freeze-thaw" technique and the apparatus was flamed while evacuating. After achieving good vacuum (50 millitorr), the system was closed and allowed to distill. The receiver flask was constantly cooled with a dry ice/isopropanol bath to facilitate distillation and to prevent polymerization of the pure, uninhibited monomer. The monomer was used immediately after purification and any unused monomer was returned to the inhibited stock.

b) <u>t-Butylstyrene</u> (Dow Chemical) and <u>p-acetoxystyrene</u> (Celanese) were purified according to the same procedure as described for styrene.

c) <u>Isoprene</u> (Goodyear) and <u>butadiene</u> (Phillips) were generally purified by passing through columns containing silica, alumina and molecular sieves. This was accomplished under nitrogen atmosphere and the column-pure monomer was subsequently transferred by nitrogen pressure to calibrated holding tanks. The monomers were directly charged into a high pressure polymerization reactor. This closed system facilitated the purification of volatile monomers such as butadiene and minimized inhalation during transfer.

In addition, the diene monomers could be distilled from dibutyl magnesium according to the procedures described for styrene. Vacuum distillation was only necessary to ensure that the monomer was exceptionally pure. In many instances, diene monomers such as isoprene will undergo Diels-Alder reactions to generate unsaturated cyclic species which contain allylic protons [267]. The allylic protons are sufficiently acidic to interact with alkyl lithium initiators and propagating anions. For example, after long storage periods of isoprene at room temperature, limonene or 4-isopropenyl-1-methyl cyclohexene can be formed and cannot be removed by the column technique. Thus, distillation was often necessary to eliminate any suspicion.

d) <u>Methyl methacrylate</u> (MMA) (Rohm and Haas) was transferred to a clean, oven-dried round bottom flask equipped with a teflon stir bar. Finely ground calcium hydride was added to the monomer and the evolution of hydrogen was immediately evident. The flask was fitted with a rubber septum and purged with nitrogen until bubbling stopped. The monomer was allowed to stir over calcium hydride for 2-3 days. The flask was fitted to a vacuum distillation apparatus and the monomer was degassed by the "freeze-thaw" technique. After establishing good vacuum (<150 millitorr), the apparatus was flamed while pumping and the system was subsequently allowed to cool. The vacuum was turned off and the monomer (boiling pt. = 100°C) was allowed to distill while cooling the receiver with a dry ice/isopropanol bath. The monomer would typically distill at 15-20°C at the pressure specified. After complete distillation of the dry monomer, the distillate was transferred to a clean, flamed, brown bottle via a cannula. The uninhibited monomer could be stored in the freezer (-20°C) for long periods without appreciable polymer formation. The septum was covered with Parafilm^R in order to prevent ice from resting directly on top. Frequent pressurizing with nitrogen eliminated the possibility of air leaking through the septum. Typically, 750 mls of monomer were distilled and stored as a stock.

Immediately prior to polymerization, a desired amount of calcium hydride pure monomer was transferred via a cannula to a distillation apparatus. The monomer was first degassed several times using the "freeze-thaw" technique. Triethyl aluminum was slowly syringed into the cold monomer using a gas tight syringe. It was imperative to add slowly while stirring in order to avoid undesirable exotherms. Once a yellow-green (chablis) complex color formed, one could be certain that the protonic impurities had been removed. A 50% excess of the triethyl aluminum solution was added after a stable complex color persisted. The complexed monomer was allowed to stand for approximately 10 minutes prior to distillation. The distillate was clear and generally all monomer was recovered. However, if the monomer was not properly degassed, then recovered yields were less than 60%. This was explained by the formation of radical intermediates present when oxygen reacts with the trialkyl aluminum reagent. The purified monomer was frozen with liquid nitrogen and used within 24 hours. If the pure monomer was not properly frozen and was allowed to reach room temperature for even short times (1 hour), polymerization occurred and the monomer could not be utilized. Although it is not advisable, the monomer can be stored frozen over night and used the next day. In most instances, no contamination occurred provided that all ground glass joints were tight and the <u>frozen</u> monomer was covered with dark cloths. Any unused portions of the triethyl aluminum pure monomer were routinely returned to the calcium hydride pure stock. In fact, this practice resulted in the gradual purification of the MMA stock.

All alkyl methacrylate monomers were analyzed by gas chromatography before and after purification to ensure that all protic impurities were adequately removed. This was accomplished on a Gow-Mac gas liquid chromatograph (GLC) which was equipped with a thermal conductivity detector (TCD). The column employed was the nonpolar DC-200 (15%) on a Chromosorb P support. Contact times required between the aluminum reagent and the monomer were established by monitoring the disappearance of the impurity (usually the alcohol) peak at early retention times. The appearance of octane in the case of trioctyl aluminum could also be utilized without difficulty.

e) Ethyl methacrylate (EMA) (Rohm and Haas) was purified in a similar fashion as MMA. The boiling point was cited as 117°C.

f) Isopropyl methacrylate (IPMA) was generously provided by Dr. W. Wunderlich (Rohm Tech, W. Germany). The boiling point was cited as 125°C. Other grades of IPMA obtained from Dajac Laboratories (Trevose, Pa.) were significantly more impure and more difficult to purify.

The major difference in purification of monomers based on secondary alcohols was that the contact time between the trialkyl aluminum reagent and the monomer must be longer. This was a result of the fact that secondary alcoholic impurities reacted slower with aluminum alkyls than primary alcohols. Typically, the contact times ranged from 30-45 minutes to ensure complete purification. If insufficient time was allowed for the scavenging of impurities, then the complex color would fade during the distillation. The storage and handling procedures were the same as described for MMA.

g) t-Butyl methacrylate (TBMA) (bp. = 155°C) was also provided by Dr. W. Wunderlich (Rohm Tech, W. Germany). A calcium hydride pure stock was prepared by similar procedures as described for MMA. Gas chromatographic analysis indicated approximately 2-3% t-butanol as an impurity. It was presumed that esterification or transesterification reactions were utilized for monomer preparation. Consequently, the corresponding alcohol was a major impurity. This observation was noted for all alkyl methacrylate monomers studied.

Due to the decreased reactivity of hindered alcohols such as t-butanol with aluminum alkyls and the instability of the monomer complex for long times, modifications in aluminum reactivity were required. This was accomplished by preparing mixed triethyl aluminum (TEA) and diisobutyl aluminum hydride (DIBAH) solutions. Concentrations ranged from 90:10 TEA:DIBAH to 50:50 TEA:DIBAH and purification contact times were approximately 40 minutes. Unless the mixed reagent was added while the monomer was cold, significant polymer formation occurred. Despite the known reduction capabilities of aluminum hydrides, there was no indication of reduced products in the distillate.

Inductively Coupled Plasma (ICP) analysis was utilized to confirm the absence of aluminum in the distillate. This was suspected due to the higher distillation temperatures required for the higher boiling monomers such as TBMA. A control sample which had not been treated with the aluminum reagents was also submitted. A detailed description of this analytical technique and applications can be found in the literature [268].

h) 2-Ethylhexyl methacrylate (EHMA) (Polysciences Inc.)

was vacuum distilled from calcium hydride according to the procedures described for MMA. The high boiling point of the monomer (bp. = 110°C/14 mm) required that the vacuum was constantly applied throughout the distillation and distilling flask temperatures reached 60-70°C. This was accomplished without significant polymer formation and recovered yields were generally greater than 90%. The stock was stored and handled as described for all alkyl methacrylate monomers,

The monomer was similarly vacuum distilled from TEA immediately prior to polymerization. The contact times between the monomer and aluminum purification reagent ranged from 45-90 minutes without premature polymerization. Alkyl methacrylates have been shown to polymerize in the presence of triethyl aluminum, but only under ultraviolet or visible light; a radical chain is thought to be involved [269]. The complexed monomer seemed more stable compared to other monomers studied. The distillation proceeded with constant vacuum and the distilling flask generally reached 70°C. Recovered yields were generally greater than 90% despite the high temperatures and absence of inhibitor. A more complete understanding of the effect of monomer structure on the complex stability and resistance to thermal polymerization would be useful.

i) <u>2,2,2-Trifluoroethyl methacrylate</u> (TFEMA) (Dajac) was purified in a similar manner as other normal ester alkyl methacrylates such as MMA and EMA.

j) Allyl methacrylate (AMA) was obtained from Dr. W. Wunderlich (Rohm Tech, W. Germany) and purified in a similar fashion as other linear ester alkyl methacrylates.

B. Polymer Synthesis

1) Poly(alkyl methacrylate) Homopolymers

All anionic polymerizations were performed in scrupulously cleaned and dried glassware under a prepurified nitrogen atmosphere. The nitrogen was passed through a column (3 ft.x 2 in.) of molecular sieves, alumina and silica to ensure dryness. Round bottom, one-neck flasks were thoroughly cleaned several days prior to polymerization and allowed to dry in a convection oven at 110°C. Teflon-coated magnetic stir bars were also cleaned and allowed to dry in the appropriate flask. Immediately prior to use, the flasks were removed from the oven and quickly fitted with a rubber septum. The flasks were flamed and allowed to cool while purging with nitrogen.

The polymerization solvent was transferred to the round bottom flask using a cannula under a nitrogen atmosphere. The amount of solvent charged was based on the weight percent solids and final molecular weight desired. Typically, 5-10 weight percent in all cases allowed for low enough viscosity for adequate stirring. Toluene and tetrahydrofuran were commonly used for all homopolymer syntheses. The relative amounts of initiator and monomer were determined according to the example calculation in Figure 14 for a 30,000 g/mole poly(alkyl methacrylate) homopolymer. Diphenylethylene was required to form a more sterically hindered, less basic initiator anion. Alkyl lithium initiators based on DPE have been shown to be quite efficient initiators for alkyl methacrylate polymerizations [54,104]. Typically, a 3-4 molar excess of diphenylethylene compared to initiator was utilized. In fact, equal volume charges of diphenylethylene and initiator conveniently corresponded to a 4 molar excess of diphenylethylene.

The excess DPE was charged to the reaction vessel and the initiator formation temperature was allowed to reach thermal equilibrium. This temperature was a function of the desired polymerization solvent. For ethereal solvents such as THF, the vessel was cooled to -78°C and for hydrocarbon solvents such as toluene, the initiator formation temperature was maintained at room temperature. s-Butyl lithium was added dropwise into the solution until the red color associated with the formation of diphenylhexyl lithium (DPHL) began to stabilize. At this moment, the calculated amount of s-butyl lithium was syringed into the DPE solution which quickly generated a strong red anion of DPHL. Scheme XX depicts the sequential addition of reagents to form the hindered DPHL initiator. The length of time required for this reaction was a function of both polymerization

Let's make 10g of a 30,000 g/mole homopolymer

$$\bar{M}n = \frac{g\ monomer}{moles\ initiator}$$

Rearranging to solve for moles of initiator yields,

$$moles\ initiator = \frac{g\ monomer}{\bar{M}n}$$

Substituting,

$$moles\ initiator = \frac{10g}{30{,}000\ g/mole}$$

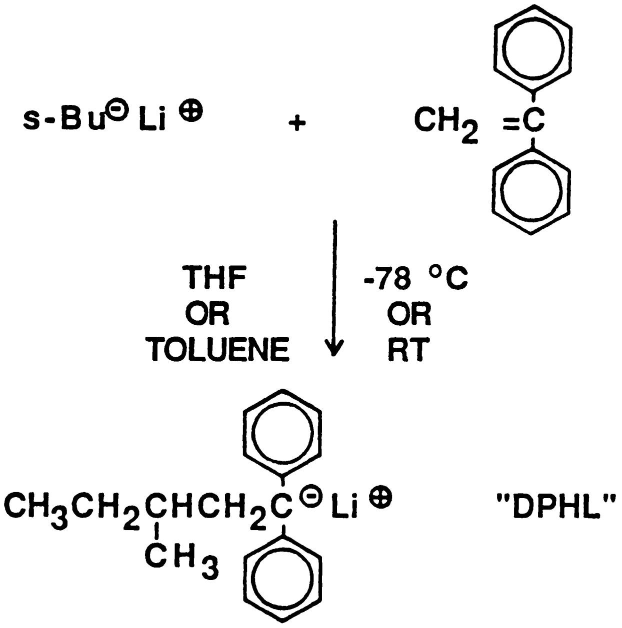
moles initiator = 0.00033 moles = 0.33 mmoles

Thus, by knowing the concentration of a sec-butyl lithium solution (ml/mmole), the charge of initiator can be determined to obtain a 30,000 g/mole sample.

Figure 14: Example Molecular Weight Calculation for a "Living" Polymerization

Scheme XX

Diphenylhexyl Lithium (DPHL) Initiator Formation

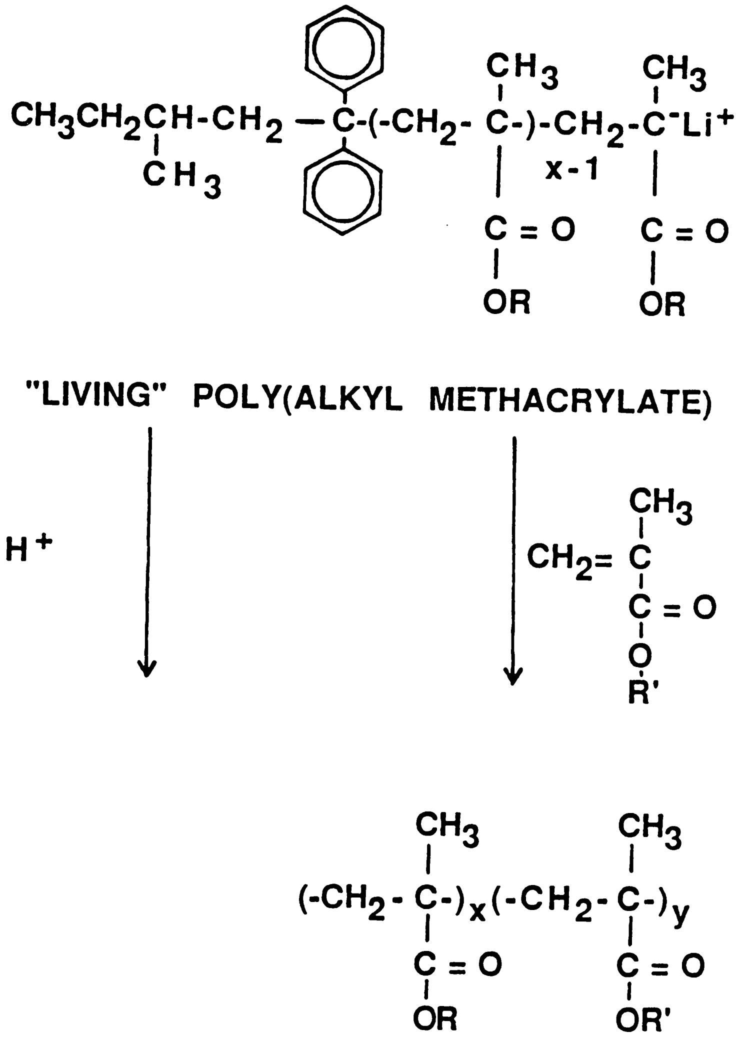


temperature and solvent. In toluene, this reaction was allowed to proceed for 60 minutes at room temperature. However, in polar solvents at -78°C, the reaction was complete in a matter of seconds. It was not advisable to allow the initiator to stand after complete conversion due to the possibility of premature termination. A stock solution of DPHL in toluene could also routinely be prepared and aliquots could be removed as needed to initiate polymerizations. However, this latter approach did not allow for facile titration of the polymerization vessel or polymerization solvent.

The trialkyl aluminum purified alkyl methacrylate monomer was slowly added to the initiator solution to avoid any undesirable exotherms, which could lead to premature termination in some cases. Initiation was rapid and was evident by the rapid disappearance of the red color. The polymerization time was a function of both polymerization solvent and polymerization temperature. For example, at -78°C, the polymerization of MMA (though probably quickly completed) usually was allowed to proceed for 20-30 minutes in polar solvents. Two hours were allowed for the polymerizations to occur in toluene. Scheme XXI depicts the chemistry involved in the generation of the propagating enolate. Once the polymerization was complete, 0.2-0.5 mls of degassed, HPLC grade methanol were syringed into the reactor. The homopolymer was precipitated in an appropriate

Scheme XXI

Anionic Propagation and Termination of Lithium Enolate



nonsolvent (10X excess) depending on the solubility characteristics of the polymer. For example, poly(methyl methacrylate) was quantitatively recovered when precipitated in petroleum ether. However, moderate molecular weight samples show limited solubility in methanol and only 90% recovered yields were obtained. The polymerization solvent must be miscible with the precipitation solvent. If the polymerization solvent was not miscible with the precipitation solvent, the polymerization solvent was removed by rotoevaporation and the polymer was redissolved in an appropriate solvent. After vacuum filtration of the precipitated polymer, the sample was allowed to dry in vacuo at the glass transition temperature for approximately 24 hours.

Poly(alkyl methacrylate) homopolymers could also be synthesized using free radical initiators such as AIBN. The bulk polymerization typically required 10g of monomer (CaH_2 pure) and 0.1 wt. percent initiator (0.011g). The reactants were charged to a round bottom flask fitted with a septum under nitrogen atmosphere. The flask was submerged in a constant temperature water bath at 65°C for 10-12 hours. The polymer was dissolved in THF and precipitated as described above. Yields were generally greater than 90%. If a solution polymerization was desired, toluene was an appropriate solvent at 25-30 weight percent solids.

2) <u>Poly(styrene-b-alkyl methacrylates)</u>

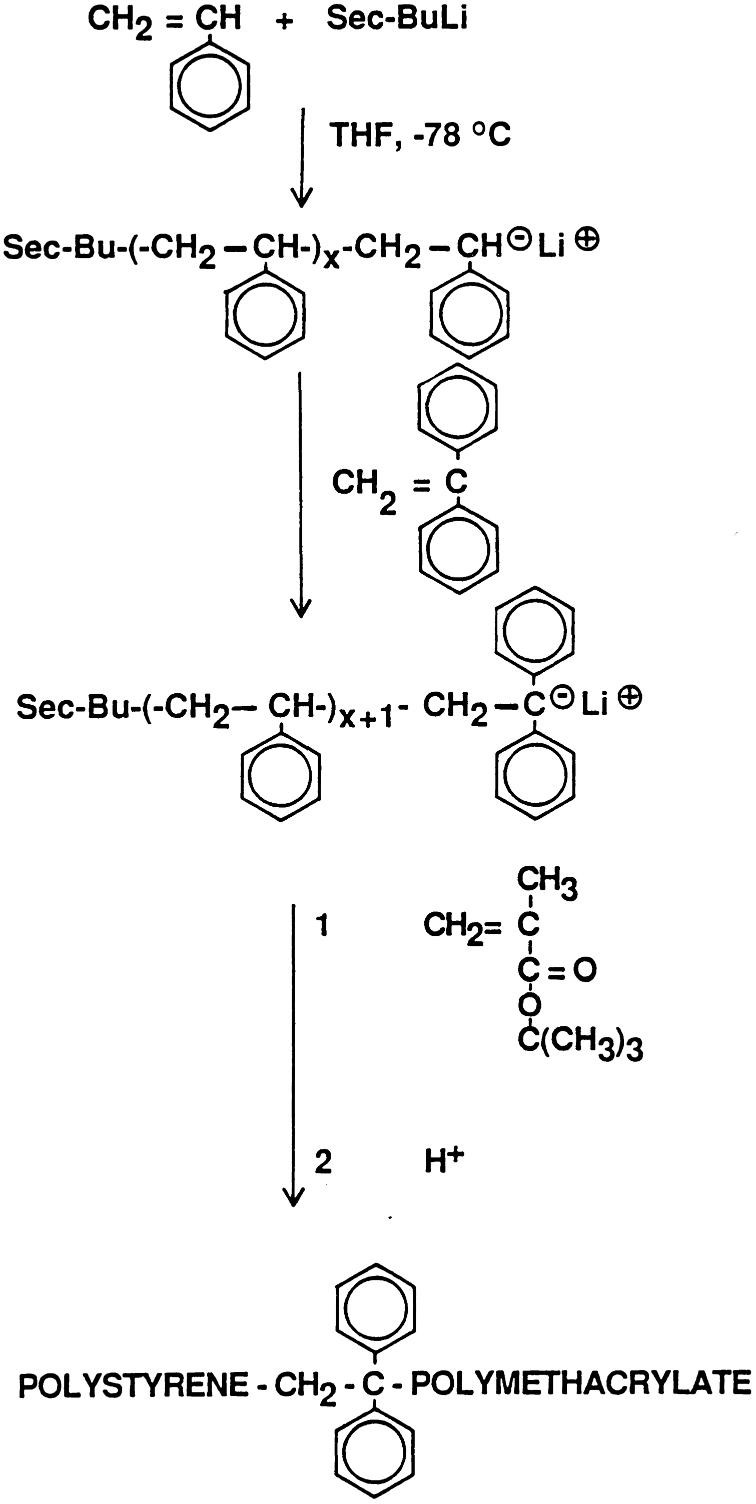
All glassware was rigorously cleaned and dried prior to use. For small scale polymerizations, the reactor consisted of a 250 ml, 1 neck, round bottom flask equipped with a magnetic stirrer and a rubber septum. The septum was secured in place with copper wire in order that 6-8 psi of prepurified nitrogen could be maintained. The reactor was assembled while hot and subsequently flamed under a nitrogen purge. After the flask had cooled, tetrahydrofuran was added to the reactor via a double-ended needle. The reactor was submerged in a -78°C bath and allowed to reach thermal equilibrium. Purified styrene monomer was charged into the reactor with a syringe. The calculated charge of s-butyl lithium was syringed into the reactor and immediately one could see the formation of the orange poly(styryl) anion. The first block was allowed to polymerize for over 20 minutes to ensure complete conversion. A slight excess of diphenylethylene (2-3 molar excess compared to lithium) was syringed into the reactor to cap the first block. It was possible to use an excess since DPE does not homopolymerize and the generated enolate will not reinitiate DPE. This capping procedure was essential in most cases to prevent carbonyl attack (1,2-addition) of the alkyl methacrylate monomer. The successful conversion to the highly delocalized diphenylethylene derived anion was witnessed by the rapid formation of a deep red color. After several minutes, highly purified alkyl methacrylate monomer was slowly added to the living capped first block. Initiation of the second block was rapid and characterized by the formation of a colorless poly(alkyl methacrylate) lithium enolate anion. After 15-20 minutes, the polymerization was terminated with a few drops of degassed, HPLC grade methanol. Scheme XXII shows the required sequential addition of reagents and the chemistry involved. The polymer can be obtained by precipitation in a large excess (10X) of nonsolvent such as methanol or methanol/isopropanol depending on the solubility characteristics of the polymer.

Due to the rapid polymerization of styrene, it is difficult to "titrate" the reactor prior to initiation in order to scavenge any impurities. Consequently, it was desirable to do a separate controlled reaction where a reactor was titrated quickly until a faint orange poly(styryl) anion appeared. In most instances, the polymerization proceeded to very high molecular weight before the calculated charge of initiator was added. However, the required amount of base needed to scavenge impurities in a reactor was determined. This amount could be added to the calculated initiator charge for the block copolymer syntheses and the total volume was charged into the styrene and tetrahydrofuran solutions. This technique allowed for excellent control of block copolymer molecular weight.

3) Poly(alkyl methacrylate-b-alkyl methacrylates)

Scheme XXII

Synthesis of Poly(styrene-b-alkyl methacrylates)



All-acrylic block copolymers were prepared by simple sequential addition techniques. The first block was prepared according to the procedures outlined for homopolymer preparation. After complete conversion of the first block, the second monomer was added by syringe to the living lithium enolate. Approximately 15-20 minutes were allowed for the complete conversion of each block. In all instances, all-acrylic block copolymers were prepared in THF. The sequential addition of the monomers is depicted in Scheme XXIII. Some monomers would be amenable to block copolymer synthesis in hydrocarbon solvents, resulting in more elastomeric materials. The polymerizations were terminated and worked-up in a manner similar to styrene based copolymers.

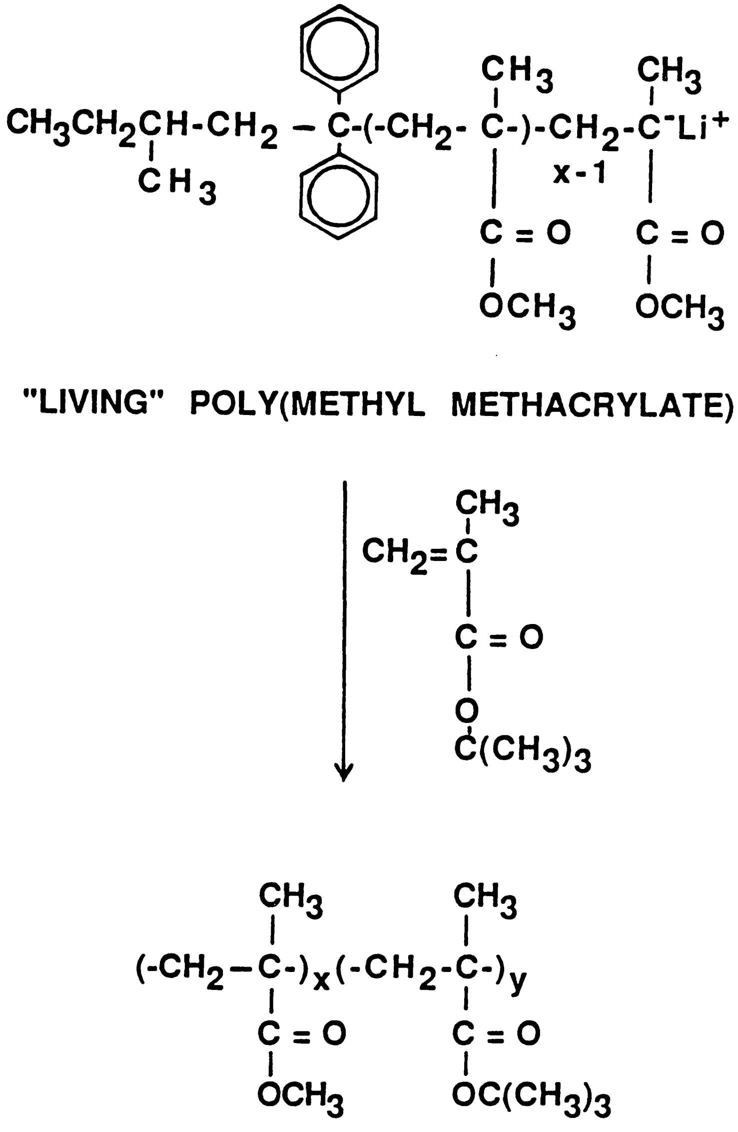
Most important was the realization that due to the structural similarity of most alkyl methacrylates, the order of addition could be varied. This opportunity was not possible in the styrene or the diene based systems; the poly(alkyl methacrylate) enolate was not basic enough to initiate styrene or a diene. This concept and the resulting ramifications will be discussed in detail later.

4) Poly(diene-b-alkyl methacrylates)

The synthesis of diene-methacrylate diblock copolymers was conducted in a variety of ways. In each case, the diene, i.e. isoprene or butadiene, was polymerized in a high pressure reactor. Hoover and McGrath have described in

Scheme XXIII

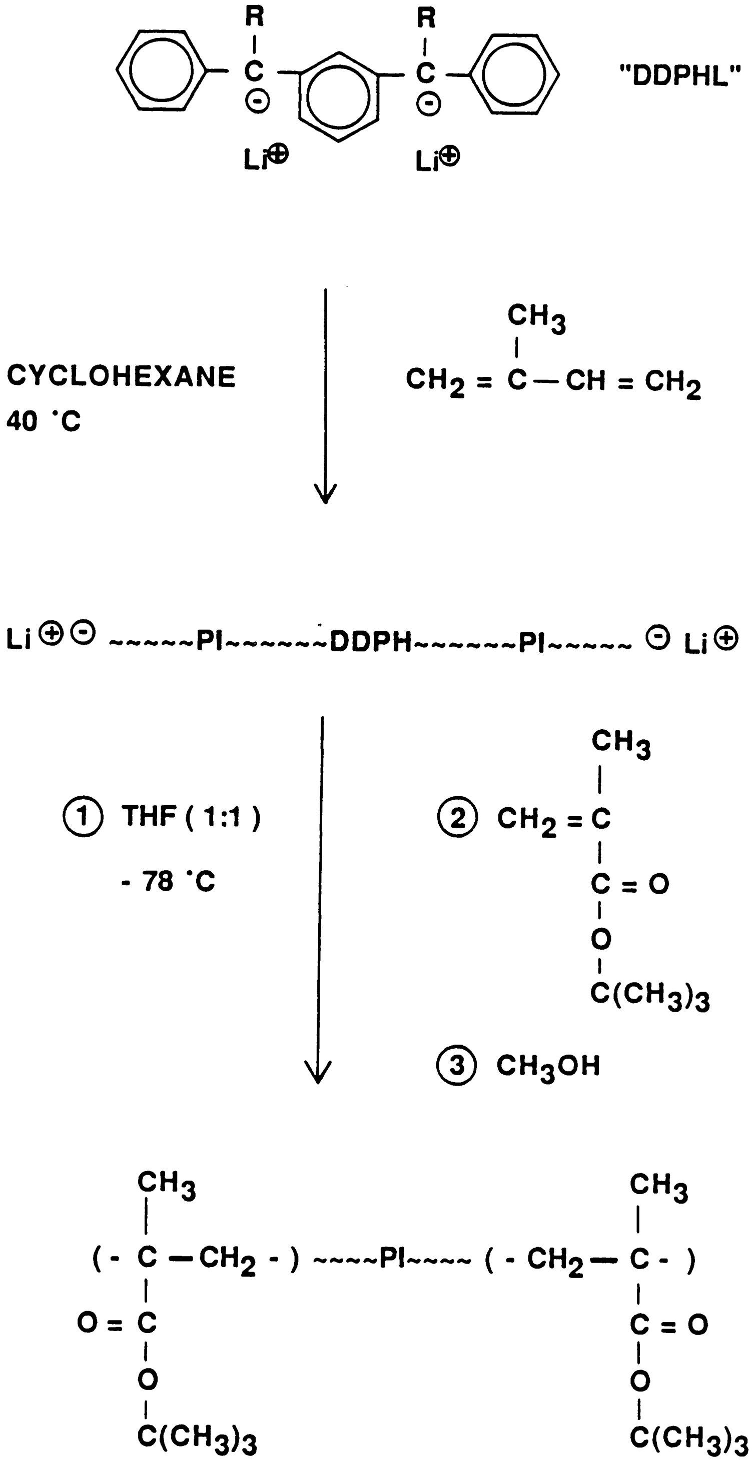
Synthesis of All-Methacrylic Block Copolymers



detail the assembly and utility of this anionic polymerization reactor [270]. Approximately 500 mls of prepurified cyclohexane or toluene were charged into the reactor through the septum port located on top of the reactor. The reactor system was designed with the capability of directly charging diene monomers from holding tanks into the reactor. The exact charge was determined by first pressurizing the diene with nitrogen from the holding tank into a precalibrated cylinder. The known amount (typically 40 g) was then charged into the cyclohexane by nitrogen pressure and the reactor temperature was allowed to reach 60°C. The calculated amount of s-butyllithium (0.50 mmoles for a 80,000 g/mole polymer) was syringed into the reactor through the septum port and the polymerization was allowed to proceed for approximately 2 hours. The sequential addition of reagents and the chemistry involved are depicted in Scheme XXIV. For polymerizations in toluene, the reaction was performed at 40°C for approximately 10 hours. This large amount of poly(dienyl) anion was used as a stock and aliquots were transferred to 250 ml round bottom flasks which were previously fitted with septa. It was critical that the flasks be very clean and flame dried in order to eliminate any possibility of termination of the poly(dienyl) anion. Since the anion concentration of the stock was known and a known volume was transferred to the round bottom flask, the anion

Scheme XXIV

Synthesis of Poly(isoprene-b-t-butyl methacrylate)



concentration in the flask could be calculated.

Tetrahydrofuran which had been distilled twice from sodium/benzophenone was added via a cannula to the 250 ml flask. It was determined that large volumes of THF were necessary and typically an equal volume of THF and cyclohexane was utilized. The reactor was cooled with a dry ice/isopropanol bath while adding THF in order to eliminate the possibility of attack on the protons of the THF ring [271]. The necessity of cooling was not investigated in detail, but all precautions were taken to avoid premature termination. The flask had to be cooled slowly in order to prevent freezing of the cyclohexane. However, after a significant amount of THF had been added, the flask could be completely submerged and allowed to reach -78°C. t-Butyl methacrylate was added slowly with a syringe and the viscosity noticeably increased quickly. The monomer had been vacuum distilled from a trialkyl aluminum/dialkyl aluminum hydride reagent immediately prior to use. The polymerization of the acrylic block was allowed to continue for approximately one hour. The generation of the second block is shown in Scheme XXIV. After the polymerization was terminated with several drops of degassed, HPLC grade methanol, the polymer was precipitated into an 80:20 methanol/water mixture. The addition of isopropanol (10%) to the precipitation solvent enhanced solubility of the cyclohexane and facilitated precipitation. The polymer was also stabilized with Irganox 1010 Antioxidant (0.1 wt. % compared to polymer), vacuum filtered and dried in vacuo at room temperature for 24-48 hours. The samples were typically stored in the freezer until further use or testing due to the propensity of poly(isoprene) to undergo scission.

t-Butyl methacrylate was chosen due to the facile polymerizability of this monomer and the exceptionally stable enolate that forms after crossover. In addition, the polymeric t-butyl group could be easily hydrolyzed by simple acid catalyzed hydrolysis. This capability allowed for the preparation of interesting ion-containing block copolymers. However, it is believed that the polymerization procedure described would be amenable to a variety of alkyl methacrylate monomers.

The chemistry involved in the preparation of triblock structures of poly(alkyl methacrylate-b-diene-b-alkyl methacrylate) was significantly different. It is important to recall that the poly (alkyl methacrylate) enolate is not capable of initiating a diene monomer. Thus, the triblock could not be synthesized using the sequential addition approaches described. Consequently, the use of a difunctional alkyllithium initiator was considered. Broske and McGrath have outlined in detail the utility of 1,3-bis(phenylethenyl)benzene (DDPE) as a hydrocarbon soluble difunctional alkyl lithium initiator [272].

The formation of the difunctional initiator is shown in

Scheme XXV. The 1,3-bis(phenylethenyl)benzene was typically stored as a solution in cyclohexane. After syringing a known amount of 1,3-bis(phenylethenyl)benzene into the reactor, a 2:1 molar ratio of s-butyllithium compared to DDPE was subsequently added. The reaction was performed in cyclohexane at 40°C for 6-8 hours and complete formation of the dianion was monitored by gas chromatography. Formation of the dianion was also confirmed by observing the rapid formation of a stable red color associated with the highly delocalized carbanion. After complete formation of the dianion, a desired amount of isoprene was charged into the reactor and allowed to polymerize at 60°C for 2 hours. In a fashion similar to the diblock synthesis, aliquots were removed and equal volumes of prepurified THF were added. Polymerizations of the acrylic block proceeded at -78°C for 1 hour and were terminated by the addition of methanol. The samples were worked-up and stored in a fashion similar to that described for the diblock materials.

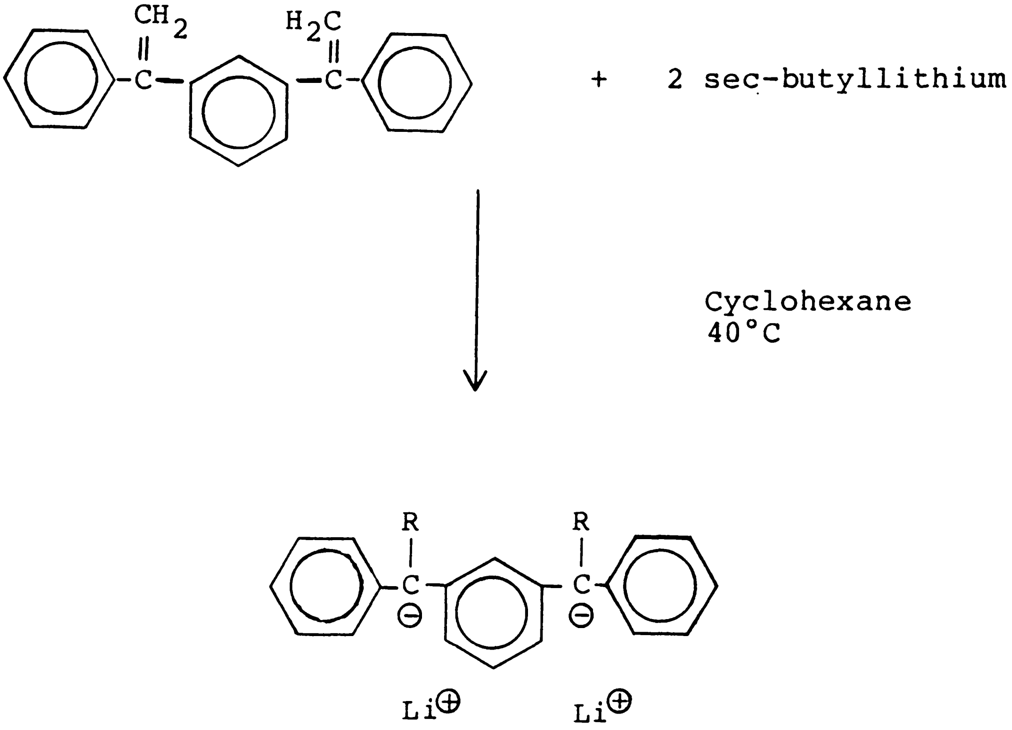
C. Polymer Modification

1) Ester Hydrolysis

Most poly(alkyl methacrylate) esters were quite resistant to classical hydrolysis routes and generally required very harsh conditions for long times to introduce only small amounts of carboxylic acid. In fact, PMMA generally requires stirring in 80 vol. % of aqueous sulfuric acid at 30°C for 5-7 days [273]. Consequently, efforts were

Scheme XXV

Difunctional Initiator Preparation [272]



directed toward the hydrolysis of t-butyl methacrylate (TBMA) which underwent acid catalyzed hydrolysis to very high conversion. In addition to the hydrolysis of poly(t-butyl methacrylate) homopolymers, poly(t-butyl methacrylate) containing block copolymers were studied.

t-Butyl methacrylate homopolymers and block copolymers were hydrolyzed using catalytic amounts of p-toluenesulfonic acid monohydrate (PTSA) in solution at mild temperatures (60-80°C). The reactor consisted of a 3-neck flask equipped with a condenser and drying tube on the center neck, a thermocouple and nitrogen inlet on the other two necks. Adequate stirring was accomplished using a magnetic stir bar. The amount of acid catalyst was calculated based on 5-10 weight percent of the amount of hydrolyzable ester present, i.e. TBMA composition. The acid was readily soluble in toluene (100 ml) and the hydrolysis temperature was allowed to stabilize at 80°C. The polymer (5.0g) was added to the acidic solution via a powder funnel and the reaction was allowed to proceed for 8 hours. Subsequent conversion studies have demonstrated that the reactions were typically completed after only 90 minutes. The temperature variable was not studied; however, it was believed that the reaction could be run at the reflux temperature of toluene or higher if another solvent, e.g. xylene, was utilized. The hydrolysis of a poly(t-butylstyrene-b-t-butyl methacrylate) copolymer is depicted in

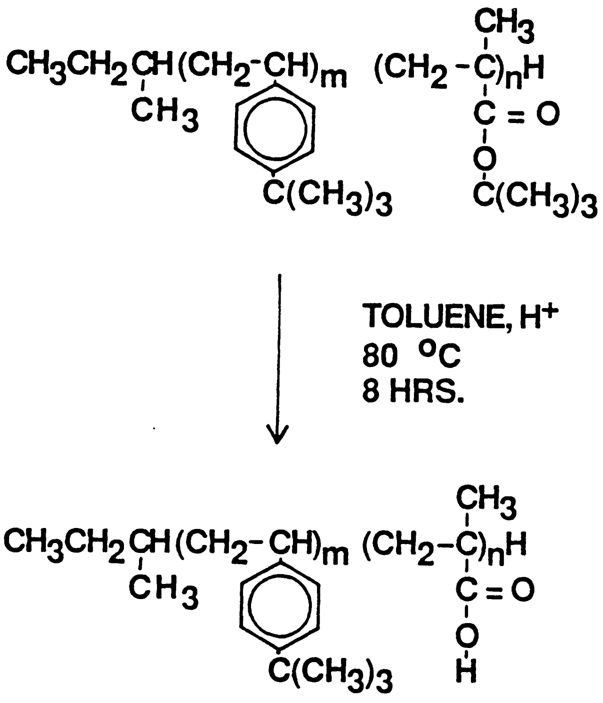
Scheme XXVI.

It was important to note that maintaining solubility during the hydrolysis lead to higher degrees of conversion. This was particularly true for the hydrolysis of PTBMA homopolymers since the solubility parameter upon hydrolysis drastically increased as the acid units were formed. Consequently, the derived acid containing polymer would precipitate after only 8-10 minutes at the hydrolysis conditions. An alcohol such as methanol was required to restore solubility and the reaction was allowed to proceed to quantitative conversion. Methanol could be used as a hydrolysis solvent with acid catalysts, but the ultimate goal was to hydrolyze block copolymers which were always insoluble in alcohols. Thus, an understanding of the hydrolysis reaction in hydrocarbon solvents such as toluene was desired. For most block copolymers, precipitation was not a problem because the unhydrolyzed block helped to maintain solubility in the hydrocarbon media. The role of the unhydrolyzed block in defining solubility considerations and reaction kinetics would be enlightening.

The reaction mixture could be worked-up in a variety of ways, but generally the percent of derived poly(methacrylic acid) dictated the solubility characteristics and the method of isolation. In most cases, the toluene was removed and the sample was redissolved in tetrahydrofuran. The removal of toluene was necessary because most samples were

Scheme XXVI

Hydrolysis of Poly(t-butylstyrene-b-t-butyl methacrylate) Copolymers



precipitated into either water or methanol/water. Toluene is not miscible with water at room temperature and two phases can develop during precipitation. THF is miscible with water and a homogeneous precipitation media results. The ratio of the methanol/water mixture was a function of the percent derived acid and the nature of the unhydrolyzed block. However, in most cases, the amount of derived acid was low enough (2-20 mole %) that the same precipitation solvent composition for isolating the precursor could be utilized for the derived polymer. The primary purpose for precipitation was to remove the residual acid catalyst. If the acid catalyst was not removed, the polymer would often turn tan colored during drying. In addition, the required amount of titrant to neutralize the acid groups to metal carboxylates would not be an indication of the polymeric acid composition.

Drying of the acid containing polymers was accomplished at 90-100°C for 24 hours. Higher temperatures (>120°C) often led to the formation of anhydride linkages and rendered the material less soluble. Anhydride crosslinked polymers could be stirred in a tetrahydrofuran/water mixture and solubility could be restored.

2) Esterification

A block copolymer containing t-butyl methacrylate was dissolved in a long chain alcohol of interest. Homopolymers were also considered, but the acid intermediate precipitated and another alcohol was the only solvent capable of restoring solubility. Initial studies were focused on the use of dodecanol as both the reaction solvent and the reactant. It was presumed that the large excess of alcohol would lead to higher conversions. A catalytic amount of p-toluenesulfonic acid (5-10 wt. % relative to ester) was also dissolved in the alcohol. The reaction was allowed to proceed for 12-24 hours at 110°C and water was removed by distillation. The esterification of a styrene based block copolymer is depicted in Scheme XXVII.

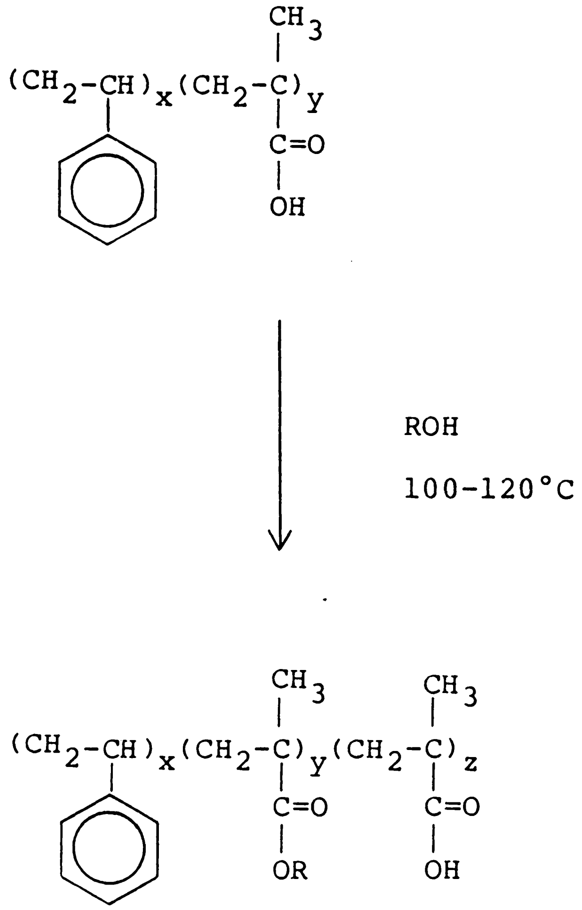
More efficient removal of water was accomplished by adding toluene to the alcohol solution and azeotroping the water. It was imperative to maintain a constant flow of nitrogen (2 psi) through the reactor in order to facilitate the collection of the azeotrope. The amount of toluene added was dependent on the size of the Dean Stark flask that was utilized. The polymer could be precipitated into a methanol/water mixture and dried in vacuo at 80°C for 24 hours.

3) Neutralization to Metal Carboxylates

The acid containing polymers were dissolved in THF (3-5 weight/volume percent). Several drops of a phenolphthalein solution in isopropanol were added to the polymer solution. Dilute potassium hydroxide (0.1N in methanol) was titrated into the solution with a buret. Turbidity often developed for the samples containing greater than 10 mole percent

Scheme XXVII

Esterification of Poly(methacrylic acid) Containing Block Copolymers



poly(methacrylic acid). The endpoint was a characteristic purple color that persisted for longer than 20 minutes. The solution was concentrated by removing 50% of the THF and precipitated into a nonsolvent. The ion-containing polymers were dried in vacuo at 100°C for 24-48 hours and stored in a desiccator until further analysis.

D. Structural Analysis

1) Fourier Transform Infrared Spectroscopy (FTIR) was performed on a Nicolet MX-1 spectrometer (resolution = 4.0 cm-1). The method was rapid, direct, nondestructive and required only small amounts of sample. Polymer solutions were generally cast onto salt plates and the solvent was allowed to evaporate to form a thin film on the plate. The evaporation rate was enhanced by placing the salt plate directly on a hot plate at low temperature. Tetrahydrofuran dissolved most acrylic polymers and evaporated at a convenient rate. In addition, free standing thin films were analyzed directly by suspending the film in front of the laser. Thus, it was not essential to have a solution for analysis. Typically the samples were scanned from 4000 cm-1 to 600 cm-1 and individual regions were expanded for closer inspection. Quantitative analysis was accomplished in the absorbance mode and construction of baselines could either be performed by the computer or by hand. In order to normalize for film thickness, a constant peak was selected in the spectrum and used as a reference.

a) Polymer analysis was routinely performed due to the ease and speed of the technique [274]. The technique was particularly suited for ascertaining the environment of a particular functional group. For example, extensive analysis of the methacrylate ester carbonyl frequency as a function of monomer structure aided in understanding and predicting polymerization capabilities. In addition, the relative ratio of geometric isomers in poly(dienes) could be determined quite easily in the absorbance mode. Although some analyses were accomplished more easily by other techniques, the availability of the infrared technique and the relative ease of obtaining and interpreting data made this a routinely used method.

b) Derived polymer characterization was especially suited for routine FTIR analysis prior to more complex analytical approaches. The analysis of hydrolyzed products verified conversion of the ester carbonyl (1723-1732 cm-1) to the carboxylic acid carbonyl (1703cm-1). Conversion of the acid to the metal carboxylate (1565-1575cm-1) was best monitored by FTIR due to the absence of overlapping peaks in the carboxylate region. Finally, esterification reactions leading to the formation of a new ester carbonyl could be observed.

Rates of conversion of polymer modification reactions were routinely determined and these analyses properly defined appropriate reaction times. For example, the hydrogenation of poly(isoprene) could be easily followed by observing the disappearance of the carbon-carbon double bond stretching frequency (1640cm-1) with time. Also, the appearance of the acid carbonyl with time at the expense of the ester carbonyl during hydrolysis was observed.

Finally, compositions in multicomponent polymeric systems could be verified by witnessing the increase of a particular absorbance with an increase in monomer charge. The lower limit of detection for compositional verification was approximately 3-5 weight percent.

The course of a polymerization was also monitored by observing the disappearance of monomer absorbances and the appearance of polymer absorbances. For example, in the polymerization of methyl methacrylate, one could witness the disappearance of the double bond at approximately 1630 cm-1. Also, the methyl group shifted from 1020 cm-1 to 980 cm-1 after polymerization. Residual amounts of monomer could detected within 2-3 mole percent. The endgroups of a polymer were also observed; however, for molecular weights greater than 5000 g/mole, the absorbance was generally difficult to quantify.

c) Polymer Stereochemistry generally did give rise to a change in the intensity and frequency of various absorbances. The peaks generally overlapped and the data was difficult to quantify. Consequently, ^{1}H NMR was a more facile and quantitative technique for determining stereochemistry of alkyl methacrylate containing polymeric systems.

2) Nuclear Magnetic Resonance (^1H) was performed on a Bruker 270 SL instrument and spectra were obtained in $CDCl_3$ solutions (3-5% wt./vol.). Several drops of tetramethylsilane (TMS) was often added as a lock; however, in most cases, the instrument was locked on the $CHCl_3$ impurity at 7.29 ppm. Deuterated dimethyl sulfoxide (DMSO-d6) was often used for the dissolution of more polar polymers such as poly(methacrylic acid) homopolymers and some copolymers.

High resolution 50 MHz ^{13}C NMR spectra of the polymers were generally obtained in $CDCl_3$ solutions (15% ca. wt./volume) using a Bruker WP 200 SY spectrometer. Inverse-gated proton decoupling in combination with the addition of a small amount (0.1 M) of $Cr(AcAc)_3$ to the samples assured quantitative accuracy of the data. Typically, 1000 free induction decays with a recycle delay of 5.0 seconds and a flip angle of approximately 40° were accumulated and Fourier transformed. Electronic integrals were used in the calculation after ensuring adequate digitization of the spectra.

^{19}F NMR was also performed on a Varian EM-390 90 MHz spectrometer. Similar solutions and concentrations were used as described for proton analysis. In most cases, it was not necessary to ascertain the exact chemical shift, but only the number of resonances were desired.

a) Structural and stereochemical analysis of polymers were the primary purposes for utilizing high resolution NMR. The utility and advantages of NMR for low molecular weight compound structural analysis were similarly realized for the identification of polymeric materials [275,276]. The major difference was that the solution concentrations had to be significantly less. High molecular weight samples dissolved at concentrations greater than 15% often were too viscous to achieve adequate Brownian motion. However, polymeric proton resonances were always significantly broader than low molecular weight compounds. This apparent limitation of resolution rarely hindered interpretation or identification of the sample. For more discriminatory analysis, ^{13}C NMR proved to be the method of choice due to the wider range of chemical shifts that were possible.

The identification of stereochemical or tactic sequences such as triad or pentad determination were accomplished routinely using NMR. ^{1}H NMR was adequate for poly(methyl methacrylate) (PMMA) stereochemistry elucidation; however, overlapping resonances in most other poly(alkyl methacrylates) prohibited quantitative use. Consequently, ^{13}C NMR was used for the analysis of stereochemistry for all poly(alkyl methacrylates) [277]. The quaternary carbon (40-45 ppm) in the polymer backbone and the carbonyl carbon (175-179 ppm) gave triad and pentad information respectively. The methyl group was solely used during proton analysis of PMMA due to the excellent resolution of the various triad resonances. If the larger ester alkyl group did not overlap with the methyl protons, it often induced a change in the chemical shift resulting in poorer resolution. It should be noted that tactic compositions of PMMA which were determined by both carbon and proton analysis agreed within 2 percent.

Similarly NMR was utilized for the quantification of geometric isomerism in poly(isoprene) and poly(butadiene), i.e. the relative ratio of the cis-1,4 and trans-1,4 isomers. In addition, the amount of 1,2-addition versus 1,4-addition in the diene polymerization was determined. In both cases, the unsaturated protons which appear near 5.0 ppm were utilized. The obtained values were often compared with the results determined by infrared spectroscopy and agreed within 3%.

b) Molecular weight determination was accomplished in situations when a significantly different structure was located at only the end(s) of a polymer chain. The integral of the resonance associated with the chain end was compared to the integral of a resonance that occurred in each repeat unit. If one assumed that all chains contained the terminal group(s), then the number average molecular weight was determined. The upper limit of detection was dependent on the relative number of protons and the molecular weight of the sample. For instance, PMMA molecular weights less than 10,000 g/mole could be reproducibly determined by ratioing the aromatic protons of the initiator to the methyl ester. This approach was utilized for a variety of poly(alkyl methacrylate) homopolymers that were initiated with diphenylhexyllithium.

c) Compositional determination was achieved by comparing a resonance associated with one monomer unit to the resonance of another comonomer. This allowed the verification of successful incorporation at the desired mole percentage. For example, the composition of a poly(styrene-b-methyl methacrylate) copolymer was verified by ratioing the aromatic resonance at approximately 7.0 ppm with the methyl ester at 3.5 ppm. In a similar fashion, the composition of a poly(diene-b-t-butyl methacrylate) copolymer was determined by ratioing the resonance of the protons attached to the double bond near 5.0 ppm with the methyls of the ester group at 1.39 ppm. All-acrylic block copolymers were analyzed by ^{13}C NMR in a similar manner.

3) Ultraviolet-Visible spectroscopy was performed using a Perkin-Elmer Model 552 spectrophotometer. Standard cell sizes were utilized (typically 1.0 cm diameter) and solutions were prepared by classical volumetric techniques. If a series of concentrations were desired, then dilutions of a stock solution were performed using volumetric pipettes. In many instances, only the wavelength of an

absorbance was desired and not the molar absorptivity. Thus, only one concentration with an absorbance between 0.3 and 2.0 was desired. An excellent discussion of the utility of ultraviolet and visible spectroscopy of polymers has appeared in the literature [278].

The spectrophotometer was zeroed automatically by the instrument at a wavelength where no species absorbed. The scan rate, wavelength limits and chart speed were chosen depending on the particular system being analyzed. Typically for poly(alkyl methacrylate) analysis, the scan rate was 120 nm/min from 190 nm to 400 nm and the chart speed was 20 nm/min. Generally, all studies where the absence of absorbance was required in the ultraviolet region were performed in distilled tetrahydrofuran. The lower limit for using tetrahydrofuran as a solvent was approximately 210 nm. Prior to analysis of unknown samples, a THF blank was scanned in order to verify solvent purity and establish a baseline. In fact, for this model, the instrument was turned on with both cells filled with THF and the baseline process was automatically initiated from 190nm to 700nm. The absorbance was read directly from the digital display located on the front of the instrument. It was also advisable to allow the spectrophotometer to warm up for approximately 2 hours prior to analysis.

a) Molecular weight determination was attempted by measuring the absorbance of the phenyl rings on the initiator chain end and determining the concentration by a Beers-Lambert relationship. The calibration curve was constructed using diphenylmethane (261 nm, molar absorptivity = 5100 l/cm mole) as a standard and the absorbance of the polymer solution was located on the linear calibration curve. The determined concentration of the phenyl rings and the known concentration of the polymer solution allowed for the calculation of molecular weight. The polymer solutions were typically diluted from a 0.1000g/100ml THF stock solution. The required concentrations of the desired standard were determined using the Beers-Lambert relationship. The molar absorptivity and an absorbance range from 0.3-1.0 (cell length = 10 cm) were required to calculate the appropriate standard concentration range.

b) Stabilities of anionic species in a particular solvent were estimated by observing a decrease in an absorbance as a function of time. Most anions have either an ultraviolet or visible absorption and the exact wavelength was a function of the solvent polarity. The anion was formed in a glass reactor equipped with UV-Visible cells. The vessel could be inverted causing the solution to fill the cells. The cells were fitted into the spectrophotometer and the absorbance was noted at various time intervals.

The vessel was rinsed with an anionic species prior to the reaction in order to avoid termination due to impurities present in the extremities of the reactor cells. In addition, the septum fitted neck was removed under vacuum to eliminate the possibility of leaking.

c) Conversion analysis was also performed in a similar fashion as the stability experiments. However, the only difference was that the reaction to form the anion was followed. This required that the reaction was slow enough to have sufficient time in the spectrophotometer. Once the absorbance of the product reached an equilibrium value, one was sure that the reaction was complete. This approach was routinely utilized for the analysis of diphenylhexyllithium formation from diphenylethylene and sec-butyllithium.

d) Solvent polarity effects on anions were ascertained by varying the solvent polarity and witnessing the appropriate shift in wavelength. Typically, the more polar the medium, the higher the wavelength. This observation also demonstrated the effect of solvent polarity on the reactivity of the anion, i.e., more solvated ion pairs resulted in enhanced reactivity.

4) Gel Permeation Chromatography (GPC) was performed using a variable temperature Waters 590 GPC equipped with ultrastyragel columns of 500 Å, 10^3 Å, 10^4 Å and 10^5 Å. A Waters 490 programmable wavelength detector and a Waters R401 differential refractive index detector were utilized. Uninhibited tetrahydrofuran was commonly used as the solvent

and the flow rate was 1.0 ml/min at 30 °C. The UV wavelength was chosen based on the polymer system. For example, poly(dienes) and poly(alkyl methacrylates) were analyzed at 218 nm for the double bond and carbonyl respectively. Styrenic polymers were analyzed at 254 nm due to the aromatic ring absorbance. In some instances, a viscometric detector introduced by Viscotech Corp. was utilized for the determination of Mark-Houwink constants [279,280]. For this latter detector, molecular weights and distributions were determined using a universal calibration curve. This eliminated the comparison to polymer standards of different hydrodynamic volume.

a) Molecular weight and molecular weight distribution were calculated using both poly(styrene) and poly(methyl methacrylate) standards. The calibration curves were fitted with linear and cubic equations. Sets of polymer standards were available over a wide molecular weight range (10^6-10^3 g/mole) from Polymer Laboratories Inc..

5) Vapor Phase Osmometry was utilized for the determination of absolute number average molecular weights less than 30,000 g/mole. A Wescan Vapor Phase Osmometer Model 233 was utilized for all analyses. The analyses were performed using toluene as the solvent at 30°C. Solution concentrations ranged from 0.7 g/l to 7.0 g/l. The detection limit of the instrument in toluene was 5x10-5 mole/l.

6) Thermal Analysis (DSC, TMA, TGA) was performed with either a Perkin-Elmer Model 2 or Model 4. In addition to the determination of glass transition temperatures, polymer modification reactions, crystalline melting points and thermal stability were also routinely determined. Microphase separation in multiphase systems was also investigated by the detection of multiple glass transition temperatures.

a) Differential Scanning Calorimetry (DSC) heating rates were 10°C/min and the experiment was conducted in a nitrogen atmosphere. In order to obtain significant thermal transitions, the sample size was greater than 10 mg. The glass transition temperature that was reported corresponded to the midpoint of the transition. Significant discrepancy exists in the literature for many glass transition temperatures on account of the method of determination. Many authors report the onset of the glass transition temperature and these values may be as much as 20°C lower than midpoint values.

b) Thermomechanical Analysis (TMA) was conducted by resting a weighted probe on a polymer film and penetration was plotted versus temperature. The heating rate was generally 10°C/min using a 5-10g weight and the experiment was conducted in a nitrogen atmosphere. The film had to be void of any imperfections and thicker films were easier to analyze. This method was particularly useful for the analysis of multiphase block copolymers. In this case, one could see significant penetration at the glass transition of each phase.

c) Thermogravimetric Analysis (TGA) monitored the polymer weight loss as a function of temperature for a powdered sample or a film. When comparing a series of polymer samples, it was desirable to use the same form, i.e., film or powder for the sample. The analysis was conducted in either a nitrogen or oxygen environment in order to determine the effect of atmosphere. In addition, the purging gas and volatile degradation products were analyzed by mass spectrometry (MS). A similar experiment was performed by placing a sample on the probe in a mass spectrometer and increasing the temperature of the probe. Although the weight loss could not be detected, the degradation products were identified. Sample sizes in either case were 0.5-5.0 mg and the temperature range was 50-600°C.

7) Mechanical Analysis

a) Dynamic Mechanical Thermal Analysis (DMTA) of polymeric films was performed in the two point single cantilever bending mode using a Polymer Laboratories DMTA. Since the accuracy of the measured values was dependent on the optimization of several parameters (sample geometry in particular), extreme care was taken to ensure that the sample was uniform in width and thickness. In addition, the samples were generally heated at a slow rate (5°C/min). The accuracy of the technique was determined on the basis of reproducibility using several test specimens and by comparison of the Tg obtained with DSC. Agreement was always better than ±2%. A frequency of 1 Hz over a temperature range from -150°C to 150°C was selected.

b) Dielectric Analysis

In the dielectric experiments, the dissipation factor and capacitance values were determined over a frequency range of 50 Hz to 10 KHz and a temperature range of -150°C to 200°C. A General Radio 1620A capacitance bridge measuring assembly was used in conjunction with a three-terminal guarded electrode sample cell. The cell was contained in a Delta Design 2850 temperature test chamber which maintains the temperature to ±0.1°C. The samples were placed in direct contact with the electrodes and the dielectric constant ε',and tan delta were measured. In a typical experiment, the cell containing the sample was first cooled to the desired temperature and the data was collected as the system warmed. Walstrom and Ward have described these techniques and their utility in polymer characterization in detail earlier [281].

c) Stress-Strain Analysis

Young's modulus, tensile strength and elongation at break were determined on polymer films using an Instron Model 1123 at room temperature and atmospheric conditions.

Dog bone shaped samples (width = 0.255 cm and gauge length = 10 mm) were cut from films that were generally 0.008-0.011 inches thick. It was imperative that no imperfections were present in the film. The cross-head speed of the instrument ranged from 20 mm/min to 50 mm/min and the strain rate was typically varied from 2 mm/min (20 %/min) to 10 mm/min (100 %/min). The selection of full scale load depended on the modulus of the material, but the general range was from 2-10 kg. All samples were elongated until break.

8) Surface Analysis

a) X-Ray Photoelectron Spectroscopy (XPS)

XPS or Electron Spectroscopy for Chemical Analysis (ESCA) was performed by utilizing a Kratos XSAM-800 instrument. Data was obtained which described the atomic composition in the upper 70-100 Å of a polymer film. Vacuums achieved during analysis generally reached 10^{-9} torr. J. Felby and J. P. Wightman have published detailed accounts of the instrument assembly and utility [282].

Variable contact angle analysis was performed from 15°-90° in order to obtain a more quantitative description of any surface domination. As the contact angle approached 15° (the grazing angle), the analysis became more surface sensitive.

b) Contact Angle

Films were either spun cast onto metal plates and allowed to dry under a watch glass or solutions were statically cast. Drying in a vacuum oven often resulted in a 2-3% silicon contamination; consequently, films were dried for long periods of time in the hood. No outgassing of residual solvent was evident in XPS studies. Thus, it was presumed that the film preparation techniques were adequate.

The polymer film on the metal substrate was placed in the goniometer at room temperature and at atmospheric conditions. Water was added dropwise usually in 0.002 ml increments until an equilibrium contact angle was measured. This angle was referred to as the advancing contact angle. The drop was subsequently removed in similar increments and the contact angle was measured until a equilibrium contact angle was established. This contact angle was referred to as the receding contact angle and the entire process of advancing and receding was referred to as contact angle hysteresis. This procedure was generally repeated 3-4 times at various locations on the film in order to ensure reproducibility and a homogeneous film. All values were averages of several readings and agreement was generally within ± 2°.

IV. RESULTS AND DISCUSSION

A) Poly(alkyl methacrylate) Homopolymer Studies

1) Monomer Purification

The initial focus of this research project was to develop further purification methodologies for alkyl methacrylate monomers. Monomer purity is a critical, but not always appreciated, aspect in anionic polymerization studies. This consideration is particularly important when high molecular weight polymers ($>5.0 \times 10^4$ g/mole) are desired, and the corresponding anion concentrations are quite low (<0.20 mmoles in 150 ml solvent). Any impurities present in the alkyl methacrylate monomer will quickly terminate the initiator anion. Significant attention had been devoted earlier in our laboratories to the use of trialkyl aluminums as purification reagents [283,284]. However, a more detailed understanding of the utility and chemistry of these compounds was required. In addition, it was desirable to demonstrate the application of these purification reagents to a wide range of alkyl methacrylate monomers. The capability of readily obtaining ultrapure, anionic-grade alkyl methacrylate monomers would allow for the careful investigation of anionic syntheses and mechanisms. Small variations in initiator or enolate stability could safely be attributed to factors inherent in the chemistry and not to the presence of side reactions associated with monomer impurities.

In order to fully appreciate the importance of monomer purity, one must consider the relative concentration of initiator to monomer that is typically employed. For example, 10.0g of monomer and 0.10 millimoles of initiator are required to synthesize a 100,000 g/mole polymer by anionic techniques. If a commercial grade of methyl methacrylate monomer contained ~3% of the esterifying alcohol (methanol), then complete deactivation of the anionic species would occur after the addition of approximately 0.11g of impure monomer (1.1% conversion). This amount of monomer would actually contain 0.0033g (0.10 millimoles) of methanol. It is important to understand that the definition of an impurity for this discussion is limited to protic species that can react with anions. This would include the esterifying alcohol, methacrylic acid and water which all may be present in commercially available grades of monomer. Impurities which do not donate a proton to anionic species can be tolerated. Table 16 depicts the purity of various hypothetical grades of methyl methacrylate monomer and the extent conversion when complete deactivation occurs. This analysis assumes that impurities are not present in the reaction vessel, atmosphere or reaction solvent. It can be shown that greater than 99.97% monomer purity is required to obtain complete conversion (100% yield). However, in order to obtain narrow molecular weight distributions and

Table 16

Effect of Monomer Purity on Extent Conversion of 100,000 g/mole PMMA

% Purity	% alcohol	g monomer complete deactivation	% conversion
97	3	0.11	1.1
98	2	0.16	1.6
99	1	0.32	3.2
99.9	0.1	3.2	32
99.95	0.05	6.4	64
99.96	0.04	8.0	80
99.97	0.03	>10	100

Theoretical Reactants Charge: Monomer = 10.0g
Initiator = 0.0001 moles

controlled molecular weights, it is necessary that less than 5% of the initiator or propagating anion be terminated. This more stringent demand would dictate that monomer purity exceed approximately 99.999 percent.

Calcium hydride has been the classical purification reagent for most alkyl methacrylate monomers. However, this reagent exhibits two disadvantages which limit its successful utility. First, the drying efficiency of calcium hydride is limited due to its heterogeneous nature. Alkyl methacrylate monomers are relatively hydrophilic due to the presence of the polar carbonyl and generally contain an appreciable amount of water. Second, the major impurities in alkyl methacrylate monomers are alcohols and carboxylic acids which result from monomer synthetic routes. In particular, alcohols are used in esterification and transesterification reactions. Calcium hydride does not react with these impurities. Thus, an effort was made to find a reagent that did not react with alkyl methacrylate monomers, but would efficiently remove protic impurities which could terminate subsequent anionic polymerization attempts.

Trialkyl aluminum (TAA) reagents readily undergo nucleophilic substitution reactions with alcohols, water, acids and amines [285]. This inherent reactivity makes these compounds viable candidates for purification reagents. Scheme XXVIII depicts the reaction of an alcohol with a

Scheme XXVIII

Reaction of Trialkyl Aluminum Reagents With Alcohols [285]

$$R_3Al + R'OH \xrightarrow{k_1} R_2AlOR' + RH$$

$$R_2AlOR' + R'OH \xrightarrow{k_2} RAl(OR')_2 + RH$$

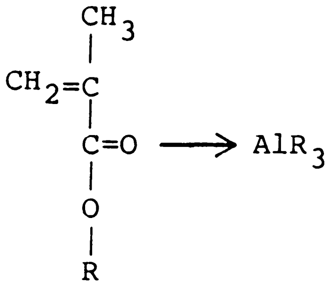
$$RAl(OR')_2 + R'OH \xrightarrow{k_3} Al(OR')_3 + RH$$

$$k_1 > k_2 >> k_3$$

* Reactions with carboxylic acids occur in a similar fashion

trialkyl aluminum reagent. Each of the alkyl groups attached to the aluminum is capable of being removed as the corresponding alkane. However, the reactivity drastically decreases as alcoholysis occurs i.e $k_1 > k_2 >> k_3$. In addition to the steric environment around the aluminum center, the rate of alcoholysis is also controlled by the size of the nucleophile i.e. bulkier impurities would react slower. Thus, it is important to realize that reactions with bulkier alcohols will require longer times. Due to the enhanced reactivity of TAA reagents with protic species, it seemed quite feasible that these compounds could be used as purification reagents [286].

P. E. M. Allen et al. had shown earlier that TAA reagents formed a colored complex with α,β-unsaturated esters such as alkyl methacrylates or acrylates [287]. Figure 15 depicts the structure of the colored complex. In addition, it was also shown that trialkyl aluminums initiate the polymerization of methacrylic monomers [269]; however, photoinitiation was required and the mechanism involved free radical species. Allen realized the possible utility of trialkyl aluminums as purification reagents [288], but later rejected this application due the presence of side reactions when the reagent came into local excess during mixing. Consequently, sodium benzil, an anionic initiator, was used to remove inhibitors and impurities. This later approach is termed "purification by



$$CH_2=C(CH_3)-C(OR)=O \longrightarrow AlR_3$$

Figure 15: Trialkyl Aluminum/Monomer Complex [287]

polymerization" and is only feasible when the polymerization proceeds very slowly. Despite this early assessment of trialkyl aluminums as purification reagents, their utility has remained unexplored over the past two decades.

If one can eliminate the possibility of side reactions of the trialkyl aluminum with the methacrylic ester, these reagents could be used in a controlled manner to scavenge protic impurities. In addition, the formation of a colored complex would allow for the "titration" of impurities prior to a distillation. This later observation assumes that the reaction with the impurities is faster than the rate of complexation, but this may not always be the case. The advantages of trialkyl aluminums as purification reagents are summarized below.

(1) The reagents do not initiate polymerization of alkyl methacrylate monomers.

(2) Reactions with a variety of protic impurities are rapid and quantitative with the liberation of an inert byproduct, i.e., an alkane.

(3) Complexation of the reagent with the ester results in a colored species which can be used as an indication of purity.

The reaction of the trialkyl aluminum reagents with impurities in various alkyl methacrylate monomers was followed by gas-liquid chromatography (GLC). In most cases, GLC also allowed for the identification of impurities in monomers and the determination of the impurity concentration prior to purification. Typically, the GLC column consisted of a nonpolar, 15% DC-200 liquid phase which was coated on a Chromosorb P solid support. Helium was routinely used as the carrier gas. The column temperature was maintained at 110°C and both the injection port and thermal conductivity detector remained constant at 160°C. Figure 16a) depicts the gas chromatogram of a commercially available methyl methacrylate sample which had been distilled from calcium hydride. The sample contains 2 component peaks which appear at 1.9cm and 2.7cm. The air peak is the first peak to appear at 0.60cm. This particular sample did not contain an alcoholic impurity, but was intentionally doped with 1% of isopropyl alcohol (1.3cm) in order to observe its disappearance upon purification (Figure 16b). Despite a calcium hydride distillation of the alcohol doped monomer, "living" polymerization attempts were unsuccessful with this impure monomer.

In order to monitor the reaction of trioctyl aluminum with the alcoholic impurity, samples were taken at various intervals and the disappearance of the alcohol peak was observed. This reaction was performed under an inert atmosphere in order to avoid reaction of the trioctyl

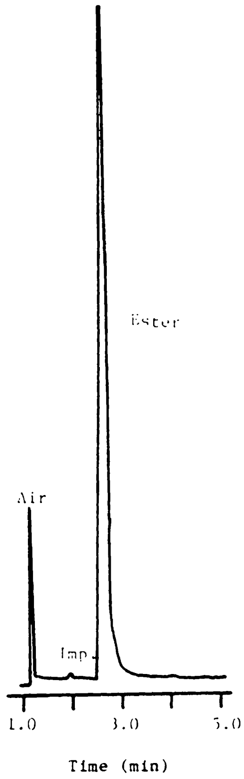


Figure 16 a): Gas Chromatogram of Commercially Available MMA

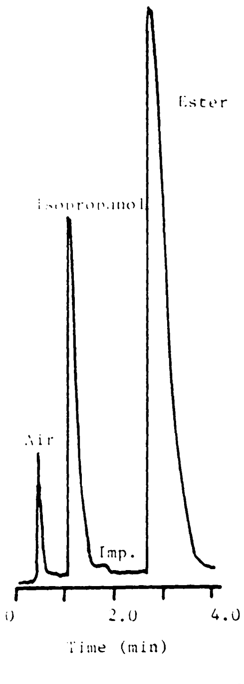
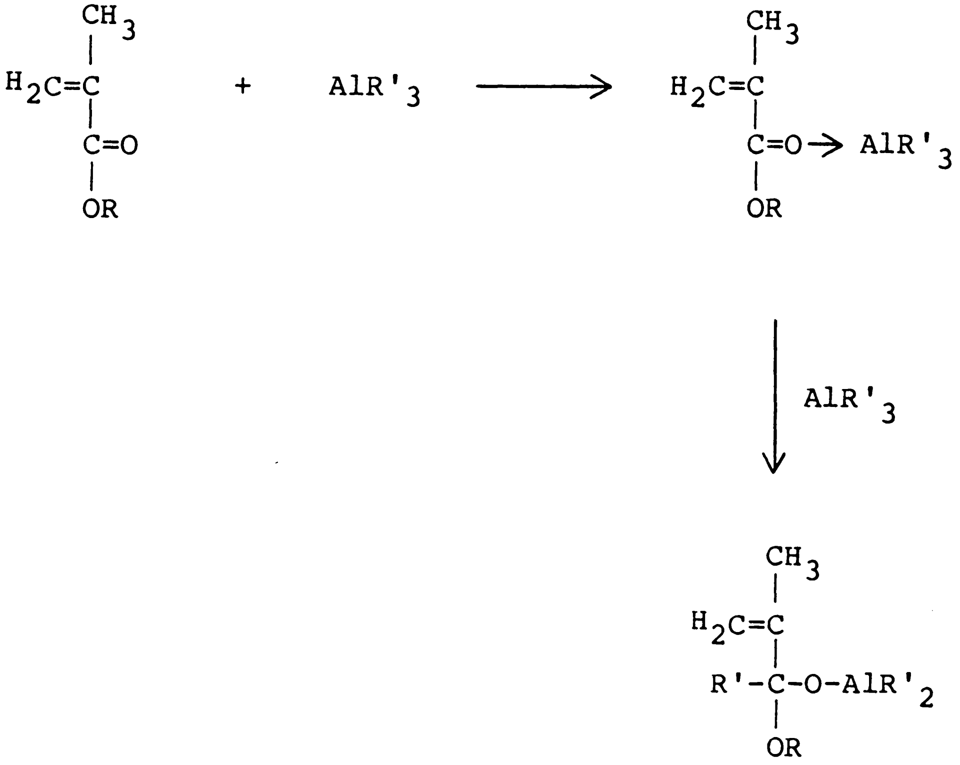


Figure 16 b): Gas Chromatogram of MMA Doped with 1% Isopropanol aluminum with moisture in the air. In addition, the purification reagent was added dropwise to the rapidly stirring monomer until the complex color formed. This was believed to eliminate the possibility of developing a local excess of reagent and inducing deleterious side reactions. A potential side reaction involving 1,2-addition across the carbonyl is shown in Scheme XXIX. A 10-20% excess of the purification reagent was typically employed in order to ensure complete purification. Figure 17 is the chromatogram of the monomer after complete removal of the alcohol (1.3cm). The ester (2.7cm) peak is unaffected and three new peaks appear. The first two peaks at 1.7-2.7 minutes are attributed to hexane isomers since the trioctyl aluminum reagent was utilized as a 25 weight % solution in hexanes. The identity of the last peak at 5.5 minutes was perplexing initially, but was later observed to increase as the alcohol peak decreased. After recalling that an alkane was the purification byproduct and trioctyl aluminum was utilized, this peak was suspected to be octane. By spiking the sample with neat octane and noting the increase in peak integration, the presence of octane was verified. After distillation of the trioctyl purified monomer, subsequent polymerization attempts resulted in quantitative conversions. Although this study did not quantify the alcohol disappearance or octane appearance with time, the time that was required for quantitative purification was

Scheme XXIX

1,2-Addition of Trialkyl Aluminum Reagents with Ester Carbonyls [285]



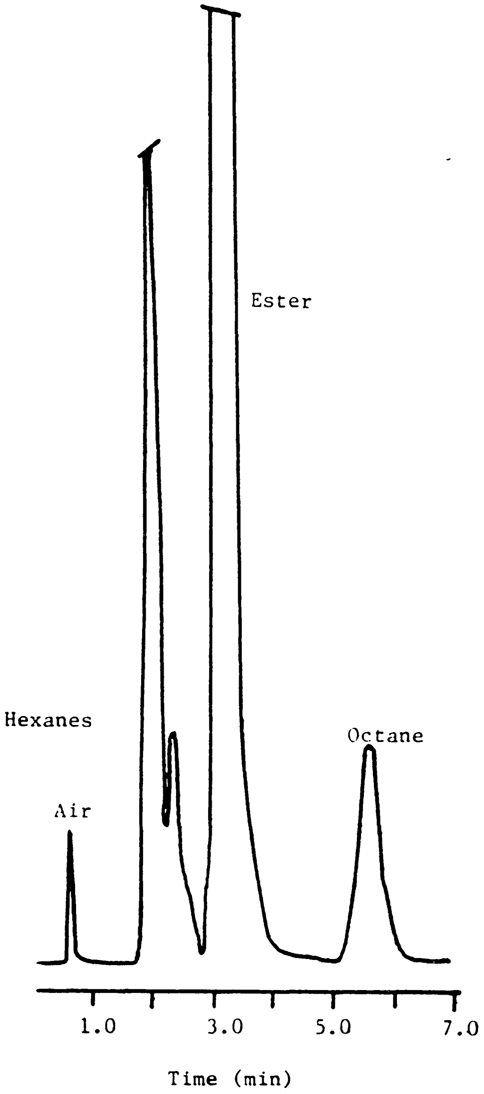


Figure 17: Gas Chromatogram of the Trialkyl Aluminum Purified MMA

determined. The example study described above for the removal of 1% isopropyl alcohol from methyl methacrylate required approximately 12 minutes after formation of the colored complex.

The absence of aluminum in the distillate was verified by Inductively Coupled Plasma (ICP) techniques. This technique is sensitive to parts per billion concentrations. The distillates generally contained 1-2 ppm of aluminum. This level of impurities would not affect the successful polymerization of the purified alkyl methacrylate monomers.

The purification of branched alkyl methacrylates such as isopropyl methacrylate was accompanied by an unusual observation. The colored complex often faded before or during distillation and GLC of the distillate indicated the presence of residual isopropyl alcohol. In addition, subsequent polymerizations resulted in materials with broad molecular weight distributions (>1.5). In order to understand further the purification reaction, the required contact times were determined by GLC for a variety of monomer and alcohol combinations. Each monomer contained approximately 1-1.5% of an alcoholic impurity and GLC was utilized to monitor the disappearance of the alcohol peak. Table 17 lists the required contact times for the purification of various monomer-alcohol combinations. These data clearly demonstrate that t-butanol (TBA) required longer reaction times than isopropanol (IPA) to result in

Table 17

Minimum Purification Reaction Times for Various Monomer-Alcohol Combinations

Monomer	(1%) Dopant	Reaction Time (min)[a]	Yield (%)
Methyl methacrylate	isopropanol	12	100
Methyl methacrylate	t-butanol	60	100
isopropyl methacrylate	isopropanol	85	100

[a] Reaction Times (± 5min) determined by disappearance of GLC alcohol peak

successful purification. In addition, these studies also indicated that there may be an effect of monomer structure due to the longer times necessary to remove isopropanol from isopropyl methacrylate versus methyl methacrylate. A possible explanation may involve the competition of complexation with alcoholysis. The larger ester alkyl groups contribute more electron density to the carbonyl of the monomer. Consequently, the trialkyl aluminum, which is a Lewis acid, forms the complex with the ester carbonyl before complete removal of the alcohol is accomplished. This theory would account for the loss of the complex color with time during isopropyl methacrylate purification.

Thus, two limitations of trialkyl aluminums as purification reagents for alkyl methacrylate monomers have been realized. First, long reaction times (>80 minutes) are required for the complete purification of branched monomers. This limitation increases the possibility of premature polymerization of the complexed monomer prior to distillation due to the instability of the complex. Second, dilution of the monomer with hexane from the trialkyl aluminum reagent solution results in loss of molecular weight control in subsequent polymerizations. However, by utilizing careful vacuum techniques, the hexane can be completely stripped prior to distillation of the pure monomer.

Despite purification attempts using longer reaction times for t-butyl methacrylate, molecular weight distributions ranged from 1.3 to 1.5. If longer contact times (>80 minutes) between the impure, branched monomer and triethyl aluminum reagent were permitted, premature polymerization often occurred. Thus, it was believed that the reactivity of the reagent had to be modified in order to enhance the rate of alcoholysis and decrease the loss of monomer to premature polymerization. This later approach involved the addition of small amounts (50 volume % or less) of diisobutyl aluminum hydride (DIBAH) to a triethyl aluminum (TEA) solution. It is known that the aluminum hydrogen bond is significantly more labile to nucleophilic substitution than the aluminum alkyl bond [285]. Scheme XXX illustrates the reaction of an aluminum hydride with a protic impurity such as an alcohol or carboxylic acid.

The mixed reagent approach (TEA:DIBAH) was necessary for two reasons. First, the aluminum hydride, unlike the trialkyl aluminum reagent, did not form a colored complex with the α,ß-unsaturated ester. Second, the mixed system was believed to tone down the reactivity of the aluminum hydride. A 25 weight % TEA:DIBAH mixture in hexanes was added dropwise to cold (-78°C) monomer until the colored complex formed. If the mixed reagent was added to the monomer at room temperature, a violent, exothermic reaction resulted and complete polymerization occurred. The reason for this observation is still unknown, but is being

Scheme XXX

Reactions of Dialkyl Aluminum Hydrides with Alcohols and Carboxylic Acids [285]

Alcohols:

$$R_2AlH \quad + \quad R'OH \longrightarrow R_2AlOR' \quad + \quad H_2$$

Carboxylic Acids:

$$R_2AlH \quad + \quad R'COOH \longrightarrow R_2AlOOCR' \quad + \quad H_2$$

investigated. In order to avoid excess aluminum hydride from causing side reactions with the ester, an excess (10-20%) of TEA alone was utilized after the endpoint. The purification reaction was allowed to proceed in the dark for approximately 60 minutes at room temperature. Distillation of the purified monomer was quantitative and the distillate was a clear, colorless liquid. Significantly narrower gel permeation chromatograms ($Mw/Mn < 1.20$) were observed for poly(t-butyl methacrylate) (PTBMA) samples prepared from TEA/DIBAH purified monomer. Table 18 illustrates the effect of TEA:DIBAH composition on the resulting PTBMA molecular weight distributions.

Despite the known reduction potential of dialkyl aluminum hydrides, reduction products were not found in the distillate. In addition, subsequent polymerizations proceeded by a "living" mechanism and spectroscopic analysis did not indicate unexplained structures. Scheme XXXI illustrates the possible reduction reaction of aluminum hydrides and esters. It is important to note that water is required to convert the aluminum alkoxide to the ketone. It is presumed that no water is available for this step to occur. Also, if the aluminum alkoxide did form, it is doubtful that it would distill at the pressures and temperatures required for monomer distillation. However, these investigations have implied that the aluminum hydride reacts faster at -78°C with protic impurities than with

Table 18

Effect of TEA:DIBAH Composition on Resulting Poly(t-butyl methacrylate) Molecular Weight Distribution

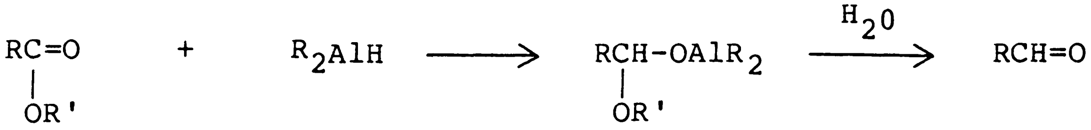
TEA:DIBAH Ratio (wt.:wt.)	(Mw/Mn)[a]
100:0	1.45
75:25	1.30-1.32
50:50	1.08-1.15

TEA: Triethyl aluminum
DIBAH: Diisobutyl aluminum hydride

[a] Determined by GPC using Polystyrene Standards (± 0.03)

Scheme XXXI

Reduction of Esters with Aluminum Hydrides [285]



$$\underset{\substack{|\\ OR'}}{RC{=}O} + R_2AlH \longrightarrow \underset{\substack{|\\ OR'}}{RCH{-}OAlR_2} \xrightarrow{H_2O} RCH{=}O$$

methacrylic esters.

Another theory which accounts for the fact that reduction products are not found is based on the decreased reactivity of the branched alkyl methacrylate monomers. The larger ester alkyl group deactivates the carbonyl by decreasing the partial positive charge on the carbonyl carbon. This can be demonstrated by noting the ^{13}C chemical shift of the carbonyl carbon. Table 19 lists the carbonyl carbon chemical shifts for various alkyl methacrylate monomers. The more deshielded or electron deficient carbon appears most downfield. For example, the carbonyl of methyl methacrylate would be more reactive than the carbonyls of isopropyl or t-butyl methacrylate. A similar trend can be noted by observing the FTIR carbonyl frequency. Table 20 lists the carbonyl frequency for various alkyl methacrylate polymers. Once again, it can be seen that isopropyl and t-butyl methacrylate carbonyls have a significantly different steric and electronic environment than the carbonyl in methyl methacrylate. The ramifications of these observations relative to anionic polymerization will be discussed in detail later.

Thus, it appears very advantageous to incorporate dialkyl aluminum hydrides with trialkyl aluminums for the purification of branched alkyl methacrylate monomers. The following advantages have been noted:

Table 19

Carbonyl Carbon Chemical Shifts for Various Alkyl Methacrylate Monomers

Monomer	ppm (^{13}C NMR) C=O[a]
methyl methacrylate	167.04
isopropyl methacrylate	166.23
t-butyl methacrylate	166.23

[a] 50 MHz, 10% in $CHCl_3$

Table 20

FTIR Carbonyl Frequencies for Various Alkyl Methacrylate Homopolymers

Poly(alkyl methacrylate)	cm-1 (FTIR)[a]
Poly(trifluoroethyl methacrylate)	1748
Poly(methyl methacrylate)	1731
Poly(isopropyl methacrylate)	1723
Poly(t-butyl methacrylate)	1723

[a] Frequencies ± 4 cm-1; Free standing films.

(1) Faster reactions with protic impurities.

(2) Less chance for premature polymerization in the distilling flask.

(3) More efficient and less time consuming.

The only disadvantages that have been realized include the inability of the hydride to form the colored complex and the possibility of side reactions with the esters. Both disadvantages have been addressed in detail and their potential limitations have been overcome.

Recent efforts have been focused on the development of a practical column technique for the purification of high boiling alkyl methacrylate monomers e.g. 2-ethylhexyl methacrylate, bpt.= 110°C at 14mm. The principal advantage of this technique is that distillation of the monomer is not required in order to remove the aluminum compounds. This aspect is particularly significant in the purification of higher molecular weight alkyl methacrylate monomers. The approach consists of the formation of a persistent colored complex under inert atmosphere followed by passage of the pure, complexed monomer through a column of alumina. The concept relies on the affinity of the trialkyl aluminum and aluminum alkoxide compounds for the alumina. The pure effluent is degassed several times and stored under a nitrogen atmosphere until use. Initial studies involved transferring the complexed, purified monomer directly into the alumina column. However, a significant heat of adsorption resulted and it was suspected that some polymerization occurred in the column. In fact, the resulting polymerizations yielded materials with bimodal gel permeation chromatograms. It was believed that one of the peaks was the polymer formed in the column and the second peak was the polymer that was subsequently prepared.

In order to circumvent this problem, later attempts involved "prewetting" the column with dry tetrahydrofuran before introducing the complexed monomer. The heat of adsorption occurred when THF was placed into the column and the column was allowed to cool before introducing the monomer. The monomer was slowly passed through the column (3 ml/min) and a significant exotherm did not occur. The effluent was degassed in a similar fashion and used immediately. The subsequent polymerizations of the column purified monomer yielded polymers with monomodal gel permeation chromatograms. In addition, when column purified 2-ethylhexyl methacrylate was used in a polymerization, significantly narrower molecular weight distributions were obtained compared to calcium hydride distilled monomer. The preliminary data is depicted in Table 21 for 2-ethylhexyl methacrylate. Although the polydispersity of the polymer prepared from the column pure monomer is still broad (1.59), the value is significantly narrower than the calcium hydride pure monomer control (2.04). It is believed that longer

Table 21

Effect of Purification Method on the Molecular Weight Distribution of Poly(2-ethylhexyl methacrylate)

Purification Technique	$\bar{M}w/\bar{M}n$[a]
Calcium Hydride Distillation	2.04
Calcium Hydride Distillation and Trialkyl Aluminum Column Technique	1.59
Calcium Hydride Distillation and Triethyl aluminum Distillation	1.35

[a] MWD Determined by GPC using Polystyrene Standards

purification reaction times or the use of dialkyl aluminum hydride/triethyl aluminum mixed reagents will sharpen the molecular weight distribution. It would be desirable to have column purified monomer result in polydispersities near the values obtained from monomer that was distilled from trialkyl aluminums (1.35).

The possibility of conducting the polymerizations in the presence of the aluminum compounds is also interesting. For example, the complexed, purified monomer could be syringed directly into the initiator solution. The success of this concept would depend on the relative reaction rates of the initiator anion with the monomer versus reaction with the trialkyl aluminums or aluminum alkoxides.

In conclusion, trialkyl aluminum and dialkyl aluminum hydride reagents are well suited as purification reagents for a variety of alkyl methacrylate monomers. A more comprehensive understanding of the reactivity of this class of compounds was achieved. In addition, it was shown that branched alkyl methacrylate monomers were more difficult to purify due to the decreased reactivity of the protic impurities. Future efforts are directed toward the development of a practical column technique and eliminating distillation of the monomer. The column approach would definitely facilitate an industrial attempt of the anionic polymerization of alkyl methacrylates.

2) Homopolymer Synthesis

a) Effect of Anionic Initiator

The selection of initiator is important in alkyl methacrylate polymerizations for a variety of reasons. Most importantly, the initiator should be sterically hindered to avoid attack on the carbonyl of the monomer. Diphenylhexyllithium (DPHL) (the reaction product of s-butyllithium with diphenylethylene) has been shown to be an efficient initiator for alkyl methacrylates [107,289]. In contrast, if sec-butyllithium is used as an initiator for MMA polymerizations, significant termination occurs, resulting in loss of molecular weight control and broadening of the distribution. However, the bulkiness of the initiator can be compromised if the ester alkyl group in the monomer is branched. For example, t-butyl methacrylate can be initiated in THF using sec-butyllithium at -78°C and the molecular weight distribution only broadens to approximately 1.3. The chromatogram is shown in Figure 18 and only a slight low molecular weight tail is evident. One should recall that sec-butyllithium can react with the monomer to form isopropenyl ketone as discussed earlier. The ketone is more reactive than the methacrylic ester and adds quickly to another propagating chain. However, the addition of more monomer to the terminal ketone anion is relatively slow. Hatada has shown by a deuterated monomer technique that the ketone group resides predominately at the chain ends after complete conversion. [70]. The relatively efficient

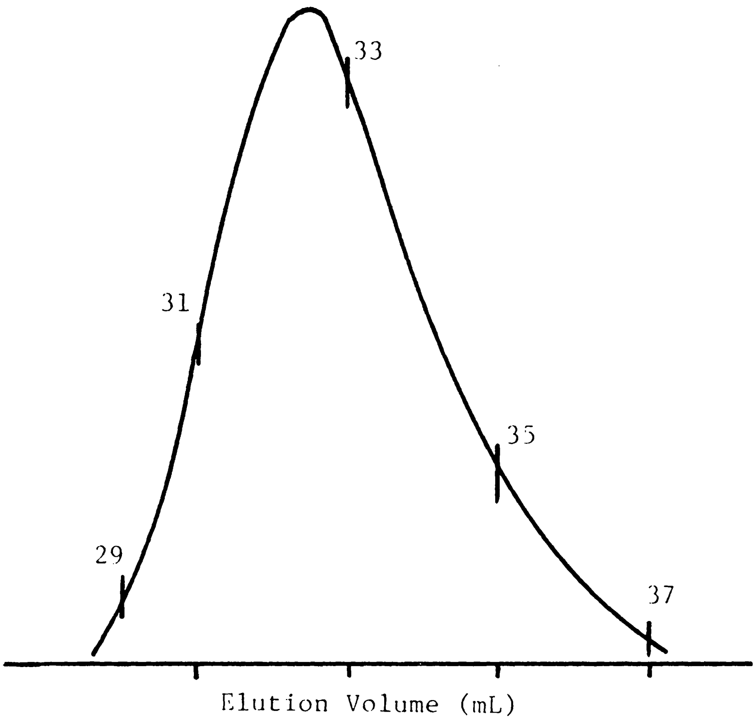


Figure 18: Gel Permeation Chromatogram of Poly(t-butyl methacrylate) Initiated with s-Butyllithium at -78°C in THF

initiation of TBMA with sec-butyllithium is in sharp contrast to most other alkyl methacrylates [286].

Despite the highly delocalized nature of DPHL, the anion is sufficiently basic to initiate alkyl methacrylates quickly. It is important that the rate of initiation be rapid relative to propagation in order obtain narrow molecular weight distributions. A broadening of the molecular weight distribution and/or loss of molecular weight control would result if significant propagation occurred before all of the initiator was consumed. For example, styrenes cannot be initiated efficiently employing DPHL, and very high molecular weights generally result [286].

It should be noted that the DPHL anion will not react at a significant rate with tetrahydrofuran at -78°C. However, complete deactivation of the anion will occur in THF at room temperature in 2-3 hours. Thus, it is advisable to form the initiator and add the monomer immediately at any temperature. Preliminary evidence has indicated that the propagating alkyl methacrylate lithium enolate does not react with THF at a rate which is competitive with polymerization. In fact, the enolate can stand at temperatures as high as 37°C and not react with the solvent. This was proven by allowing the anion to stand and later adding additional aliquots of monomer. The molecular weight still increased linearly with conversion and the molecular weight distributions remained narrow.

The fact that DPHL is a deep red color facilitates polymerization techniques. The reactor can be "titrated" in order to eliminate any impurities present in the reactor prior to monomer addition. Also, the formation of DPHL can be monitored very easily using ultraviolet-visible spectroscopy. For example, the anion absorbs very strongly at approximately 435 nm in toluene and 495 nm in tetrahydrofuran. Figure 19 depicts the DPHL absorbance versus wavelength in toluene. The increase in absorbance can be followed with time and the required reaction time can be determined. The plot of absorbance versus time for DPHL formation in toluene at 25°C is shown in Figure 20. One can see that after approximately 40 minutes, the absorbance remains constant for several hours. This is indicative that complete formation of the initiator has been accomplished. In polar solvents, the reaction is believed to be done in several minutes at temperatures ranging from -78°C to 40°C.

Diphenylhexyllithium (DPHL) was an efficient initiator for various alkyl methacrylate monomers and polymerizations proceeded in a "living" manner. All samples demonstrated good molecular weight control and narrow molecular weight distributions (<1.25). Table 22 depicts representative poly(methyl methacrylate) (PMMA) and poly(t-butyl methacrylate) (PTBMA) samples. The number average molecular weights and molecular weight distributions were determined

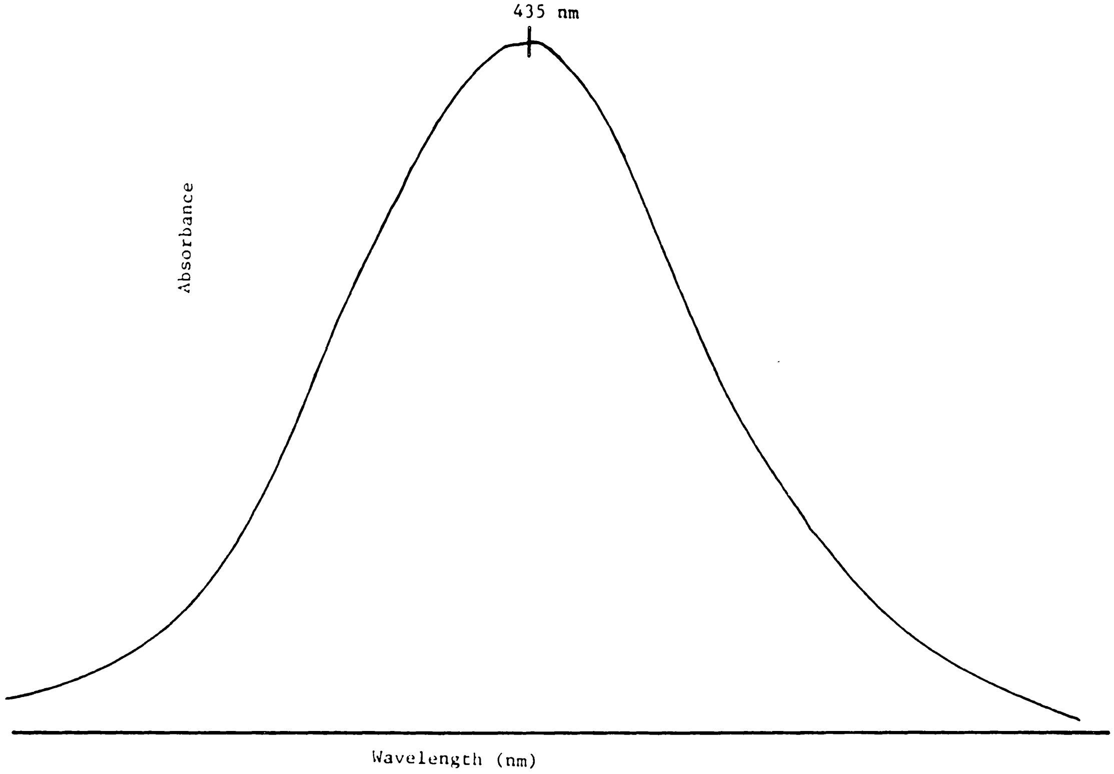


Figure 19: DPHL Absorbance Versus Wavelength in Toluene

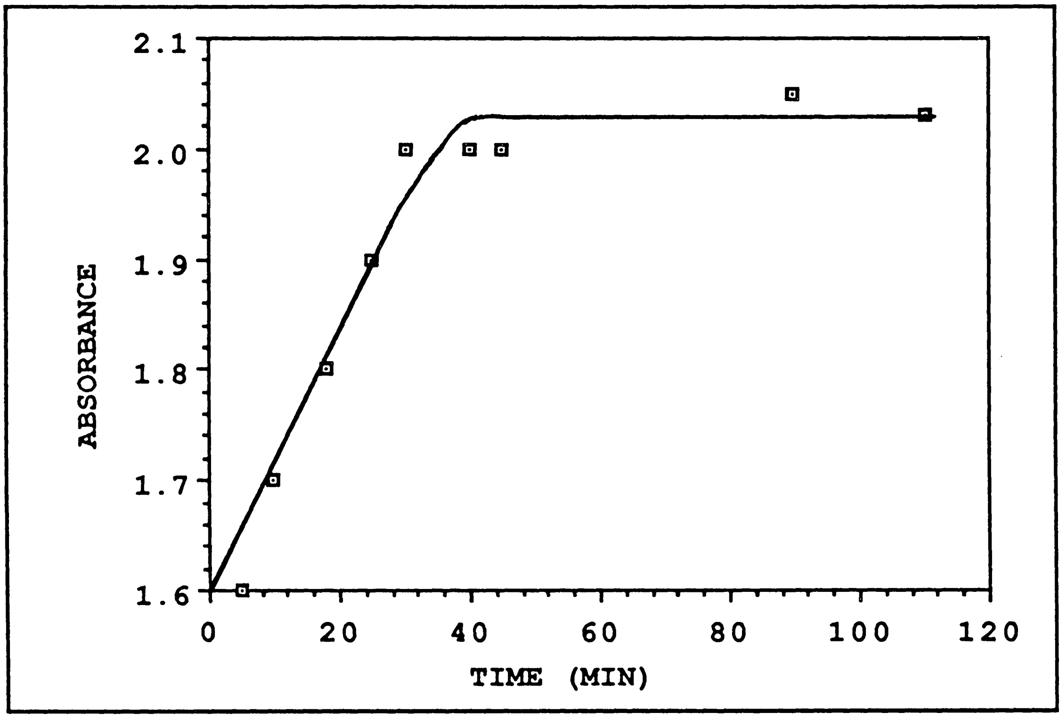


Figure 20: DPHL Absorbance Versus Time in Toluene at 25°C (435nm)

Table 22

Molecular Weight and Molecular Weight Distribution for Various Poly(alkyl methacrylates)

Sample	$\bar{M}n$ (th)[a]	$\bar{M}n$ (GPC)[b]	$\bar{M}w/\bar{M}n$
PMMA-1	7,400	10,000	1.18
PMMA-2	30,000	31,100	1.15
PTBMA-1	50,000	60,500	1.12
PTBMA-2	100,000	139,000	1.18

[a] $\bar{M}n\ (th) = \frac{\text{g monomer}}{\text{moles initiator}}$

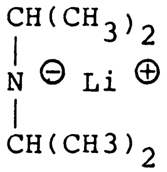
[b] Polystyrene Standards

by gel permeation chromatography (GPC) and calculated based on poly(styrene) standards for those samples described in Table 22. It is important to note that all the polymerizations were conducted in THF at -78°C. The theoretical molecular weight was calculated by dividing the grams of monomer by the moles of initiator.

It is important to realize that the monomer is added directly to the "living" initiator. This technique places stringent demands on monomer purity because impurities in the monomer can quickly terminate the initiator anion. On the other hand, if the initiator is added to a monomer solution, the impurities in the monomer can be scavenged by a certain percentage of the initiator charge and the remaining amount will initiate polymerization. This later approach has two distinct disadvantages. First, the reactor and polymerization solvent cannot be titrated before initiation. Consequently, molecular weight control is more difficult to achieve and one generally has to charge an arbitrary, excess amount of initiator to react with impurities. Second, it is more difficult to control the exotherm of the polymerization and in many instances, alkyl methacrylates will undergo side reactions at elevated temperatures. One method of avoiding these undesirable exotherms is to use a very dilute (2-3% wt./vol.) monomer solution. The role of polymerization temperature will be described in detail later.

Lithium diisopropylamide (LDA) (Figure 21) has also been found to be an efficient initiator for methyl methacrylate. LDA is a very common non-nucleophilic, strong base used in many organic reactions. Its bulkiness eliminates carbonyl attack, and narrow molecular weight distribution samples with predictable molecular weights (Table 23) are obtained. In fact, the molecular weight distributions are generally narrower than those obtained using DPHL. This may be attributed to a faster initiation rate for LDA. One disadvantage of this initiator is that it is not colored and does not allow for visual detection of initiation. In addition, LDA does not initiate diphenylethylene and reactor "titration" is not possible. The use of LDA to initiate branched alkyl methacrylate monomers has also been investigated. Table 23 lists a molecular weight distribution of 1.31 for poly(isopropyl methacrylate). This value is significantly higher compared to values routinely obtained for PMMA. The initiation reaction of LDA is generally less efficient for branched alkyl methacrylates. This may be due to the decreased reactivity of the double bond by ester alkyl, electron donation.

Many synthetic possibilities exist when an amine is located only at the polymer chain end (telechelic). For example, the tertiary amine group can be converted to the corresponding ammonium salt by a simple acid titration.



$$\begin{array}{l} \mathrm{CH(CH_3)_2} \\ | \\ \mathrm{N}^{\ominus}\ \mathrm{Li}^{\oplus} \\ | \\ \mathrm{CH(CH3)_2} \end{array}$$

Figure 21: Lithium Disopropyl Amide (LDA)

Table 23

Molecular Weight Control and Molecular Weight Distribution for LDA Initiated Alkyl Methacrylates

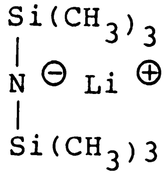
Sample	$\bar{M}n(th)$[a]	$\bar{M}n(GPC)$[b]	$\bar{M}w/\bar{M}n$
PMMA	30,000	23,100	1.16
PMMA	7,500	10,000	1.18
PIPMA	10,000	17,500	1.31

[a] $Mn(th) = \frac{\text{g monomer}}{\text{moles initiator}}$

[b] Poly(styrene) Standards

Another possibility would involve blending the tertiary amine terminated poly(alkyl methacrylate) with an acid terminated polymer. This may result in the synthesis of novel block copolymers where the blocks are linked not by a covalent bond, but by an ionic interaction [213]. Coupling reagents such as dibromoxylene would permit the synthesis of difunctional telechelic polymers.

Preliminary efforts have also been directed at the utilization of lithium bis(trimethylsilyl)amide (LBTSA) (Figure 22) as an anionic initiator for alkyl methacrylates. It was hoped that the nitrogen-silyl bonds could be hydrolyzed after polymerization and primary amine groups would remain. The primary amine groups (difunctional or monofunctional) could be used in wide variety of subsequent reactions. For example, macromonomers could be prepared by reaction with an acid chloride. In addition, methacrylates could be incorporated into a variety of multiphase segmented copolymers such as poly(urethanes), poly(ureas) or poly(imides). Unfortunately, polymerizations which utilized BTSA as the initiator resulted in low conversions (20%), and high molecular weights. However, the distributions were narrow (1.30) and spectroscopic analysis of the polymer did not show any unexplained structures. Due to the hydrolytic instability of the nitrogen-silyl bond, there may be primary amine, secondary amine or hexamethyldisiloxane impurities in the initiator solution. It was also suspected that the



$$\begin{array}{l} \mathrm{Si(CH_3)_3} \\ | \\ \mathrm{N}^{\ominus}\ \mathrm{Li}^{\oplus} \\ | \\ \mathrm{Si(CH_3)_3} \end{array}$$

Figure 22: Lithium Bis(trimethylsilyl) Amide (BTMSA)

propagating anion could backbite at the silyl-nitrogen bond after a certain percentage of conversion. Distillation or careful synthesis of BTSA may eliminate the impurities which cause termination reactions.

Lithium diisopropylamide also has been demonstrated to be a potential initiator for hexamethylcyclotrisiloxane (D_3). Initiation was allowed to proceed at room temperature in cyclohexane and propagation was promoted by the addition of 10 vol.% THF. A detailed account of the polymerization procedure has been published by McGrath and coworkers [290]. Termination of the propagating lithium siloxanolate was accomplished by the addition of a methacrylate functional chlorosilane. The unsaturated ester functionality allowed the normally UV transparent material to be analyzed by GPC using a UV-Vis detector. Gel permeation chromatography of a 21,000 g/mole poly(dimethyl siloxane) sample reveals a molecular weight distribution of 1.19 ($\bar{M}n(th)$ = 10,000 g/mole). The fact that a chromatogram was obtainable for the functionalized poly(dimethyl siloxane) indicates that initiation and propagation did occur. The chromatogram contains a high molecular weight tail which may have resulted from hydrolysis of the nitrogen-silicon bond. Coupling of the resulting silanols would result in a polymer chain with double the molecular weight. A possible technique to avoid this problem would be the addition of a hydroxyl containing molecule such as phenol to the anionic polymerization flask. The phenol could quantitatively replace the tertiary amide chain end. A more practical approach would involve the addition of a phenolic terminated oligomer.

Many reviews have been published describing the determination of number average molecular weights by end group analysis [291]. In the anionic polymerization of alkyl methacrylates, at least one chain end is defined by the initiator fragment. Thus, one can develop various techniques to determine the number average molecular weight based on the determination of the end group concentration. ^1H NMR has been utilized to determine Mn for a variety of poly(alkyl methacrylates). This is easily accomplished by ratioing the integration associated with the 10 aromatic protons to an integration associated with the ester alkyl, e.g. the methyl ester at approximately 3.5 ppm for poly(methyl methacrylate). As the number of protons in the ester group decreases, the maximum Mn that can be determined is increased. For example, PIPMA number average molecular weights can be determined routinely from 20,000 g/mole-30,000 g/mole by using the single proton in the ester alkyl group. On the other hand, the maximum molecular weight for PMMA is approximately 10,000 g/mole. Table 24 compares the Mn values determined by NMR with the theoretical values based on the ratio of monomer to initiator. It is important that all residual diphenylethylene is removed from the

Table 24

Number Average Molecular Weight Determination by ^{1}H Nuclear Magnetic Resonance

Sample	$\bar{M}n(th)$[a]	$\bar{M}n(NMR)$[b]
PMMA	10,000	11,700
PIPMA	20,000	19,800

[a] $\bar{M}n\ (th) = \dfrac{\text{g monomer}}{\text{moles initiator}}$

[b] Ratio aromatic resonance to methyl ester protons for PMMA and tertiary proton in PIPMA (270MHz, 5% $CDCl_3$).

sample by precipitation before analysis. The purity of the sample can be witnessed by noting the absence of the unsaturated protons of diphenylethylene. This technique could not be extended to LDA initiated homopolymers because the signals associated with the initiator fragment were hidden by the polymer resonances.

A very sensitive technique for molecular weight determination based on ultraviolet-visible spectroscopy has also been considered. This approach takes advantage of the ultraviolet absorbance of the initiator phenyl rings. A calibration curve (abs. vs. conc.) was constructed using either diphenylmethane or protonated DPHL (DPHH) as the standard in tetrahydrofuran. For example, a calibration curve for diphenylmethane (corr. coeff.= 0.999) at 262nm was routinely constructed. The molar absorbtivity which was determined from the slope of the linear plot is 5150 liter/mole·cm. A precise weight of the polymer which contains the diphenylhexyl initiator fragment was dissolved in tetrahydrofuran. It is important to remember that the Beer-Lambert relationship is valid for quantitative analysis for absorbance values ranging from 0.3 to 0.8. The absorbance of the polymer sample was scanned from 190nm to 300nm. Figure 23 depicts the absorbance versus wavelength for a poly(methyl methacrylate) sample. However, when one selects a concentration that gives an absorbance between 0.3 and 0.8, the strong absorbance associated with the carbonyl

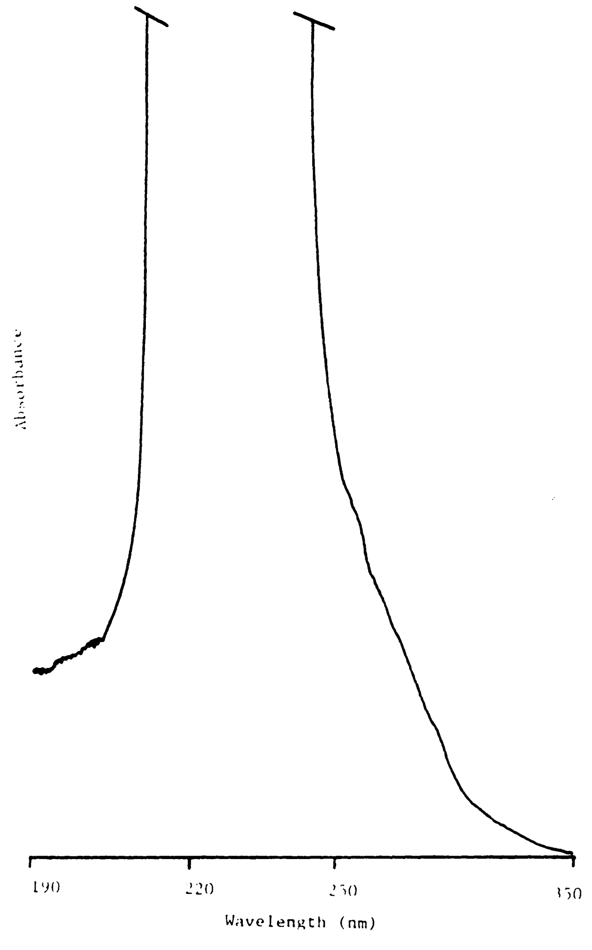


Figure 23: Absorbance Versus Wavelength for DPHL Initiated PMMA

of the polymer at 212nm overwhelms the aromatic absorbance. At more dilute concentrations, the K band (254nm) of the polymer phenyl rings can be resolved from the large carbonyl signal. Figure 24 shows the improved resolution of the aromatic absorbance at more dilute concentrations. The procedure and considerations have been established for the routine determination of molecular weight in the future.

Elemental analysis can also be utilized for the determination of number average molecular weights when a hetero atom is present in the initiator fragment. For example, the percentage of nitrogen can be compared to the amount of oxygen in the repeat unit of poly(methyl methacrylate). The values generally agree within 5 % of the molecular weights obtained by GPC.

b) Effect of Polymerization Solvent

Excellent molecular weight control and narrow molecular weight distributions are possible when a polar polymerization solvent is utilized (Table 22). However, termination mechanisms generally occur during alkyl methacrylate polymerizations in hydrocarbon solvents such as toluene. Figure 25 illustrates a typical gel permeation chromatogram for poly(ethyl methacrylate) that was prepared in toluene at
-78°C. In addition, the molecular weight control is quite poor. As stated earlier, it is believed that the absence of peripheral solvation by the solvent results in increased

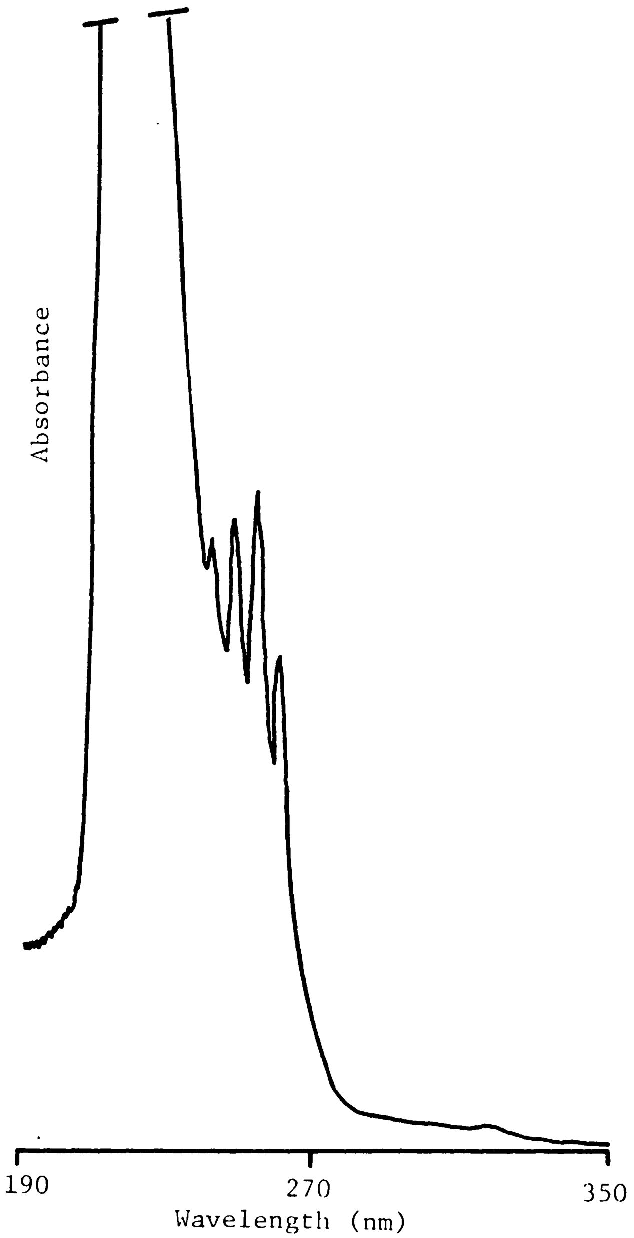


Figure 24: Absorbance Versus Wavelength for DPHL Initiated PMMA (Dilute Solution)

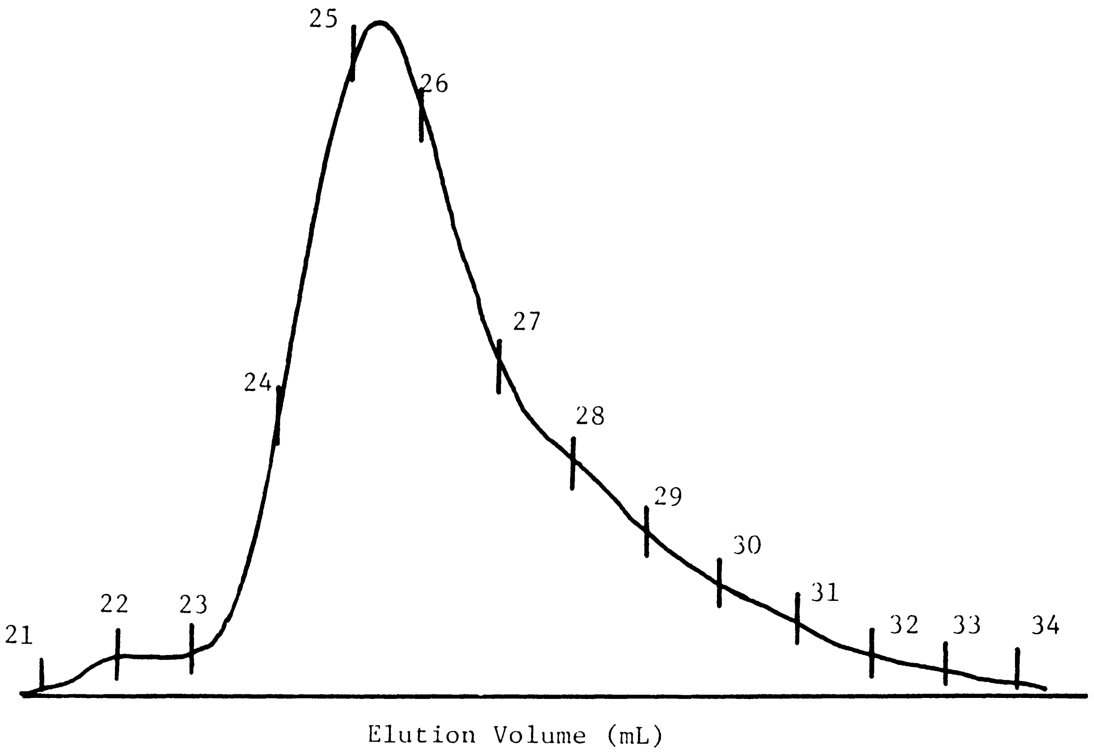


Figure 25: GPC of Poly(ethyl methacrylate) Initiated with DPHL in Toluene at -78°C

interactions of the enolate with the penultimate ester functionality. The closer proximity of the propagating anion with the reactive ester carbonyl facilitates the liberation of lithium alkoxide. The termination mechanisms have been investigated in detail by Hatada and coworkers [70].

However, the bulkiness of the ester alkyl group has a dramatic effect on the ease of polymerization of alkyl methacrylates in toluene. Due to the steric and electronic deactivation of the carbonyl by the larger ester alkyl, the propensity of side reactions is decreased. In fact, t-butyl methacrylate can be polymerized in toluene by a "living" mechanism and molecular weight distributions less than 1.15 are possible. Figure 26 is the gel permeation chromatogram of a poly(t-butyl methacrylate) sample that was synthesized in toluene at -78°C using DPHL as an initiator. Both differential refractive index and viscometric detectors were utilized. Thus, TBMA is a unique monomer compared to other alkyl methacrylates. However, TBMA polymerizations in toluene at 25°C yielded broader molecular weight distributions (1.5), but the chromatograms were always monomodal.

Although narrow molecular weight distribution PTBMA samples can be obtained in hydrocarbon solvents, molecular weight control has been difficult to obtain. Table 25 illustrates the molecular weight control for various samples

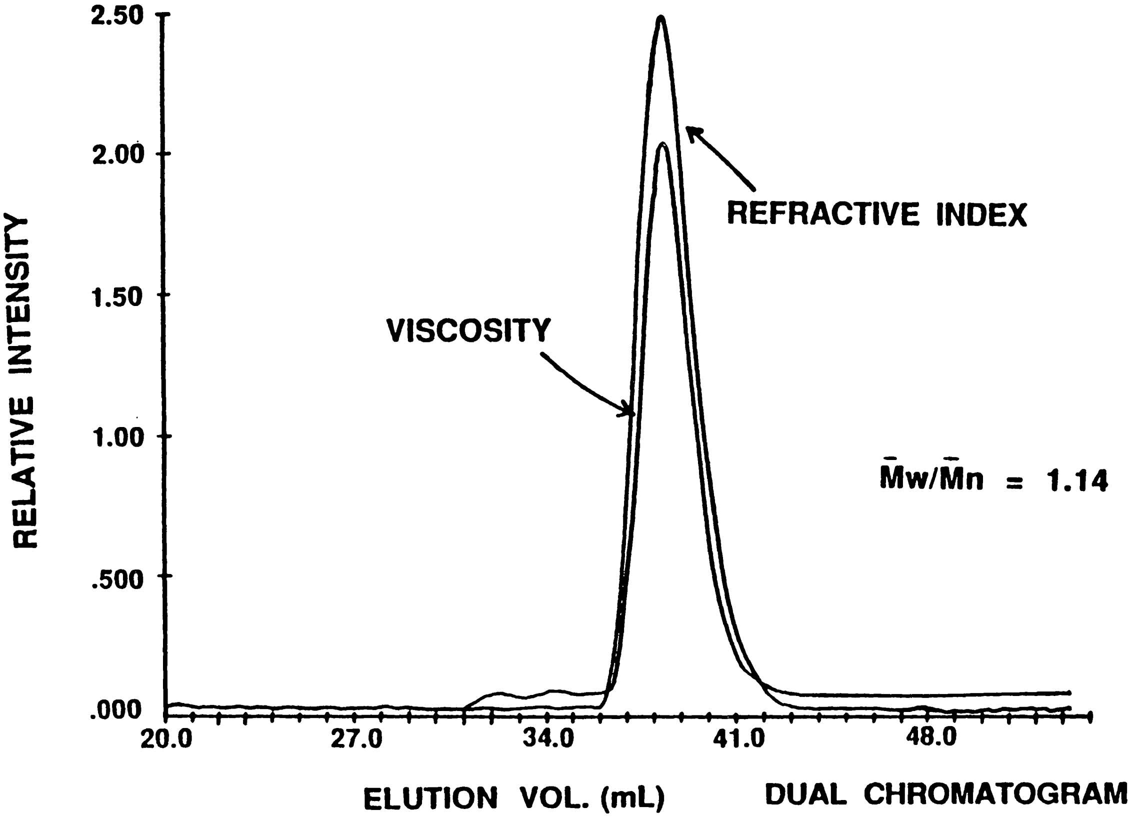


Figure 26: GPC of Poly(t-butyl methacrylate) Initiated in Toluene with DPHL at -78°C

Table 25

$\bar{M}n$ Control for Isotactic PTBMA Prepared in Toluene (4% solids)

Sample	$\bar{M}n$(th)[a]	$\bar{M}n$(GPC)[b]	$\bar{M}w/\bar{M}n$
PTBMA-331	10,000	35,400	1.11
PTBMA-332	10,000	52,100	1.10
PTBMA-333	10,000	36,100	1.15
PTBMA-334	30,000	75,800	1.19

[a] $\bar{M}n(\text{th}) = \dfrac{\text{g monomer}}{\text{moles initiator}}$

[b] Polystyrene Standards

prepared in toluene (ca. 4 wt./vol.%) and the molecular weight distribution. The resultant molecular weight is generally 2-5 times higher than the calculated number. The control becomes worse as the percent solids of the polymerization increases. For example, Table 26 lists three samples that were prepared according to the same procedures; however 10-12 wt./vol. percent solutions were used. At the higher concentrations, molecular weights can be 9-13 times higher than the predicted value. Two theories have been postulated to account for this observation. First, the initiator anion may be highly associated in the nonpolar media and the initiation reaction could be inefficient. Only a certain percentage of the initiator would be active for polymerization. Second, a side reaction which occurs very early in the polymerization would terminate a percentage of the growing chains. The yield would still be quantitative if the side reaction occurred at very low conversion (1-2%).

The kinetics of alkyl methacrylate polymerizations using anionic initiators in polar solvents have been extensively investigated [80,292]. This is due to the absence during polymerization of side reactions which would complicate interpretations. On the other hand, the kinetics in hydrocarbon solvents have remained unexplored due to many termination mechanisms. The "living" polymerization of t-butyl methacrylate in toluene offers a unique opportunity to

Table 26

$\bar{M}n$ Control for Isotactic PTBMA Prepared in Toluene (10-12% solids)

Sample	$\bar{M}n(th)^a$	$\bar{M}n(GPC)^b$	$\bar{M}w/\bar{M}n$
PTBMA-172	30,000	274,000	1.18
PTBMA-173	60,000	816,000	1.15

[a] $\bar{M}n(th) = \frac{\text{g monomer}}{\text{moles initiator}}$

[b] Poly(styrene) standards

investigate important synthetic considerations such conversion versus time at various temperatures. It is well appreciated that polymerizations in polar solvent such as THF are complete in seconds, but the required reaction time for polymerization in toluene have been undefined.

Thus, a study was conducted to quantify conversion versus time for a t-butyl methacrylate polymerization in toluene at different temperatures. Figure 27 depicts conversion versus time for a TBMA polymerization at -60°C. The initiator was charged to a monomer solution at the appropriate polymerization temperature in order to obtain a valid t_o. The conversion was calculated at each interval by dividing the molecular weight at each time by the final molecular weight (both determined by GPC). The data clearly shows that complete conversion was obtained after approximately 20 minutes. In order to ensure that complete conversion was obtained, the polymerization was allowed to proceed for 90 minutes. The molecular weight after 90 minutes was within 0.5% (GPC error) of the value that was obtained after 20 minutes. All recovered yields after precipitation in 80:20 methanol/water were quantitative (100%). A similar study was conducted at -80°C, but complete conversion was never obtained due to the slow reaction. Figure 28 describes the conversion versus time for a TBMA polymerization at -80°C in toluene. After 20 minutes of polymerization, the conversion was less than 30

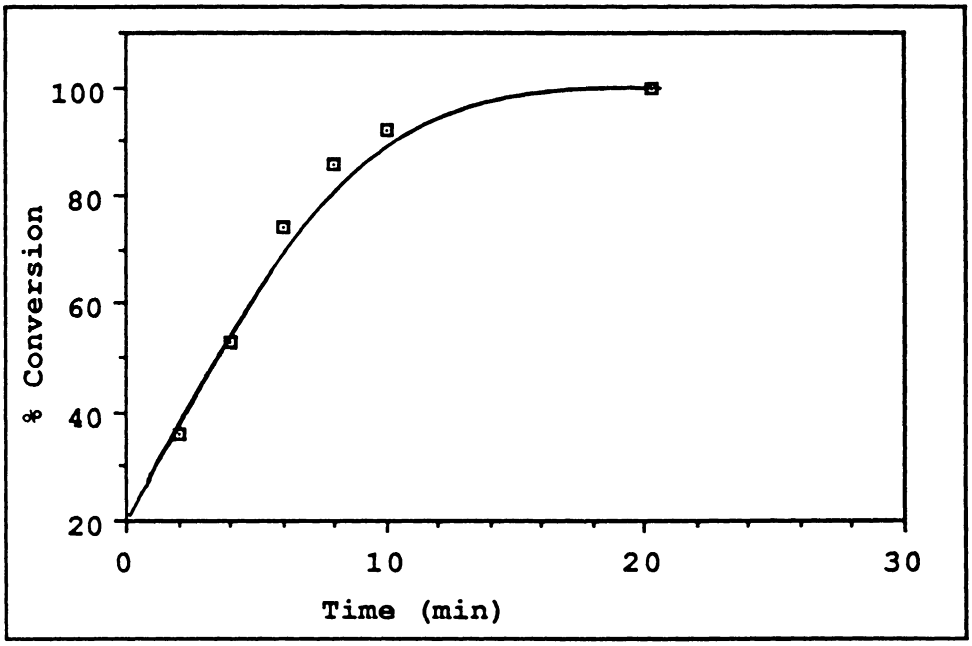


Figure 27: Conversion Versus Time for Poly(t-butyl methacrylate) Synthesis in Toluene at -60°C

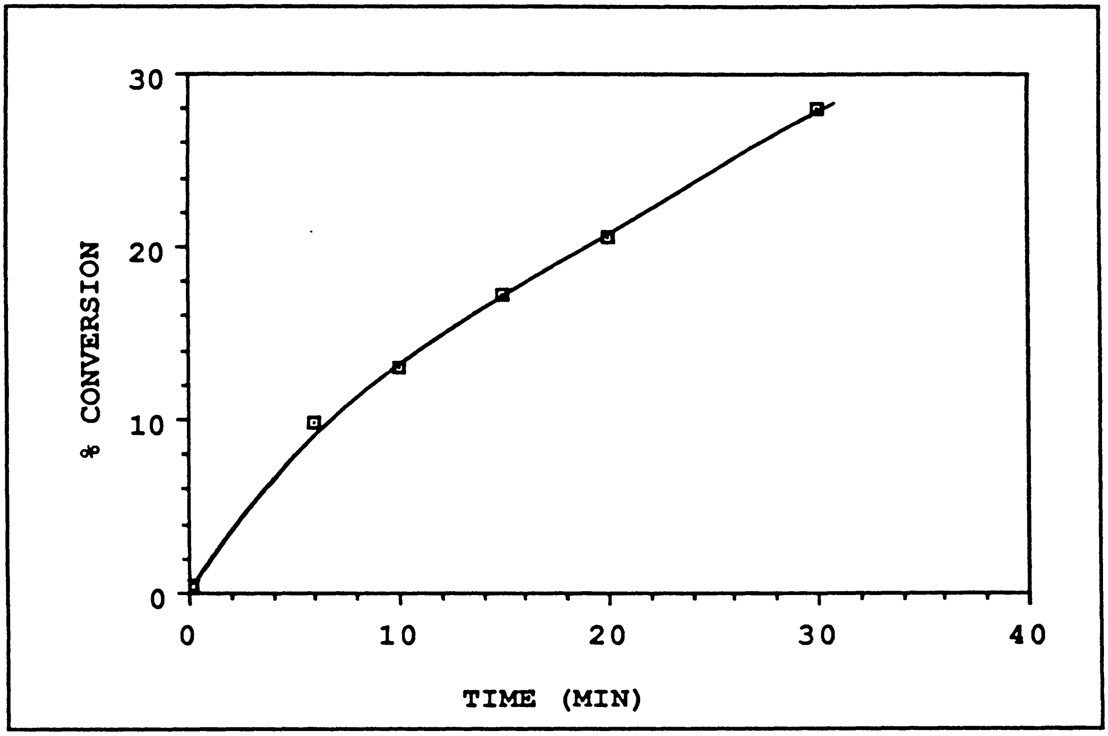


Figure 28: Conversion Versus Time for Poly(t-butyl methacrylate) Synthesis in Toluene at -80°C

percent. However, after 90 minutes, the reaction is 94% complete. It should be noted that all samples had narrow molecular weight distributions (<1.25), but the molecular weights were 3 times higher than the theoretical values.

It was surprising that the polymerization at -60°C required only 20 minutes to ensure complete conversion. If one conducts an isoprene polymerization in toluene at 35°C (95°C higher), the reaction requires 11 hours. Figure 29 depicts the conversion versus time for isoprene which was initiated with sec-butyllithium in toluene at 35°C. One could postulate that the polar backbone intermolecularly solvates the propagating enolate and the large t-butyl group "protects" the carbonyl from attack by the enolate. Muller has investigated the relative reactivity of various alkyl methacrylate monomers and has shown that t-butyl methacrylate is less reactive than other linear ester alkyl methacrylates in THF. This has been attributed to the electronic donation of the ester alkyl group to the carbon-carbon double bond. The more electron-rich double bond is less receptive to the anionic initiator. Thus, other linear alkyl methacrylates such as methyl or ethyl methacrylate should polymerize faster than TBMA in toluene.

Toluene is not typically described in the literature as an anionic polymerization solvent due to the possibility of proton abstraction to form the benzylic anion. Benzene is often employed by many workers, but was discouraged in this

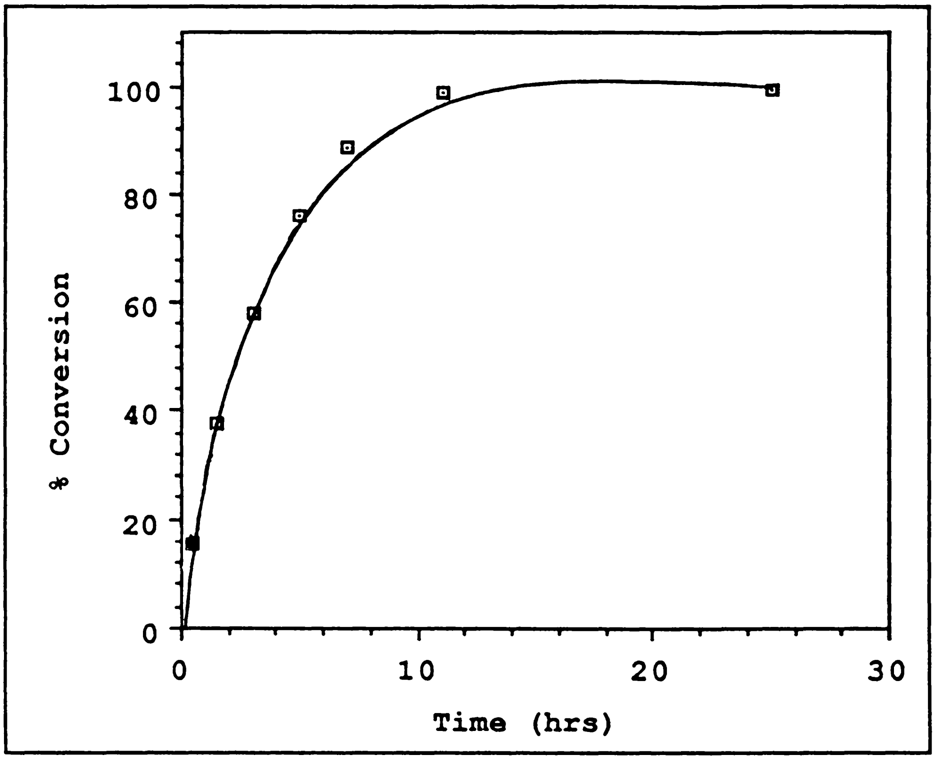


Figure 29: Conversion Versus Time for Isoprene Polymerization at 35°C in Toluene

work on account of its carcinogenic properties. Consequently, it was necessary to prove that toluene could be utilized without significant termination of the propagating anion. This was demonstrated in the polymerization of isoprene at 35°C as described above (Figure 29). The gel permeation chromatogram of the poly(isoprene) sample does not indicate high or low molecular weight tailing. In addition, if one plots number average molecular weight versus conversion, the plot is linear as shown in Figure 30. This observation is essential in order to define a polymerization as "living". The molecular weight distribution of the poly(isoprene) samples broadens slightly as complete conversion is approached. Figure 31 describes the molecular weight distribution as a function of conversion. This behavior has been reported in the literature and ascribed to possible backbiting mechanisms in the absence of monomer. Hence, it is advisable to terminate the polymerization or add another monomer at 95-98% conversion. This study demonstrated the stability of toluene in the presence of poly(isopropenyl) lithium for long times (11 hours). Further evidence was obtained by monitoring the absorbance of diphenylhexyllithium (DPHL) in toluene for long times. This was described earlier for observing the formation of DPHL in toluene. The DPHL anion concentration remained constant after complete conversion. Finally, the fact that narrow

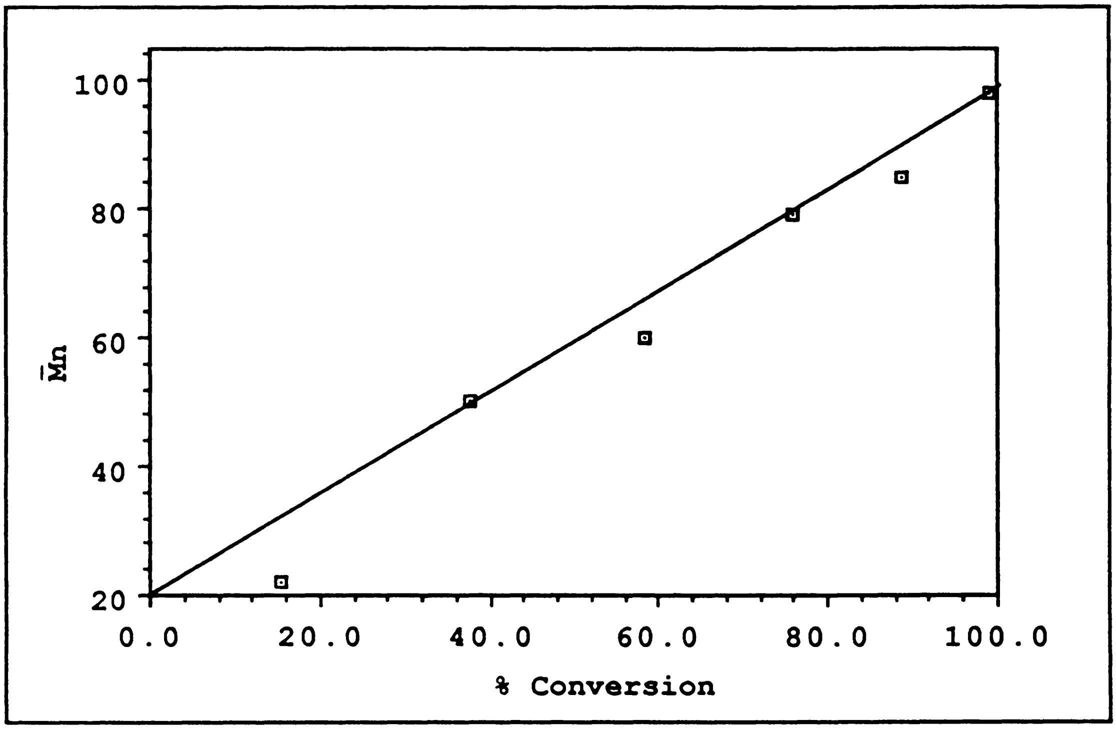


Figure 30: M̄n Versus Conversion for Poly(isoprene) (PI) Initiated with s-Butyllithium in Toluene at 35°C

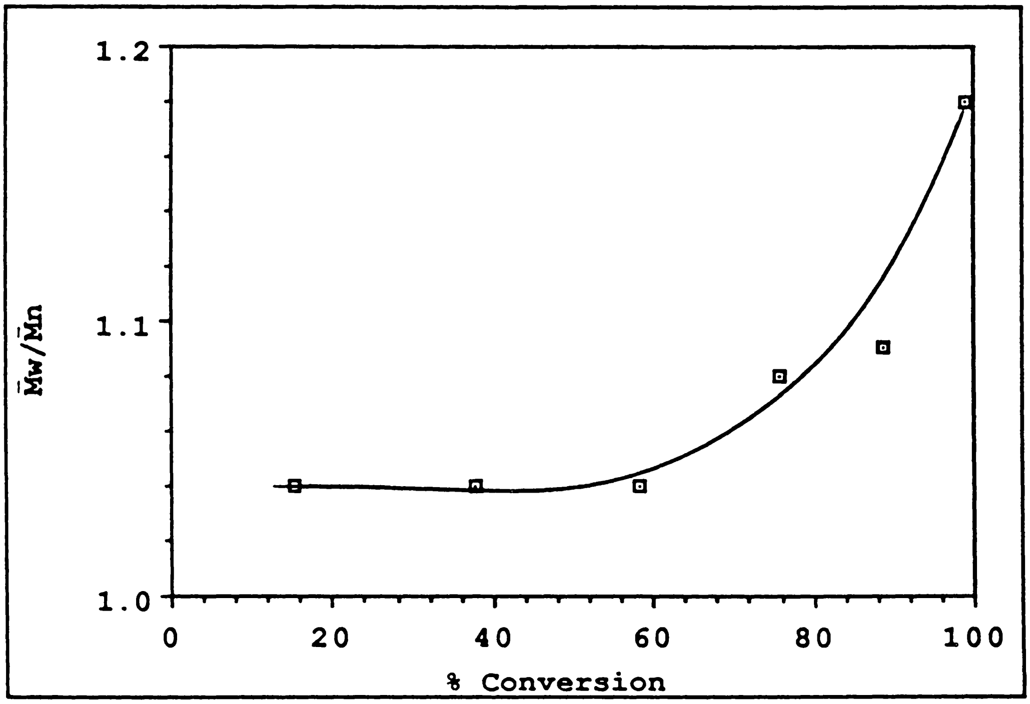


Figure 31: Molecular Weight Distribution Versus Conversion for Poly(isoprene)

molecular weight distribution poly(t-butyl methacrylate) samples were prepared indicates that a reaction with toluene is not competitive with propagation.

Based on the above observations, it is believed that toluene can be used as an anionic polymerization solvent. The primary difficulty associated with the use of toluene is the availability of pure grades. If one distills the solvent from a sodium dispersion, a slow termination reaction still is present during subsequent polymerizations. However, if the solvent is also allowed to stir in the presence of a poly(styryl) lithium anion for 3 days followed by vacuum distillation, termination reactions due to impurities are eliminated.

In addition to defining the polymerization mechanism, the polymerization solvent also influences the polymer tacticity. The mode of stereochemical addition of incoming monomer to the propagating enolate is altered by the presence of peripheral solvation. Polar solvents will separate the ion pair leading to higher levels of syndiotacticity and enhanced reaction rates. On the other hand, hydrocarbons do not effectively solvent separate the pair, leading to an isotactic addition and decreased reaction rates. The difference in reaction rates was exemplified earlier in the formation of diphenylhexyllithium by the reaction of sec-butyllithium and diphenylethylene. The polar solvent also shifted the ultraviolet absorbance of DPHL from 435 nm in toluene to 495nm in tetrahydrofuran. Thus, a polar solvent and the corresponding solvated chain end will play a more critical role in defining polymer tacticity than a hydrocarbon solvent. In a nonpolar media, it is presumed that the intermolecular solvation of the polymer chain will be the dominant factor.

Table 27 illustrates the effect of polymerization solvent on the tacticity for a variety of alkyl methacrylate monomers. All of the polymers that are described in Table 27 were synthesized in either tetrahydrofuran (THF) or toluene (TOL) using DPHL as the initiator at -78°C. In addition, the homopolymers have a number average molecular weight of approximately 100,000 g/mole and narrow molecular weight distributions (<1.25). It is evident that THF promotes high levels of syndiotacticity, but as the ester group is substituted at the carbon adjacent to the ester alkyl oxygen, the steric control is diminished. In fact, PTBMA exhibits only approximately 52% syndiotacticity when polymerized in polar solvents. This is lower than the syndiotactic levels obtainable by most free radical mechanisms. Typically, a free radical polymerization of alkyl methacrylates yields 55-60% syndiotacticity (Table 28). Despite the low level of syndiotactic placement, the polymer will be described as "syndiotactic" in order to imply reaction conditions. However, when the ester alkyl

Table 27

Effect of Polymerization Solvent on Tacticity of Various Poly(alkyl methacrylates)

Sample	Polymerization Solvent	% Tacticity[a] iso	hetero	syndio
Poly (alkyl methacrylate)				
methyl	THF	1	21	78
	Toluene	82	15	3
ethyl	THF	2	21	77
	Toluene	90	10	0
isopropyl	THF	6	29	65
	Toluene	83	17	0
allyl	THF	5	25	70
t-butyl	THF	2	46	52
	Toluene	100	0	0
2-ethylhexyl	THF	0	10	90

[a] Mole fractions (in %) of isotactic (iso), heterotactic (hetero) and syndiotactic (syndio) triads from ^{13}C NMR (50 MHz, 5-10% $CDCl_3$).

Table 28

Tacticity of Poly(alkyl methacrylates) Prepared by Free Radical Initiators

Sample	% Tacticity[a] iso	 hetero	 syndio
Poly(methyl methacrylate)	5	35	60
Poly(trifluoroethyl methacrylate)	4	41	55
Poly(t-butyl methacrylate)	0	39	61

[a] Mole fractions (in %) from 270 MHz ^1H NMR for PMMA and PTFEMA and ^{13}C NMR for PTBMA

group is substituted at the second carbon removed from the ester oxygen, e.g. poly(2-ethylhexyl methacrylate), the syndiotacticity is comparable to poly(ethyl methacrylate) (PEMA).

When the polymerizations are conducted in a hydrocarbon medium, the various poly(alkyl methacrylates) exhibit high levels of isotacticity. In fact, in each case, it is easier to synthesize predominantly isotactic polymers and poly(t-butyl methacrylate) can be prepared with exclusively (100%) isotactic triads. This stereochemical control is beginning to approach the control obtainable by Ziegler-Natta catalysts. The 100% isotactic PTBMA samples also have narrow molecular weight distributions as depicted earlier in Figure 26. Thus, PTBMA is a very unique monomer compared to other alkyl methacrylates. The possibility of hydrolysis of the t-butyl ester followed by esterification would yield a variety of purely isotactic poly(alkyl methacrylates). This aspect will be described in detail later.

The tactic compositions that have been discussed in Tables 22 and 23 were determined by ^{13}C Nuclear Magnetic Resonance. Although 1H NMR can utilized to determine the stereochemistry of poly(methyl methacrylate), resonance overlap precludes the analysis of higher order poly(alkyl methacrylates). Table 29 illustrates the proton chemical shift regions which describe the triad composition for various stereoregular PMMA samples. The syndiotactic triad

Table 29

Typical 270 MHz Proton Chemical Shift Values for PMMA

Assignment	Chemical Shift Range (ppm)[a]
s-CH_3	0.7-0.8
h-CH_3	0.9-0.95
i-CH_3	1.1-1.15
i-CH_2-	1.4-2.2
s-CH_2-	1.8-2.0
O-CH_3	3.5-3.6

[a] in $CDCl_3$

(rr) appears near 0.75ppm, the heterotactic triad (mr) near 0.93 ppm, and the isotactic triad (mm) at approximately 1.12ppm. This excellent resolution of the various triad resonances is not possible for any higher order poly(alkyl methacrylates). Triad resolution is not possible in ^{1}H NMR analysis of a poly(isopropyl methacrylate) sample that was prepared in THF at -78°C. Figure 32 is a spectrum of poly(t-butyl methacrylate) and again one can see the loss of resolution. In fact, as the ester group becomes branched, it appears that the syndiotactic and heterotactic resonances shift toward each other. It is very obvious that ^{1}H can not be used to quantify the tactic composition of most poly(alkyl methacrylates).

^{13}C NMR is useful due to the wider range of chemical shift values and the absence of overlapping chemical shifts in the α-methyl region. In addition, higher order sequence distributions, e.g. pentad, can be discerned quite easily. Figure 33 describes the chemical shift regions of interest for a poly(methyl methacrylate) homopolymer. Stereochemical information is obtainable from both the quaternary (44-46ppm) and carbonyl (176-179ppm) carbon regions. In particular, triad and pentad sequences can be ascertained by studying the quaternary and carbonyl carbon respectively. The PMMA tactic compositions that were determined by 1H and 13C NMR were compared and found to agree within 2 percent. Despite increased substitution of the ester alkyl group,

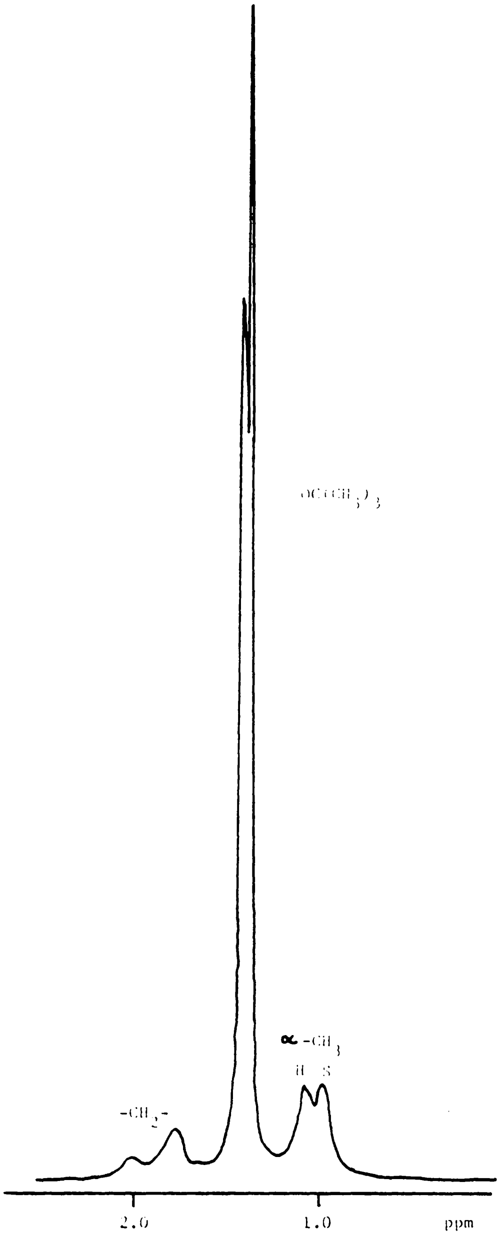


Figure 32: ^1H NMR Spectrum of Poly(t-butyl methacrylate) Prepared in Tetrahydrofuran

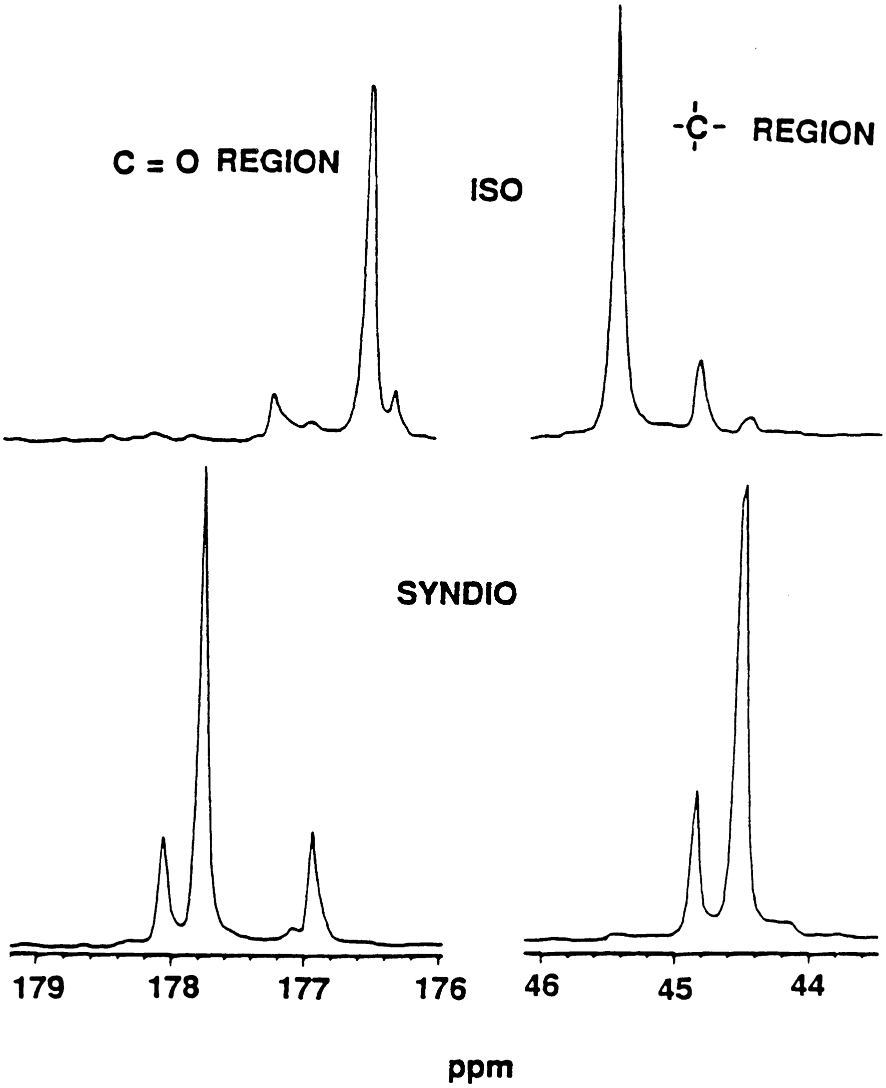


Figure 33: ^{13}C NMR Regions for Syndiotactic and Isotactic PMMA

good resolution exists in both regions of interest. Figure 34 depicts the ^{13}C regions of interest for the predominantly syndiotactic and isotactic poly(t-butyl methacrylate) materials. The isotactic assignment for PTBMA was made based on the chemical shift values determined for PMMA. It is interesting to observe that only one resonance appears for the isotactic sample and this indicates exclusive stereoregularity. A similar observation is seen in the ^{1}H NMR spectrum of isotactic PTBMA (Figure 35). Only one resonance appears for the α-methyl protons and the t-butyl group is resolved at 1.36ppm. The resolution of the isotactic triad indicates that the typical resolution problem may result from a shifting of the syndiotactic and heterotactic chemical shifts for higher order poly(alkyl methacrylates).

The solvent polarity can be finely controlled by varying the ratio of polar to nonpolar solvent. This ideally would allow for the prediction of the resulting tacticity based on the solvent composition. The highest syndiotactic content would be obtained in a polar solvent and the highest isotactic content would be possible in hydrocarbon solvents. The tactic composition could be controlled between these two extremes by adding small amounts of a polar solvent to a polymerization in hydrocarbon media or vice versa. For example, DPHL was formed in a 90:10 toluene/THF mixture and t-butyl

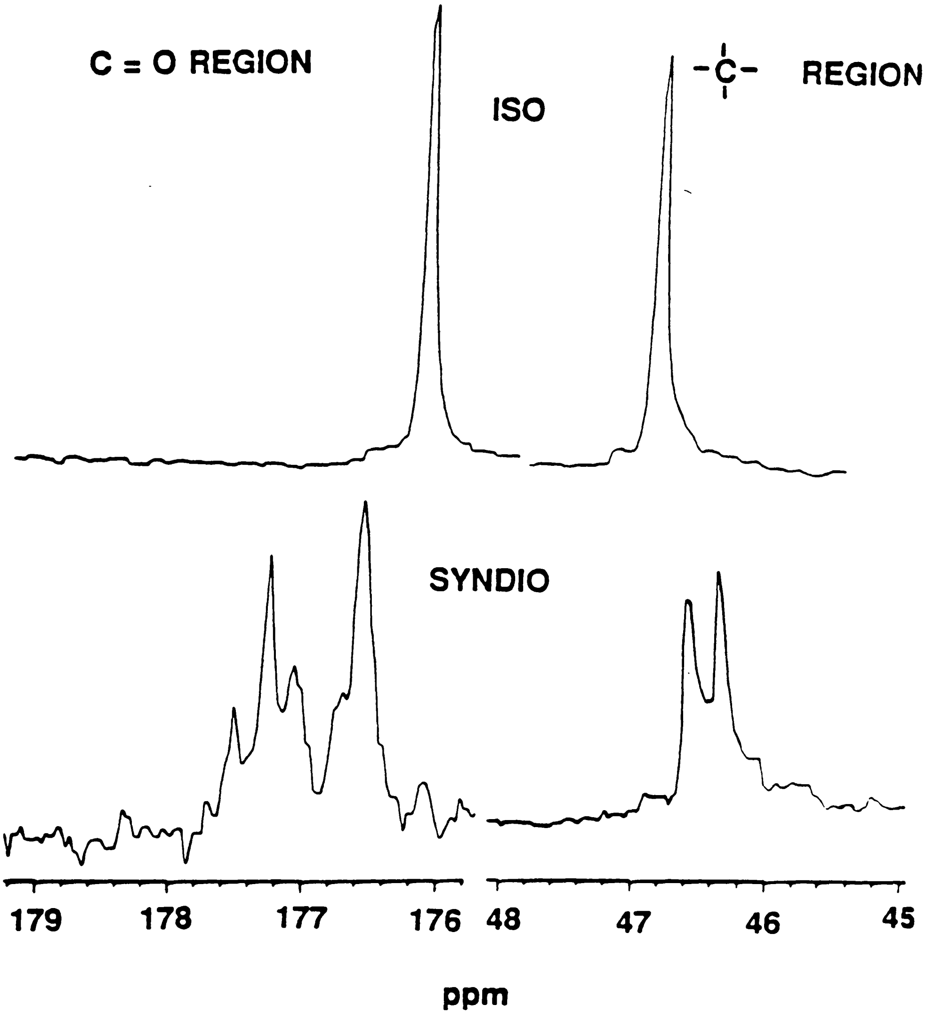


Figure 34: ^{13}C NMR Regions for Syndiotactic and Isotactic PTBMA

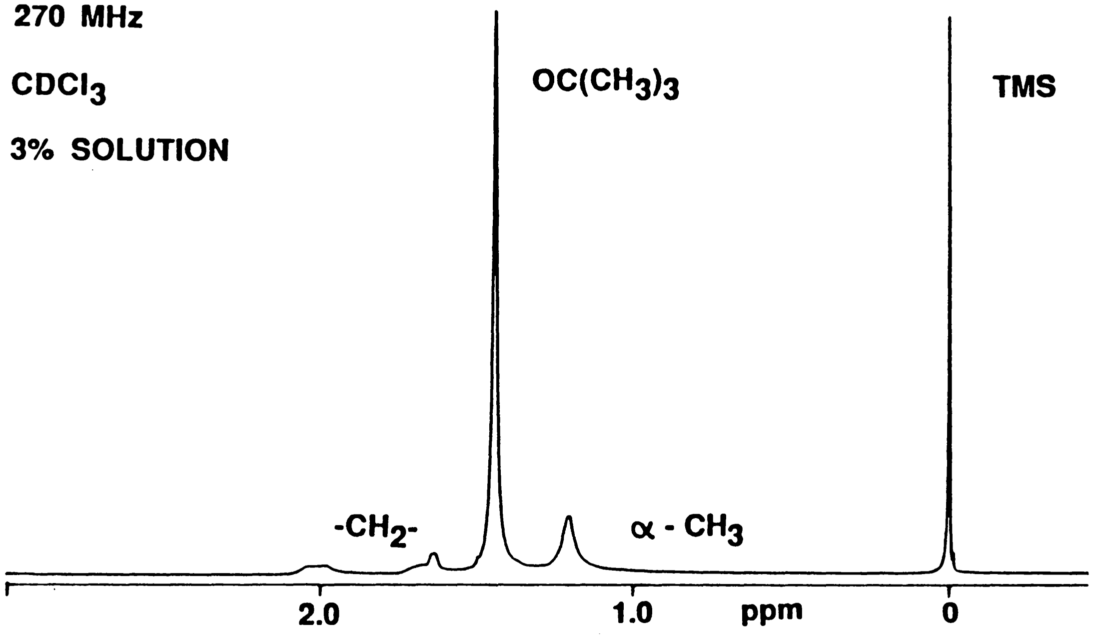


Figure 35: ^{1}H NMR Spectrum of Isotactic PTBMA

methacrylate was added at -78°C. The polymerization proceeded in a homogeneous fashion, but the molecular weight distribution was approximately 1.30 (monomodal). The ^{1}H NMR spectrum of the polymer (Figure 36) indicates the presence of nearly equal percentages of each tactic form. A ^{13}C NMR analysis would be more precise, but ^{1}H NMR does indicate a substantial change in the relative tactic compositions. An interesting plot would be solvent composition versus tactic composition. This data may be used as a predictive tool for polymer properties and facilitate the correlation of physical properties with polymer stereochemistry. The effect of polymer tacticity on various physical properties will be described in detail later.

Polymerizations in mixed solvents are complicated in some instances by the formation of a stereoblock or stereogel. The gel results from the association of isotactic sequences with syndiotactic sequences in the polymer backbone. The presence of isotactic PMMA is required in order for the gel to occur and the syndiotactic polymer can be various alkyl methacrylates. Thus, if one attempts to modify a MMA polymerization with a polar solvent such as THF, gelation will occur. Preliminary efforts in this area included the modification of a MMA polymerization in toluene with dipiperodinoethane (DIPIP). DIPIP is well known for its ability to coordinate with anionic species in a similar fashion as THF. The polymerization gelled due to

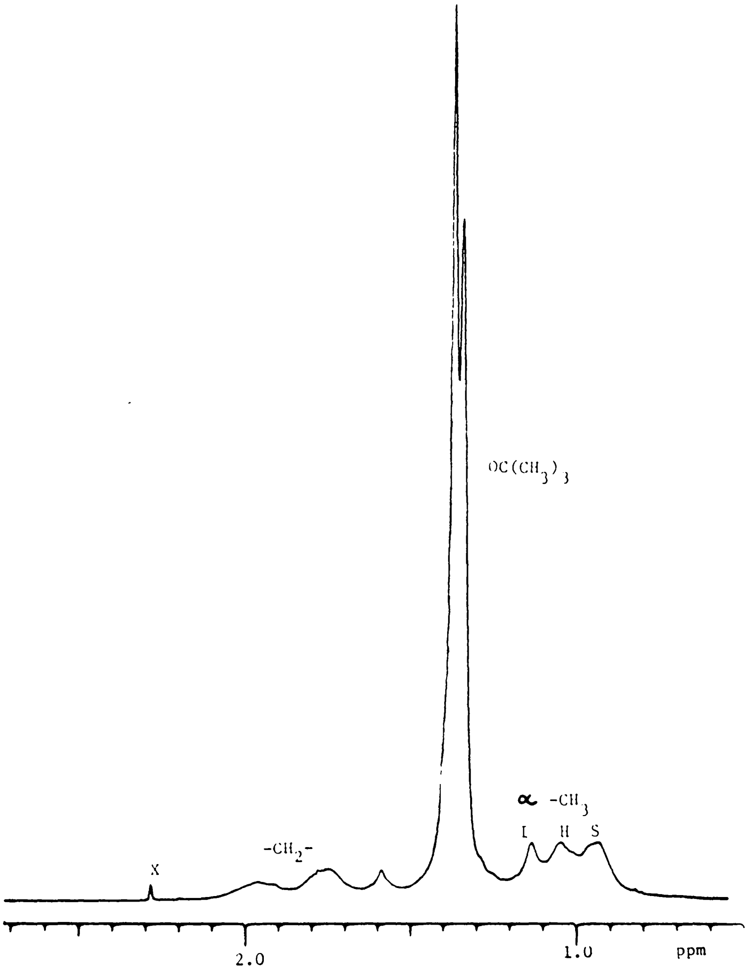


Figure 36: ^{1}H NMR Spectrum of PTBMA Prepared in Mixed Solvent (90:10 Toluene:THF)

the formation of the stereocomplex; however, this situation did not arise in other alkyl methacrylate polymerizations.

Another method for forming the stereocomplex is the blending of the appropriate stereoregular polymers. For example, 2-3 wt. percent acetone solutions of isotactic and syndiotactic PMMA (60i/40s) were mixed at room temperature. Immediately, turbidity developed which was indicative of the formation of the insoluble stereocomplex. Despite annealing studies on the stereocomplex at 140°C, the appearance of a melting point for the stereocomplex was not detected. An interesting future investigation would be to analyze the effect of ester alkyl group on the ease of complex formation, especially the hindered t-butyl ester.

c) Effect of Polymerization Temperature

The polymerization temperature plays a very critical role in defining the propagating enolate stability. The anionic polymerization of alkyl methacrylates has been conducted typically at -78°C in order to suppress the side reactions associated with the carbonyl. This fact has discouraged industrial research and prompted the development of Group Transfer Polymerization (GTP) and Iniferter Polymerization. However, by judicious choice of the ester alkyl group, higher polymerization temperatures during anionic polymerization are possible. In particular, a branched ester alkyl group "protects" the carbonyl from side reactions at higher polymerization temperatures. It is presumed that both inductive and steric effects are responsible for the deactivation of the carbonyl. This hypothesis is based on FTIR and NMR characterization of the alkyl methacrylate carbonyl in the monomer as described earlier. One can recall that the steric and electronic environment of the branched ester carbonyl was significantly different than the carbonyl of linear ester alkyl methacrylates.

Table 30 illustrates the effect of increased PMMA polymerization temperature on molecular weight control. In each case, a theoretical $\bar{M}n$ = 30,000 g/mole was desired based on initiator and monomer charges. The data clearly depict a loss in molecular weight control with increasing temperature while the yield decreases to <10% at 0°C. The $\bar{M}n$ values were determined by vapor phase osmometry (VPO) utilizing toluene as a solvent. The loss of molecular weight control depends on the percentage of the anions that have been terminated. In particular, higher molecular weights are obtained if only a portion of the anions are terminated. Yields would also be fairly high in this situation e.g. at -48°C. On the other hand, if all of the chains terminated at low conversion, both the molecular weights and yields would be low e.g. at 0°C. The mechanisms are quite complex and the molecular weight control depends on the extent conversion when termination reactions begin to occur.

Table 30

Effect of PMMA Polymerization Temperature on Molecular Weight Control and Yield

Temperature (°C)	$\bar{M}n(th)$[a]	$\bar{M}n(VPO)$[b]	Yield (%)
-90	30,000	32,500	100
-78	30,000	29,900	100
-48	30,000	40,700	86
-20	30,000	23,500	80
0	30,000	5,300	8

[a] $\bar{M}n(th) = \frac{\text{g monomer}}{\text{moles initiator}}$

[b] in Toluene, 25°C

Molecular weight distributions (MWD) also broaden with increasing PMMA polymerization temperature. Table 31 depicts the effect of polymerization temperature on the MWD of PMMA. The values for the polymers prepared at -78°C and -90°C are both 1.25;this indicates that -78°C is adequate for the elimination of termination reactions. The samples that were prepared at -48°C and -20°C exhibit significant low molecular weight tailing in the gel permeation chromatogram. Many workers continue to attempt novel anionic syntheses of poly(alkyl methacrylates) at -20°C and termination reactions certainly occur at this temperature. The molecular weight distributions can often appear artificially narrow due to the dissolution of lower molecular weight chains in the precipitation solvent (petroleum ether). This is especially true for the PMMA sample that was prepared at 0°C.

The propensity for side reactions at elevated temperatures (>-78°C) can be decreased by increasing the steric bulk near the carbonyl carbon. This is accomplished by introducing substitution at the carbon adjacent to the ester oxygen in the alkyl methacrylate monomer. Thus, methyl, ethyl, isopropyl and t-butyl methacrylate monomers represent an excellent series for elucidating many effects on the enolate stability. Essentially, this series involves the replacement of each proton on the methyl ester group of PMMA with an additional methyl group i.e. replacement of the

Table 31

Effect of PMMA Polymerization Temperature on the Molecular Weight Distribution

Polymerization Temp.(°C)	$\bar{M}w/\bar{M}n$ (GPC)[a]
-90	1.25
-78	1.26
-48	1.90
-20	4.95
0	2.89

[a] Poly(methyl methacrylate) standards (all MWD values ± 0.03)

first proton results in PEMA, the second results in PIPMA and the third yields PTBMA.

Table 32 summarizes the polymer yields obtained at higher polymerization temperatures for the series of poly(alkyl methacrylates). All the polymers were prepared in THF using DPHL as the initiator at the specified temperature. Alkyl methacrylates with linear, normal ester alkyl groups behave in a similar fashion to PMMA. For example, PEMA polymerizations at 0°C also result in low yields. However, if one polymerizes IPMA at 0°C, quantitative yields of polymer are obtained with narrow molecular weight distributions. Quantiative yields of poly(t-butyl methacrylate) are also obtained even at polymerization temperatures exceeding 25°C. It is clear that as the ester group becomes bulkier, the stability of the propagating enolate increases. This realization has many important experimental ramifications. Unlike in a PMMA polymerization at -78°C, one does not need to be concerned with large exotherms (>10°C) causing side reactions in the branched alkyl methacrylate polymerization. This eliminates both the necessity to monitor polymerization temperature and the tedious slow addition of monomer. Recent investigations with C. D. DePorter indicate that substitution at the second carbon from the ester alkyl oxygen is not sufficient to protect the carbonyl from attack. A polymerization of 2-ethylhexyl methacrylate at 25°C failed to yield polymer.

Table 32

Polymer Yields at Higher Polymerization Temperatures for Various Alkyl Methacrylates

Sample	Temp. (°C)	Yield (%)
Poly(alkyl methacrylate)		
methyl	0	8
ethyl	0	15
isopropyl	0	quantitative
t-butyl	0	quantitative
t-butyl	26	quantitative
t-butyl	37	quantitative
t-butyl	44	90

Muller has reported earlier that the poly(t-butyl methacrylate enolate was stable at 25°C using different initiator systems with cesium and sodium counterions [80]. However, the investigation of lithium enolates has remained unexplored. It was believed that the lithium enolate would exhibit the lowest stability due to the small size of the cation. Despite this early presumption, the TBMA lithium enolate exhibited exceptional stability at temperatures as high as 37°C. Table 33 describes the enhanced enolate stability over a wide thermal range (-78°-37°C). All polymers obtained over this range demonstrated quantitative yields, good molecular weight control and narrow molecular weight distributions. It is important to note that initiation and propagation proceeded at the specified temperatures. It would be interesting to decouple the temperature dependence of initiation and propagation. The molecular weight distribution begins to broaden significantly at 44°C; this indicates that termination reactions are beginning to occur. However, narrow molecular weight distributions are obtained at temperatures as high as 37°C. Also, the molecular weight control is good, indicating the absence of termination mechanisms. Figure 37 depicts a gel permeation chromatogram of a PTBMA sample polymerized with DPHL as an initiator in THF at room temperature. Also, poly(styrene) and poly(methyl methacrylate) standards are shown for reference. As one can

Table 33

Polymerization of t-butyl methacrylate at Various Temperatures: Molecular Weight Control and Distribution[a]

Polymerization Temperature (°C)	$\bar{M}n(th)$[b]	$\bar{M}n(GPC)$[c]	$\bar{M}w/\bar{M}n$
-78	100,000	139,000	1.18
0	10,000	7,800	1.32
22	30,000	31,000	1.14
26	50,000	60,500	1.12
44	30,000	23,600	1.76

[a] Reaction Conditions: THF, DPHL, N_2

[b] $\bar{M}n(th) = \frac{\text{g monomer}}{\text{moles initiator}}$

[c] Poly(styrene) Standards

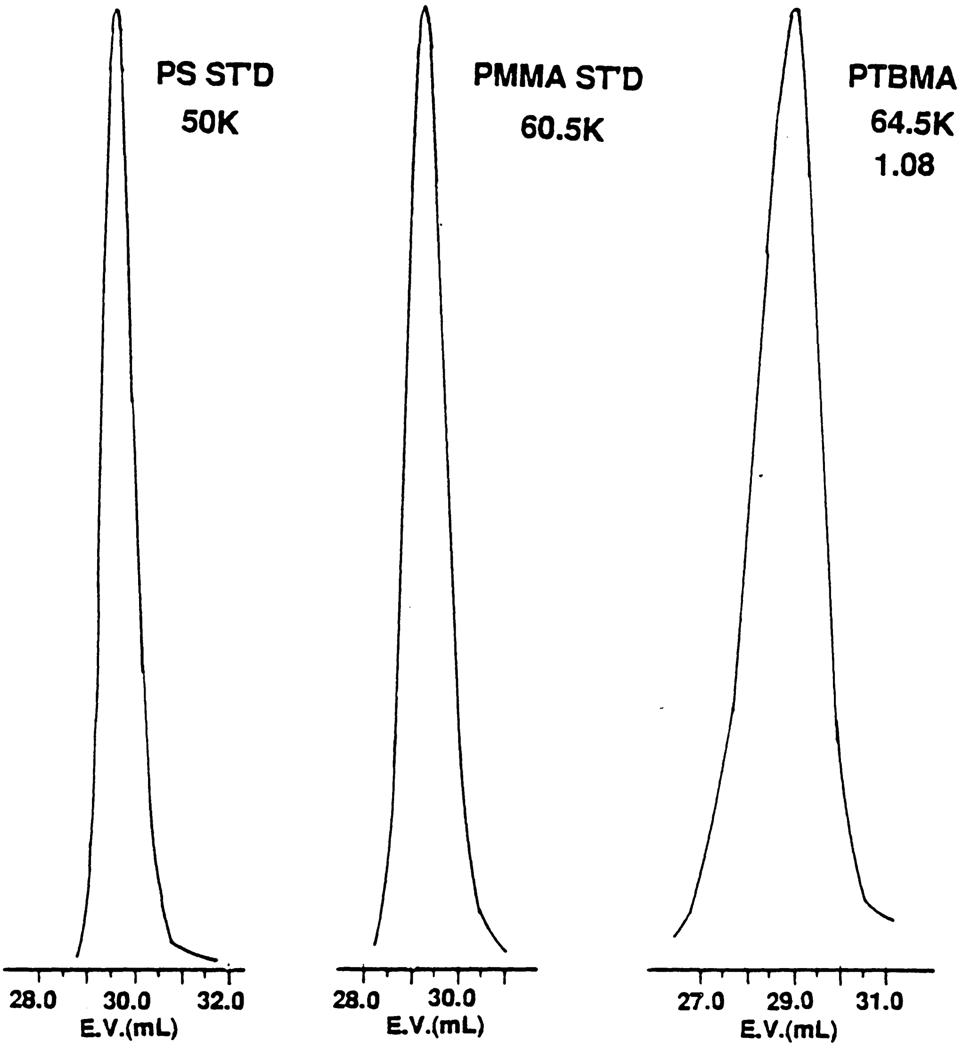


Figure 37: GPC of PTBMA Prepared in THF at Room Temperature Using Diphenylhexyllithium

see, the distribution appears narrow with no evidence of high or low molecular weight tailing.

Anionic polymerization attempts of 2,2,2-trifluoroethyl methacrylate were conducted in an attempt to investigate the effect of the electron withdrawing fluorines on the reactivity of the carbonyl. This would represent the opposite extreme to t-butyl methacrylate. All polymerizations were conducted in a typical fashion using DPHL in THF at -78°C. Yields ranged from 44% to 60% after precipitation in a methanol/water mixture. Initial attempts to characterize the molecular weight and distribution were impeded by the fact that the refractive index of the polymer and THF (GPC solvent) were too close. Thus, the differential refractive index detector could not be utilized. However, by taking advantage of the carbonyl absorbance at approximately 218nm, chromatograms were obtained. In each case, bimodal peaks of similar intensity in the gel permeation chromatogram were found. This was indicative that termination was occurring at an appreciable extent. Two theories were postulated to account for this behavior. First, it was believed that the fluorine groups were activating the carbonyl carbon by electron withdrawing effects and termination reactions were occurring with the ester carbonyl during anionic polymerization. This theory was substantiated by noting the high FTIR carbonyl frequency, i.e., 1748 cm-1 compared to isopropyl and t-butyl methacrylate. The second theory attributed the bimodal behavior to the less reactive 2,2,2-trifluoroethanol impurity in the monomer. The reaction of the alcohol and triethyl aluminum purification reagents may require longer contact times. In fact, both situations may have been important simultaneously. It should be noted that ^{1}H NMR did not indicate any unexplained structures and only one resonance was present in the ^{19}F NMR. A gas chromatographic analysis to determine the required purification times would prove which theory was correct. After repeated polymerization attempts, free radical polymerization techniques were ultimately used to prepare high molecular weight polymeric samples.

In addition to the effect of polymerization temperature on the stability of the propagating enolate, the polymer tacticity is also influenced. Table 34 describes the change in stereochemistry as a function of polymerization temperature for the same series of PMMA samples described in Table 30. It is assumed that the polymer tacticity is independent of extent conversion. This is a good assumption because similar tactic compositions (±2%) were obtained for a range (10,000-100,000 g/mole) of molecular weight PMMA samples prepared at -78°C. As one can see in Table 34, the syndiotactic triad composition increases with decreasing temperature at the expense primarily of the heterotactic sequences. Insignificant changes can be seen in the

Table 34

Effect of Polymerization Temperature on PMMA Tacticity[a]

Polymerization Temperature (°C)	% syndio	Tacticity % hetero	% iso
-90	82	17	1
-78	81	18	1
-48	72	26	2
-20	69	28	3
0	63	33	4

[a] Mole % Determined by 270 MHz ^{1}H NMR triad region; all values ± 2%.

isotactic levels. All values in Table 34 were determined by ^1H NMR utilizing the α-methyl resonance. If one plots polymerization temperature versus percent syndiotacticity, a linear relationship exists (correlation coefficient = 0.99). This plot is shown in Figure 38a). Extrapolations of this line to room temperature yields tactic compositions which are similar to those obtained at room temperature via GTP. The lower polymerization temperature restricts the mobility of the polymer chain. Thus, the side groups prefer to be as far apart as possible in order to reduce steric clashes. Thus, the amount of syndiotacticity increases at colder temperatures.

The stereochemical dependence on polymerization temperature is also a function of the size of the ester alkyl group. Preliminary stereochemical investigations indicate that poly(t-butyl methacrylate) (PTBMA) behaves quite differently than PMMA. Table 35 describes the change in stereochemistry with an increase in polymerization temperature from -78°C to 44°C. Tactic compositions for PTBMA are based on ^{13}C NMR analysis doe to overlapping signals in ^1H NMR spectra. In a similar fashion as in the PMMA study, DPHL was utilized in THF. Similarly, one can note the decrease in syndiotacticity as the temperature is increased, but this occurs at the expense of the isotactic levels rather than the heterotactic levels. The desire for PTBMA to assume an isotactic configuration was seen earlier

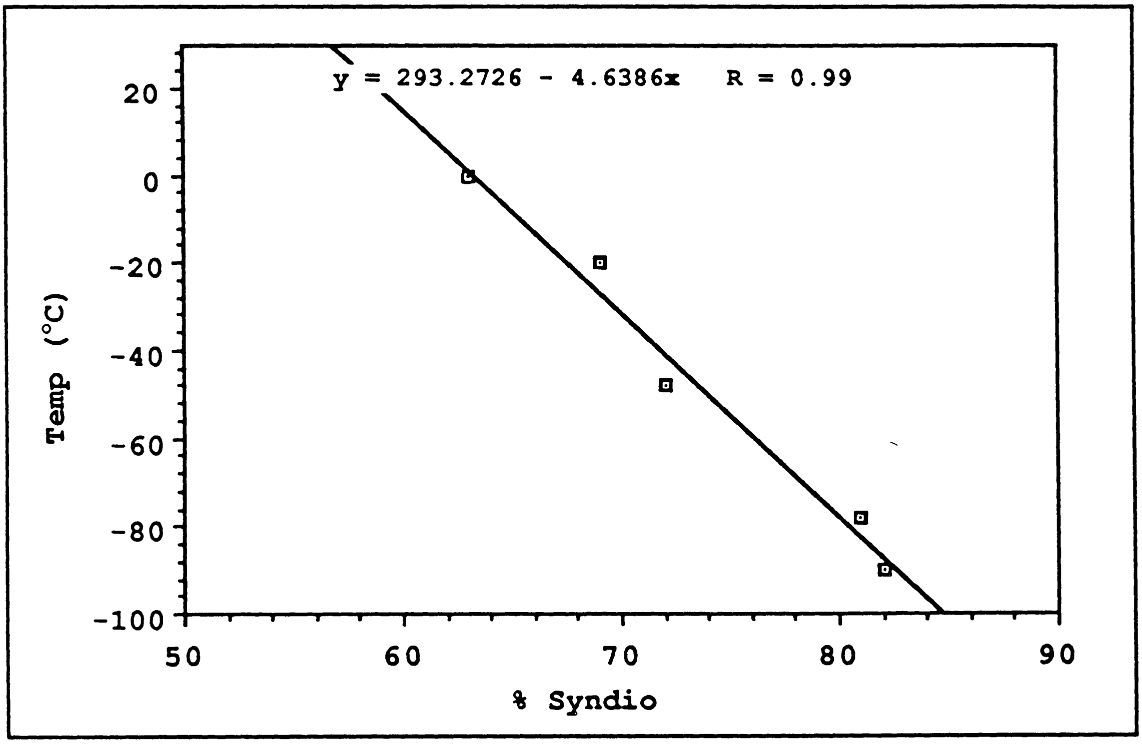


Figure 38a: PMMA Polymerization Temperature Versus Percent Syndiotacticity

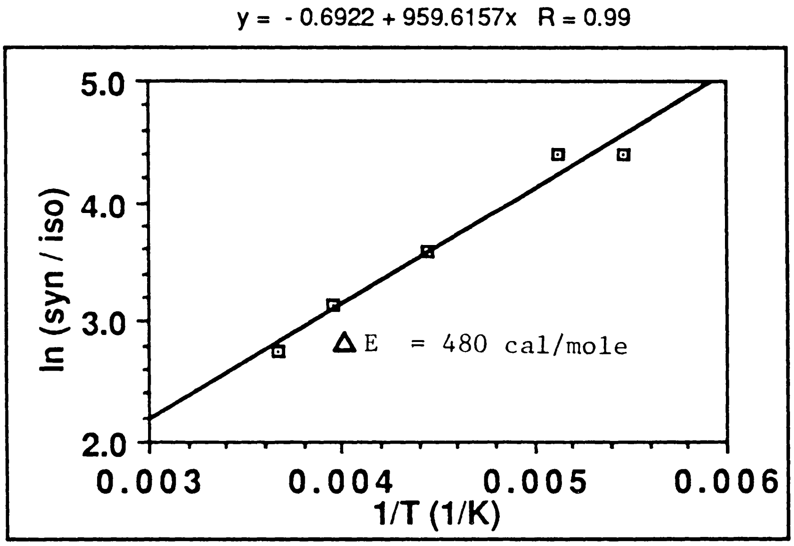


Figure 38b: % Syndiotacticity of PMMA Versus Inverse Polymerization Temperature

Table 35

Effect of Polymerization Temperature on PTBMA Tacticity[a]

Polymerization Temperature (°C)	%syndio	Tacticity % hetero	% iso
-78	52	48	0
0	46	50	4
25	41	49	10
44	38	48	14

[a] Determined by 50 MHz ^{13}C NMR backbone quaternary carbon region (5% in $CDCl_3$, 0.01M $Cr(AcAc)_3$)

in the polymerizations in hydrocarbons which yielded 100% isotactic materials. It is interesting to note that polymerizations of TBMA in toluene at 25°C retain isotactic stereoregularity.

Many advantages of t-butyl methacrylate monomer have been discussed. The primary conclusions are summarized below:

(1) "Living" polymerizations are possible in polar solvents at temperatures as high as 37°C with a lithium counterion.

(2) Narrow molecular weight distribution PTBMA is obtainable in toluene using lithium alkyl initiators at -78°C.

(3) PTBMA samples prepared at all temperatures in toluene are 100% isotactic.

Due to the enhanced stability of the poly(t-butyl methacrylate) lithium enolate, the analysis of the anion by ultraviolet-visible spectroscopy is facilitated. A stable propagating species is much easier to characterize than one which undergoes side reactions at the typical test temperatures. A DPHL initiated PTBMA lithium enolate was observed by UV-Visible spectroscopy and an absorbance was not seen. However, the lower absorbance values (<280nm) were shielded by the presence of the initiator phenyl ring absorbances. Future efforts should involve the use of sec-butyllithium as an initiator. The absorbance of the enolate should not be influenced by the broader molecular weight distribution which results from using the unsterically hindered alkyl lithium.

3) Physical Properties of Poly(alkyl methacrylates)

a) Thermal Properties

Poly(alkyl methacrylates) have received significant attention due to the wide range of physical properties that are possible within a single class of polymer. In the past, this has been achieved by the systematic alteration of the ester alkyl group in the monomer. However, the polymerization approaches have been generally limited to free radical techniques. Although the free radically prepared polymers are termed "random" or heterotactic, the materials are usually 55-60% syndiotactic. Anionic techniques allow for superior control of stereochemistry by virtue of the ionic mechanism. Tactic compositions can range from 100% isotactic to 90% syndiotactic depending on the monomer structure and polymerization solvent. The stereochemistry has a profound effect on the glass transition temperature due to changes in backbone conformational energies.

Table 36 illustrates the effect of tacticity on the glass transition temperature for various high molecular weight (ca.100,000g/mole) poly(methyl methacrylate) samples which have been synthesized by different mechanisms. All glass transition temperatures were determined at the

Table 36

Effect of PMMA Tacticity on the Glass Transition Temperature

Synthetic		% Tacticity[a]		
Route	syndio	hetero	iso	Tg(°C)[b]
DPHL, Toluene -78°C	3	15	82	54
AIBN, Bulk 64°C	60	35	5	124
DPHL, THF -78°C	78	21	1	131

[a] Determined from ^{1}H NMR -methyl region; all values ± 2%.
[b] Determined by DSC at transition midpoint

transition midpoint. A decrease in the syndiotacticity parallels a decrease in the glass transition temperature. Thus, the syndiotactic (78%) polymer which was prepared by anionic techniques in polar solvents has the highest Tg (131°C). The isotactic (82%) polymer which was prepared anionically in toluene has the lowest amount of syndiotacticity and the lowest Tg (54°C). It is clear that by employing anionic techniques the Tg of PMMA can range over 75°C. The "random" polymer has an intermediate Tg because the amount of syndiotacticity is approximately 60%. Figure 39 depicts a plot of glass transition temperature for poly(methyl methacrylate) versus percent syndiotacticity. It is interesting to note that the plot is fairly linear (correlation coeff. = 0.99) and the extrapolated Tg for 100% syndiotactic PMMA is 160°C (slope = 1.08 °C/%syndio). An analogous plot (corr. coeff. = 0.999) can be constructed for the Tg versus percent isotacticity and the extrapolated Tg for 100% isotactic PMMA is 37°C (slope = -0.93 °C/%iso). The difference in the extrapolated glass transition temperatures between the 100% tactic polymers is 123°C.

A similar analysis was performed on various poly(t-butyl methacrylate samples to investigate the effect of the ester alkyl group size. Table 37 lists the glass transition temperatures and tacticities for various PTBMA samples that were synthesized in a similar fashion as the poly(methyl methacrylates). Once again, the decrease in the amount of

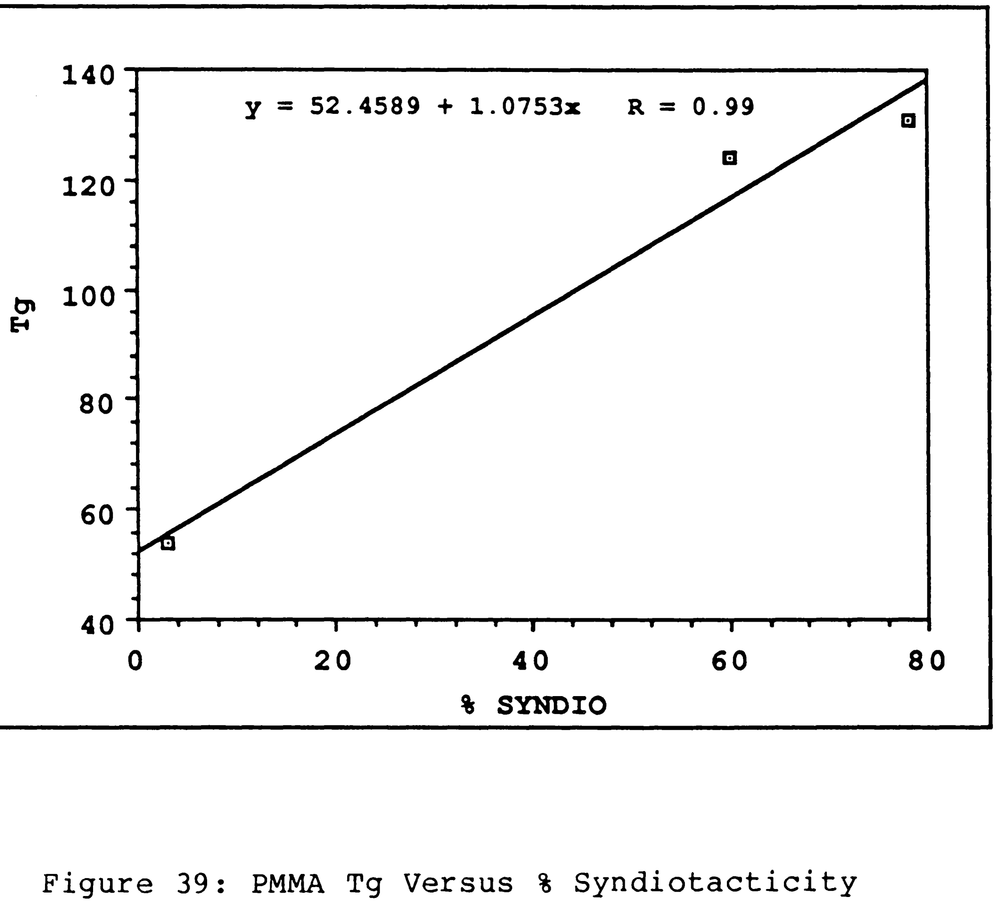


Figure 39: PMMA Tg Versus % Syndiotacticity

Table 37

Effect of PTBMA Tacticity on the Glass Transition Temperature

Synthetic Route	% tacticity[a]			Tg(°C)[b]
	syndio	hetero	iso	
DPHL, Toluene -78°C	0	0	100	84
DPHL, THF -78°C	52	46	2	118
AIBN, Bulk 64°C	61	39	0	123

[a] Determined by 50 MHz ^{13}C NMR backbone quaternary carbon; All values ± 3%.

[b] Determined by DSC at the transition midpoint.

syndiotacticity parallels the decrease in the glass transition temperature. The Tg versus percent syndiotacticity was plotted in a similar fashion (corr. coeff. = 0.999) and the extrapolated Tg for 100% syndiotactic PTBMA was determined to be 148°C (slope = 0.644°C/%syndio). This upper Tg is 12°C lower than the value determined for PMMA. The corresponding plot to determine the Tg for 100% isotactic PTBMA was not required since the material can be synthesized. Table 37 lists 84°C for the Tg of 100% isotactic PTBMA. The difference in the 100% syndiotactic and isotactic Tg for PTBMA is 64°C. This analysis reveals that a smaller difference in tactic glass transition temperatures exists for homopolymers with bulkier ester alkyl groups. This reflects a smaller difference in the conformational energy barriers for segmental rotation between the isotactic and syndiotactic forms of PTBMA versus PMMA. This may be attributed to differences in the packing of the polymer chains.

Another interesting observation is that the glass transition temperatures for methyl and t-butyl methacrylate polymers which are prepared by free radical initiators are essentially the same, i.e. 123°C for PTBMA and 124°C for PMMA. Despite the bulkier t-butyl group, similar thermal energy is required for segmental motion of the polymer backbone. It is presumed that there are differences in free volume between the two samples due to packing of the bulkier ester group. This observation is in sharp contrast to behavior noted for styrene based systems. For example, the glass transition temperature for poly(styrene) is approximately 100°C. However, the Tg for poly(t-butyl styrene) is 145°C. Alkyl substitution on the phenyl ring dramatically increases the glass transition temperature. Free radically prepared PMMA and PTBMA may be interesting to study from the perspective of a membrane application because of their similar Tg, but drastically different free volume.

The effects of ester alkyl group and polymerization solvent on the glass transition temperatures for various poly(alkyl methacrylates) are summarized in Table 38. From a quick glance, it is apparent that variations of the solvent and ester group enable one to modify the room temperature characteristics of the polymers from a glass (s-PMMA) to an elastomer (i-PEMA). In addition, longer ester alkyl methacrylate monomers such as 2-ethylhexyl methacrylate (EHMA) significantly reduce the Tg below 0°C. It should be noted that linear ester alkyl groups greater than eight carbons can crystallize and this may impart rigidity to the system. Thus, linear ester alkyl groups are generally branched in order to disturb the symmetry and prevent crystallization. Table 38 illustrates the large range of thermal properties that are obtainable from the anionic polymerization of alkyl methacrylates. Acrylates have lower glass transition temperatures than the

Table 38

Effect of Ester Alkyl Group and Polymerization Solvent on the Glass Transition Temperature

Ester Alkyl Group	Polymerization Solvent	Tg(°C)[a]
methyl	Tetrahydrofuran	131
	Toluene	54
ethyl	Tetrahydrofuran	86
	Toluene	6
isopropyl	Tetrahydrofuran	86
	Toluene	34
t-butyl	Tetrahydrofuran	118
	Toluene	84

[a] Determined at Transition Midpoint by DSC (10°C/min).

corresponding methacrylates, but anionic polymerization attempts using DPHL or LDA at -78°C failed. The literature Tg values for poly(alkyl acrylates) that were prepared by free radical initiation have been compared to the corresponding poly(alkyl methacrylates) earlier.

b) Thermal Stability

Thermogravimetric analysis (TGA) describes the thermal stability of polymeric systems in terms of weight loss as a function of temperature. Figure 40 illustrates the thermal stability for a variety of samples which were prepared using DPHL in polar solvents at -78°C. Interestingly, PTBMA reproducibly loses approximately 46% of its weight. FTIR and mass spectroscopy (MS) analysis attribute this loss to the liberation of isobutylene to form poly(methacrylic acid) followed by subsequent anhydride formation. Also, free radically prepared PMMA begins to lose weight near 160°C. This early weight loss is the consequence of thermally labile linkages resulting from free radical termination mechanisms. Anionic polymerization does not result in weak groups such as head-to-head linkages or unsaturated chain ends. Thus, the anionically prepared materials generally demonstrate enhanced thermal stability. The stabilities of PIPMA and PEMA are intermediate and degradation occurs in a single step.

Preliminary evidence has indicated that the isotactic poly(alkyl methacrylates) exhibit greater thermal stability

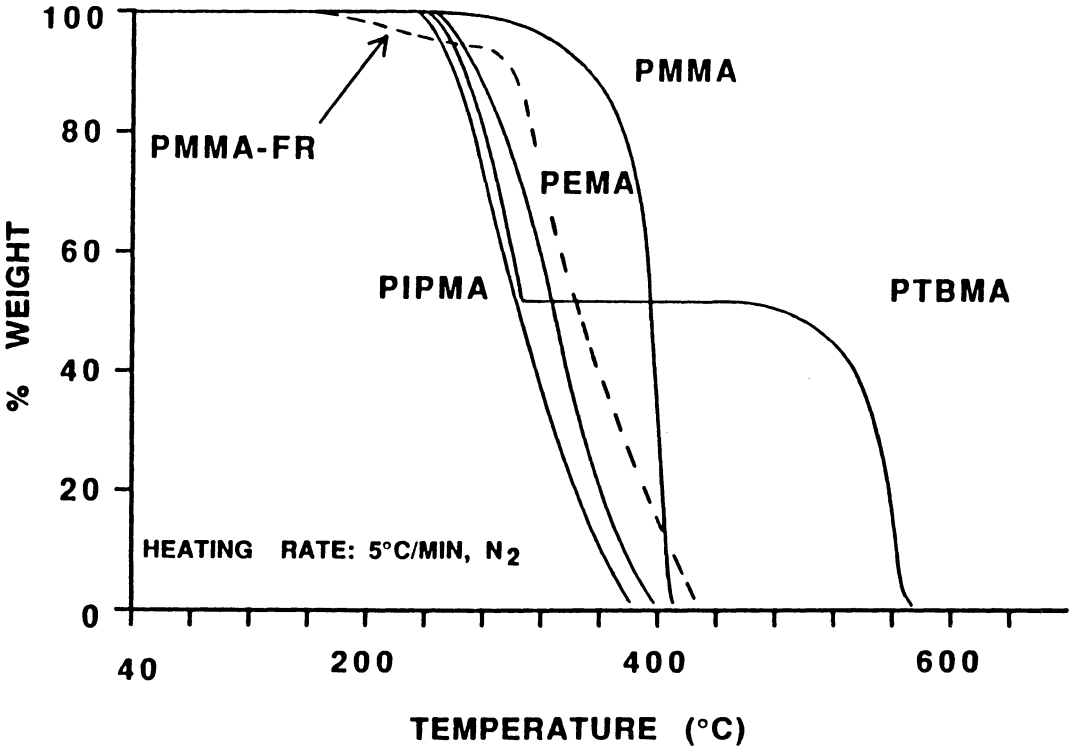


Figure 40: Thermogravimetric Analysis (TGA) of Various Poly(alkyl methacrylates) Prepared in THF at -78°C with DPHL

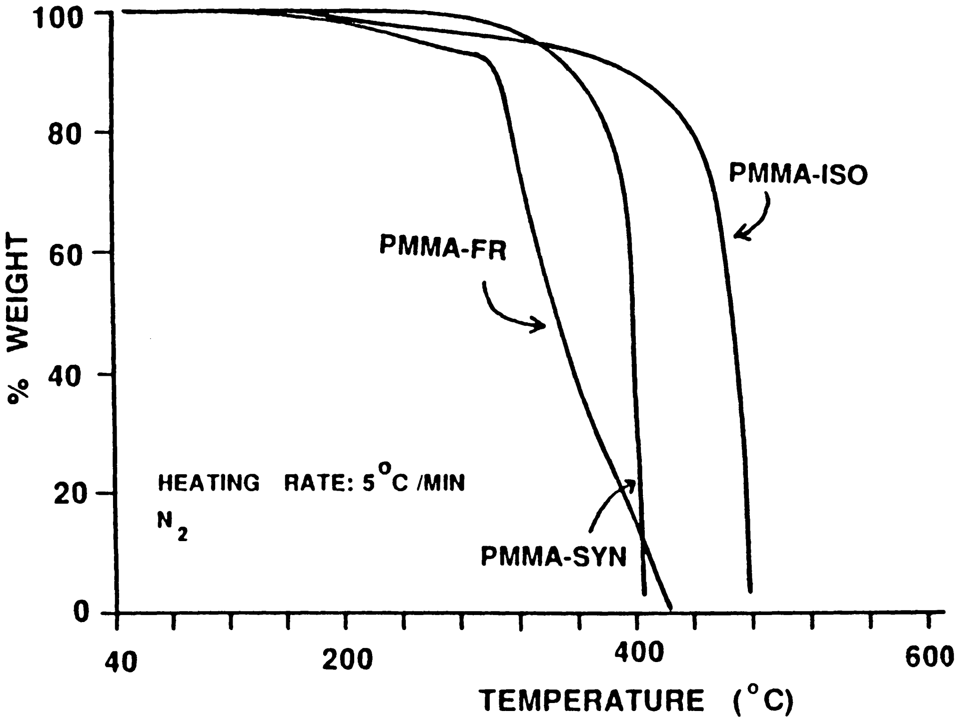


Figure 41: Effect of PMMA Polymerization Conditions on Thermal Stability

than the corresponding syndiotactic materials. Figure 41 shows a 40°C increase in thermal stability during a majority of the weight loss for isotactic PMMA. The syndiotactic and random materials are also shown for reference. The isotactic chain ends are presumed to be quite different in structure due to the termination reactions that occur during polymerization. This may alter the mode and temperature of degradation. On the other hand, t-butyl methacrylate undergoes "living" polymerizations in both polar and hydrocarbon solvents. Consequently, the weight loss versus temperature curves for i-PTBMA and s-PTBMA are superimposable. The thermal stability of poly(alkyl methacrylates) can be used as an indication that the polymerization proceeded in a nonterminating manner.

Random copolymers generally exhibit thermal stabilities which are intermediate between the thermal stabilities of the respective homopolymers. However, initial studies have demonstrated that block copolymers do not degrade at the same temperatures as the equivalent random copolymer. This was demonstrated for a poly(t-butylstyrene-b-t-butyl methacrylate) copolymer (10% wt. TBMA) versus the random copolymer which had the same composition. The free radically prepared, random copolymer demonstrated a 20°C increase in thermal stability over the block copolymer. This may indicate that the terminal units in the random copolymer are styrenic and the rate of degradation from the chain end is decreased.

c) Mechanical Properties

Dynamic Mechanical Thermal Analysis (DMTA) was performed on various stereoregular poly(alkyl methacrylates) at 1 Hz. The microstructure may play a role in determining the presence and position of and β transitions. The β-relaxation is attributed to the rotation of the ester group in the side chain and involves relatively lower activation energies than the or glass transition. Figure 42 depicts the DMTA results for both isotactic and syndiotactic PMMA homopolymers. The β-transition is evident between 0°C and 50°C for the syndiotactic material, but cannot be found in the corresponding isotactic PMMA. The activation energies for these transitions have been calculated by dielectric techniques and reported by Walstrom and Ward [293]. PTBMA did not demonstrate a β-relaxation for either the syndiotactic or isotactic material. This may be due to a shifting of the β-transition to higher temperatures and becoming hidden by the strong α-transition.

The stress-strain behavior was also examined for various isotactic poly(alkyl methacrylates). The analyses of the syndiotactic and heterotactic homopolymers have received significant attention, but the isotactic materials have remained unexplored. The behavior is dependent on the glass transition temperature relative to the test temperature (25°C). Thus, i-PMMA exhibits glassy behavior

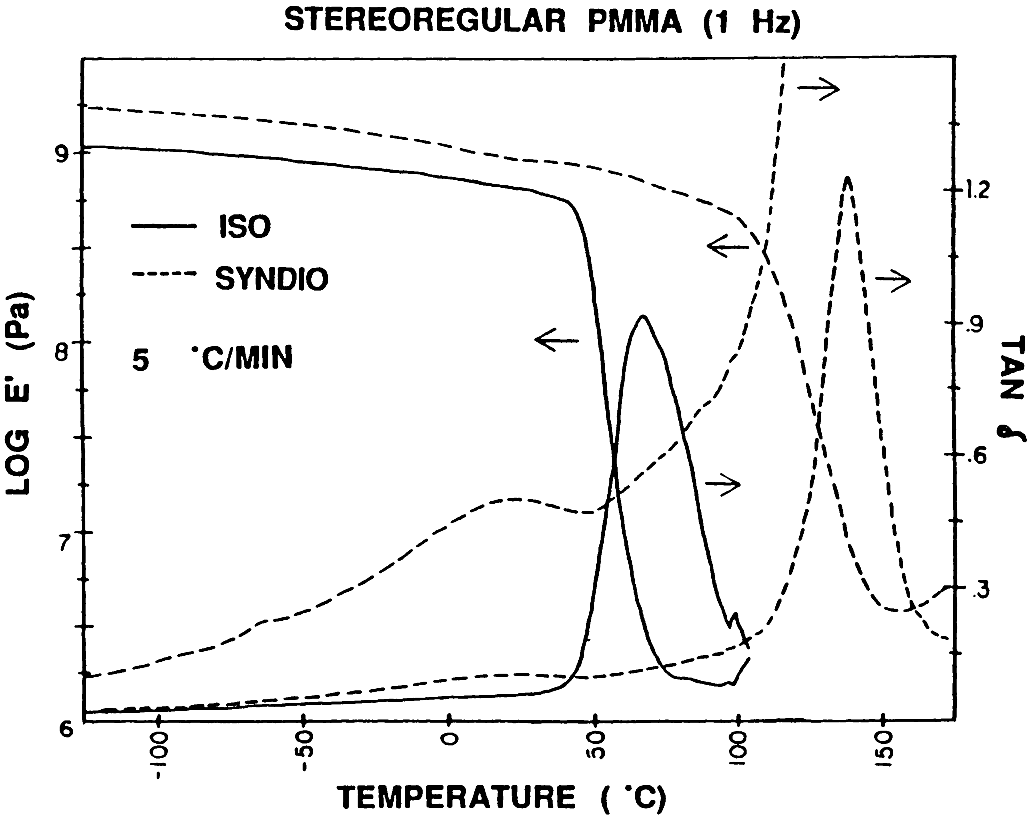


Figure 42: DMTA of Isotactic and Syndiotactic PMMA

and i-PEMA demonstrates very high elongations before fracture. i-PIPMA undergoes a yielding which is followed by elongation. The main objective of this analysis was to demonstrate that diverse mechanical behavior could be obtained with isotactic poly(alkyl methacrylates). Unfortunately, the 100% isotactic material was too brittle for sample preparation in our laboratories. However, a cooperative effort with IBM workers was unsuccessful at orienting the stereoregular polymer and typical, glassy amorphous behavior was observed. Table 39 lists the modulus, tensile strength and elongation at break for the three isotactic samples.

d) Refractive Index and Surface Properties

A variety of applications such as fiber optics require the knowledge of polymeric refractive indices. In addition, many gel permeation chromatographs are equipped with differential refractive index detectors and the refractive index of the polymer relative to the solvent is important. Thus, it seemed interesting to determine the refractive indices for various poly(alkyl methacrylates). Table 40 lists the refractive indices for several samples. Due to the similar polarizability of the carbon-hydrogen bond, the refractive indices of s-PMMA, s-PIPMA and h-PEHMA are quite similar. A common value is 1.5 for carbon-hydrogen polymers. Introduction of halogen atoms instead of hydrogen will alter the polarizability and therefore the refractive

Table 39

Mechanical Properties of Various Isotactic Poly(alkyl methacrylates)

Isotactic Homopolymer	Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
PMMA	1800	49	3
PEMA	29	4.6	426
PIPMA	478	9.5	87

Table 40

Refractive Indices of Various Poly(alkyl methacrylate) Homopolymers

Sample	Refractive Index (25°C)
s-PMMA	1.49
s-PIPMA	1.47
h-PEHMA	1.48
h-PTFEMA	1.42
Polystyrene	1.59 (Lit)
Poly(tetrafluorethylene)	1.38 (Lit)

s = syndiotactic (PMMA,78%;PIPMA,65%)
h = prepared by free radical polymerization (55-60% syndiotactic)

index. The refractive index of PTFEMA is significantly lower than most poly(alkyl methacrylates). In fact, the value is too close to THF (1.404) and the GPC differential refractive index detector cannot be utilized. Toluene (1.494) may be a suitable replacement in this type of situation. The refractive indices for poly(styrene) and poly(tetrafluoroethylene) are included in Table 40 for comparison. The refractive indices of polymers are generally 0.05 to 0.07 higher than the corresponding monomers.

Poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) was believed to possess interesting surface behavior due to the presence of fluorine and therefore an indepth analysis of the surface properties was desired. PTFEMA offers a variety of advantages that compliment the nonhalogenated poly(alkyl methacrylates). The advantages include: radiation degradation sensitivity, low surface free energy, hydrophobicity, oleophobicity, nonadhesive character, low coefficients of friction and lack of solubility in hydrocarbon solvents. Despite the inability to synthesize this polymer by anionic techniques, the free radically prepared polymer was investigated.

X-Ray Photoelectron Spectroscopy (XPS) was utilized to examine the upper 90 angstroms of the surface. By employing the depth profiling technique, any evidence of surface migration would be detected. The carbon, ester oxygen, carbonyl oxygen and fluorine signals were all evident in the full XPS scan. XPS analysis indicated that the fluorine/oxygen ratio was a constant from 90° to 15° and therefore indicated the absence of preferential migration of fluorine to the surface. In addition, the fluorine/carbon ratio was also a constant. Thus, XPS indicated that the fluorine atoms were dispersed throughout the polymer matrix.

A contact angle study was also conducted to examine the surface characteristics of PTFEMA. In particular, advancing contact angles were measured using water as the dropping liquid. The advancing contact angle for PTFEMA was 98° which was indicative of a hydrophobic, low surface energy surface. The advancing contact angle for PMMA is 75° and this value represents a more hydrophilic surface. All angles were accurate to ±2°. For comparative purposes, the water contact angle for Teflon is 120°.

e) Solubility Characteristics

Poly(alkyl methacrylates) are readily soluble in a variety of common organic solvents. In particular, tetrahydrofuran, toluene and acetone were commonly used for all applications. The homopolymers are also soluble in common NMR solvents such as dimethylsulfoxide and chloroform.

The selection of a precipitation solvent for the reaction solution is based on two criteria. First, the precipitation solvent must be a nonsolvent for the polymer.

Second, the polymerization solvent must be miscible at room temperature with the precipitation solvent. Poly(methyl methacrylate) was routinely precipitated in petroleum ether and 100% recovered yields are possible. If PMMA is precipitated into methanol, dissolution of the lower molecular weight chains occurs and can actually result in narrower molecular weight distributions. As the ester alkyl group size is increased, the polymers become more soluble in methanol and petroleum ether. In fact, high molecular weight poly(t-butyl methacrylate) is soluble in methanol. Consequently, the branched poly(alkyl methacrylates) were routinely precipitated in methanol/water mixtures (80:20). It should be noted that these precipitation solvents can be used without difficulty if THF is the polymerization solvent. Since toluene is immiscible with water at room temperature, it must be removed by rotoevaporation and the polymer redissolved in THF in order to precipitate the polymer.

B. Synthesis and Characterization of Alkyl Methacrylate Containing Block Copolymers

1) Poly(styrene-b-alkyl methacrylates)

The poly(styryl) lithium anion is sufficiently basic to initiate the polymerization of alkyl methacrylate monomers; however, the poly(alkyl methacrylate) lithium enolate is not capable of initiating styrenic monomers. Consequently, anionic techniques permit the preparation of poly(styrene-b-alkyl methacrylate) (P(S-b-AMA)) diblock copolymers. If one uses a difunctional initiator, P(AMA-b-S-b-AMA) triblock copolymers can also be prepared. Thus, the relative basicity of the propagating anions limits the potential chemical architecture of the block copolymer. The method of adding another monomer to a "living" polymer in order to prepare block copolymers is termed "sequential addition".

The preparation of block copolymers by the sequential addition of monomers places stringent demands on monomer purity. Regarding the synthesis of P(S-b-AMA), copolymers, the deleterious effects of styrene impurities are avoided since any protic impurities are scavenged by the alkyl lithium prior to initiation. However, molecular weights of the block copolymers will be high due to partial deactivation of the initiator. Monomer purity becomes more important for subsequent alkyl methacrylate monomers because the presence of impurities will quickly terminate the poly(styryl) lithium anions. If termination occurs, the resulting block copolymer would be contaminated with poly(styrene) homopolymer. Block copolymers which contain homopolymer contamination have undesirable physical properties and complicated structure-property correlations. If the homopolymer contaminant has different solubility characteristics than the block copolymer, it can be removed by selective solvent extraction. The goal of this research was to be able to prepare "clean" block copolymers which did not require subsequent extraction techniques.

The initial objective was to confirm and quantify the earlier work of Rempp et al. which reported the necessity to "cap" the poly(styryl) or substituted poly(styryl) lithium with diphenylethylene prior to the addition of the alkyl methacrylate monomer [104]. This step was performed in order to prepare a less basic, sterically hindered chain end which would not attack the alkyl methacrylate carbonyl during crossover. The "capped" poly(styrene) block was actually a macromolecular initiator analogous to diphenylhexyllithium which was used for homopolymer studies. Table 41 illustrates the effect of capping the poly(styryl) lithium with diphenylethylene on the molecular weight distribution of PS-b-PMMA copolymers. It is obvious that the molecular weight distribution of the uncapped block copolymer is significantly broader (1.44) than the capped polymer (1.29). This confirms the necessity of capping the first block in order to avoid termination during crossover. In addition, a similar study which utilized t-butyl methacrylate was conducted in order to investigate the effect of ester alkyl group size. As expected based on homopolymer studies, the t-butyl group was capable of eliminating side reactions during crossover. Thus, the synthesis of P(S-b-TBMA) copolymers does not require the capping of the poly(styrene) first block with

Table 41

Effect of Diphenylethylene (DPE) Capping Procedure on the Anionic Synthesis of Poly(styrene-*b*-methyl methacrylate)

Sample	$\bar{M}n$(th)[a]	$\bar{M}n$(GPC)[b]	$\bar{M}w/\bar{M}n$
PS	10,000	10,000	1.12
P(S-*b*-MMA)	10,000- 10,000	18,500	1.44
P(S-DPE-*b*-MMA)	10,000- 10,000	19,400	1.29

[a] $\bar{M}n(th) = \frac{\text{total g monomer}}{\text{moles initiator}}$

[b] Poly(styrene) standards

diphenylethylene.

The elimination of the capping step is quite significant for two reasons. First, diphenylethylene is difficult to purify and high vacuums are generally required. Second, the addition of reagents to a "living" system increases the risk of termination. In addition to the many advantages that were outlined earlier for t-butyl methacrylate, the ability to eliminate side reactions during crossover is also very significant.

Various substituted styrene-alkyl methacrylate block copolymers have been synthesized in a controlled fashion, demonstrating predictable molecular weight and narrow molecular weight distributions. Table 42 depicts various poly(t-butylstyrene-b-t-butyl methacrylate) (P(TBS-b-TBMA)) copolymer samples. In most cases, a maximum of 15-20 wt. percent of alkyl methacrylate was incorporated into the block copolymer. The alkyl methacrylate composition was easily verified by monitoring the increase in the FTIR absorbance of the carbonyl as the monomer charge increased. Figure 43 illustrates an FTIR spectrum of a P(TBS-b-TBMA) (10% wt. TBMA) copolymer. In particular, one should note the carbonyl absorbance (1723 cm-1) for PTBMA and the characteristic styrene band above 3000 cm-1 associated with the aromatic carbon-hydrogen stretch. ^1H NMR cannot be utilized to verify composition for the TBMA based systems due to overlapping chemical shifts. However, if methyl

Table 42

Molecular Weight Control and Molecular Weight Distribution for Poly(t-butylstyrene-*b*-t-butyl methacrylate) Copolymers

Sample	% wt. TBMA	$\bar{M}n(th)^a$	$\bar{M}n(GPC)^b$	$\bar{M}w/\bar{M}n$
PTBS	0	50,000	50,300	1.03
P(TBS-TBMA)	2	50,900	56,400	1.07
P(TBS-TBMA)	5	52,300	57,900	1.03
P(TBS-TBMA)	10	55,000	54,700	1.03
P(TBS-TBMA)	10	55,000	53,000	1.03
PTBMA	100	100,000	139,000	1.18

[a] $\bar{M}n(th) = \frac{\text{total g monomer}}{\text{moles initiator}}$; 0.30mmoles initiator

[b] Poly(styrene) Standards, THF, 30°C

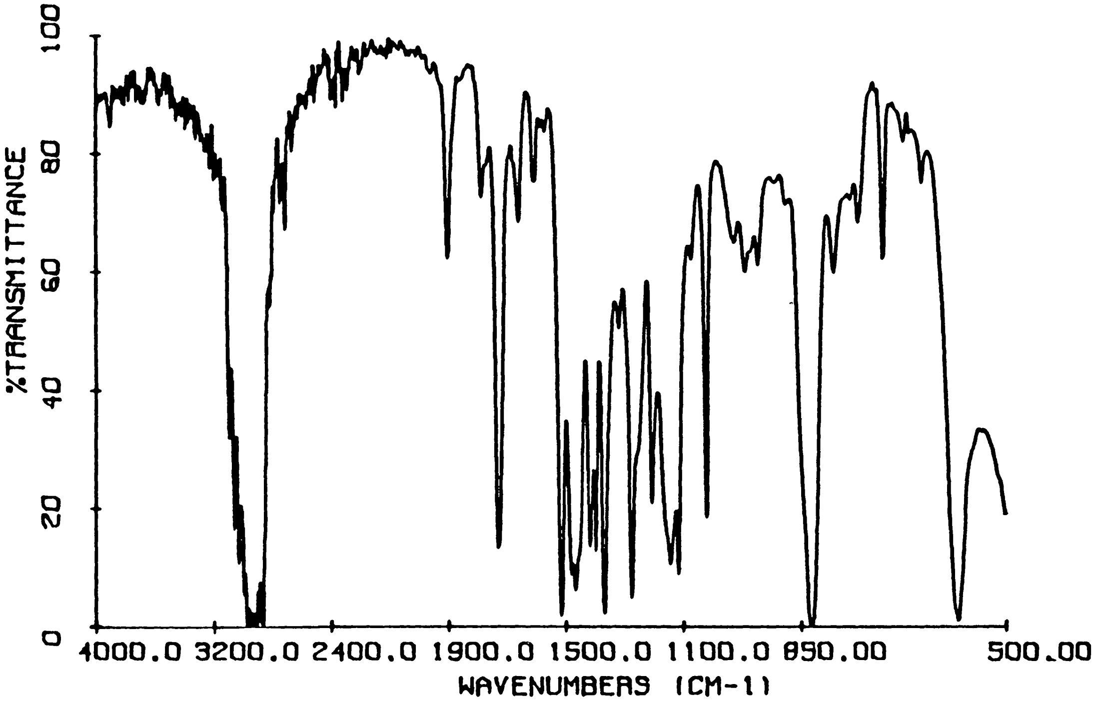


Figure 43: FTIR Spectrum of P(TBS-b-TBMA) Copolymer (10 % wt. PTBMA)

methacrylate (MMA) is used, the methyl ester resonance appears downfield (ca. 3.5 ppm) and can be used for verification of composition. This is true for all alkyl methacrylate monomers which have protons on the carbon which is adjacent to the ester oxygen. Figure 44 is the ^{1}H NMR spectrum of a P(TBS-b-MMA) (85:15 by wt.) sample ($\bar{M}n$ = 85,500 g/mole, MWD = 1.16). Compositions generally agree within 2% of the theoretical values. Cast films from THF were clear which was indicative of the absence of homopolymer contamination.

Tetrahydrofuran (THF) was chosen as the polymerization solvent because the "living" polymerization of the alkyl methacrylate block requires a polar solvent. The major concern when using THF is its reactivity with alkyl lithiums even at -78°C. In order to circumvent this problem, the sec-butyllithium initiator was charged quickly to the monomer solution at -78°C. A large exotherm can be avoided by maintaining the percent solids at 5-8 wt./vol. percent. It is presumed that the reaction of the poly(styryl) lithium anion with THF is slower than sec-butyllithium. This technique has been adequate for the preparation of poly(styrene) homopolymers which have molecular weight distributions less than 1.10. Similarly, block copolymers with narrow molecular weight distributions were obtained by this approach.

2) Poly(alkyl methacrylate-b-alkyl methacrylate)

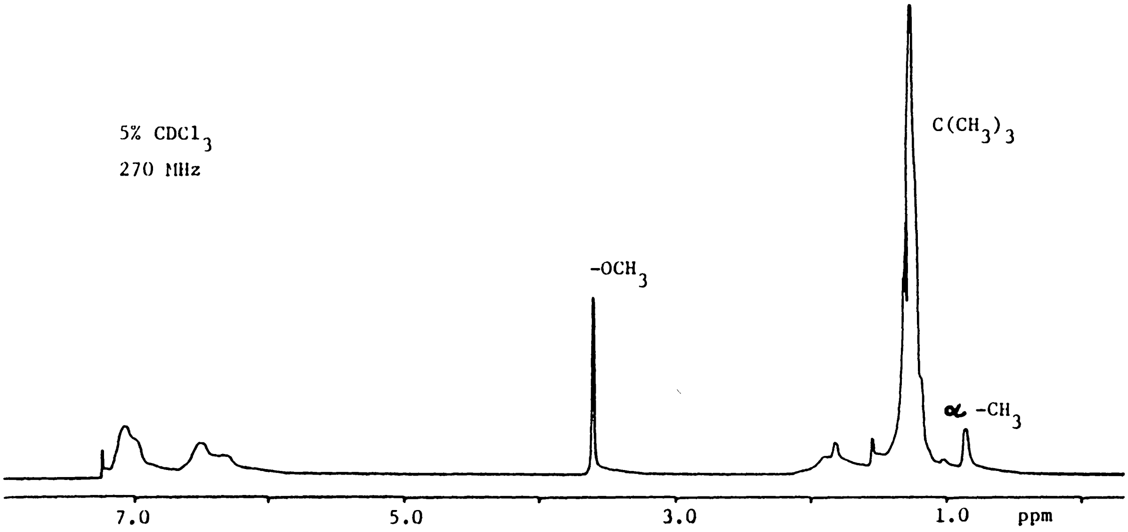


Figure 44: ^{1}H NMR Spectrum of P(TBS-b-MMA) Copolymer (85:15 by wt.)

Due to the structural similarity of most alkyl methacrylate monomers, the order of addition in block copolymer syntheses is interchangeable. This will not drastically change the physical properties of diblock copolymers, but may have many ramifications on the preparation of all-methacrylic triblock copolymers. The primary advantage of alkyl methacrylates in multiphase polymeric materials is the wide spectrum of physical properties that are available. For example, alkyl methacrylate blocks with low glass transition temperatures can be prepared by employing a monomer with a long ester alkyl group. In addition, the rubbery block could be surrounded by glassy poly(methyl methacrylate) on either side to form interesting all-methacrylic thermoplastic elastomers. The number of possibilities is tremendous due to the diverse physical properties that are available in this single class of monomer.

Despite the vast potential of all-methacrylic block copolymers, the synthesis of novel materials has been limited. The major reason for the sluggish synthetic development of these novel, multiphase materials is monomer purification. As discussed in detail earlier, most alkyl methacrylates due to their polar functionality contain many protic impurities such as esterifying alcohols and methacrylic acid. Conventional purification methodologies such as calcium hydride are not adequate for the quantitative removal of these compounds. In addition, purification by distillation often leads in premature polymerization. This is especially true for the long ester alkyl methacrylates which may have boiling points greater than 200°C. Anionic polymerization requires monomer purities greater than 99.999% and this requirement is more important in the preparation of block copolymers. Any impurities in subsequent monomer additions will lead to termination and the formation of homopolymer contamination. The trialkyl aluminum/dialkyl aluminum hydride purification reagents allow for quantitative removal of protic impurities. In addition, the application of a practical column technique would eliminate the necessity of distillation.

The major focus of the all-methacrylic block copolymer synthesis was to incorporate t-butyl methacrylate (TBMA) as one of the components. In addition to the facile anionic polymerizability of TBMA, the polymeric t-butyl ester can be quantitatively hydrolyzed to poly(methacrylic acid). This feature permits the synthesis of surfactant-like macromolecules. In addition, neutralization of the carboxylic acid groups yields metal carboxylate block copolymers. The hydrolysis reaction and conversion to the block ionomer will be discussed in detail in a subsequent section.

Table 43 illustrates the "living" nature of the all-

Table 43

Molecular Weight Control and Molecular Weight Distribution of Various All-Methacrylic Block Copolymers

Sample	% wt.TBMA	$\bar{M}n(th)^a$	$\bar{M}n(GPC)^b$	$\bar{M}w/\bar{M}n$
P(MMA-b-TBMA)	17	27,600	29,300	1.12
P(MMA-b-TBMA)	23	65,000	51,100	1.20
P(EHMA-b-TBMA)	5	62,000	82,700	1.18
P(EHMA-b-TBMA)	10	62,000	56,000	1.35
P(EHMA-b-TBMA)	50	62,000	60,300	1.27
P(EHMA-b-TBMA)	50	62,000	62,400	1.23

[a] $\bar{M}n(th) = \frac{\text{total grams monomer}}{\text{moles initiator}}$

[b] Poly(styrene) Standards, THF, 30°C

methacrylic block copolymer syntheses. Various poly(methyl methacrylate-b-t-butyl methacrylate) (P(MMA-b-TBMA)) and poly(2-ethylhexyl methacrylate-b-t-butyl methacrylate) (P(EHMA-b-TBMA)) samples are depicted. Narrow molecular weight distributions ($\bar{M}w/\bar{M}n$) are possible and good control of molecular weight is evident. All recovered yields were high (>90%) as determined by gravimetric analysis after precipitation and films cast from THF were optically clear. These observations indicate efficient crossover and the non-terminating nature of the polymerization. Figure 45 is a gel permeation chromatogram (GPC) of P(EHMA-b-TBMA) (50:50 by weight). All the monomers that were used to prepare the samples in Table 43 were distilled either from triethyl aluminum or triethyl aluminum/diisobutyl aluminum hydride. All samples were characterized by FTIR and typically two carbonyls were observed. However, at low compositions of one constituent, a shoulder rather than a resolved absorbance appeared. The PTBMA carbonyl appears at 1723 cm-1 and most other alkyl methacrylate esters appear at frequencies greater than 1731 cm-1. This difference in carbonyl position permits the facile verification of monomer incorporation by FTIR.

NMR is the most useful technique for the verification of chemical composition of the block copolymers. ^1H NMR cannot be utilized in a quantitative manner due to overlapping chemical shifts. Figure 46 illustrates the

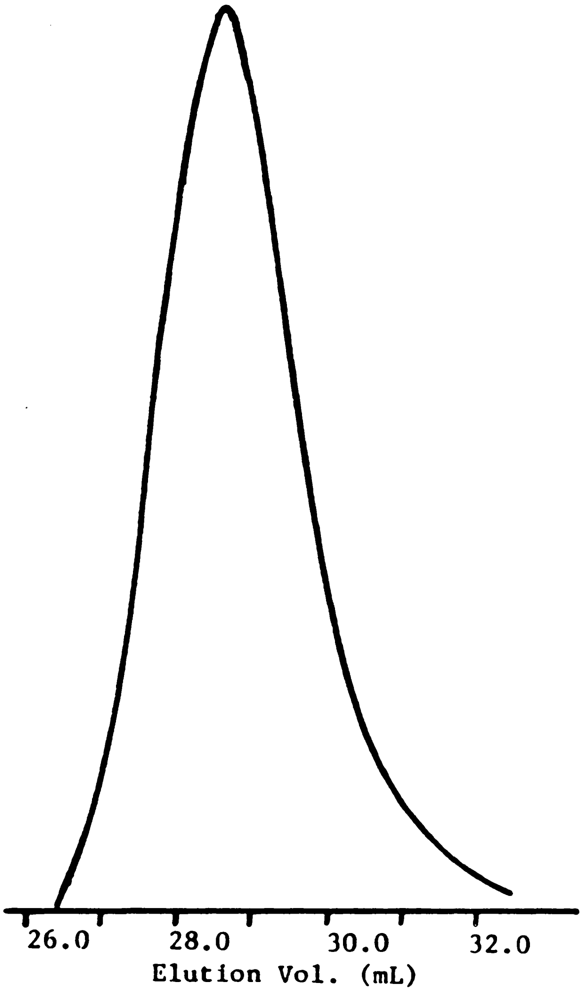


Figure 45: GPC of P(EHMA-b-TBMA) (50:50 by wt.)

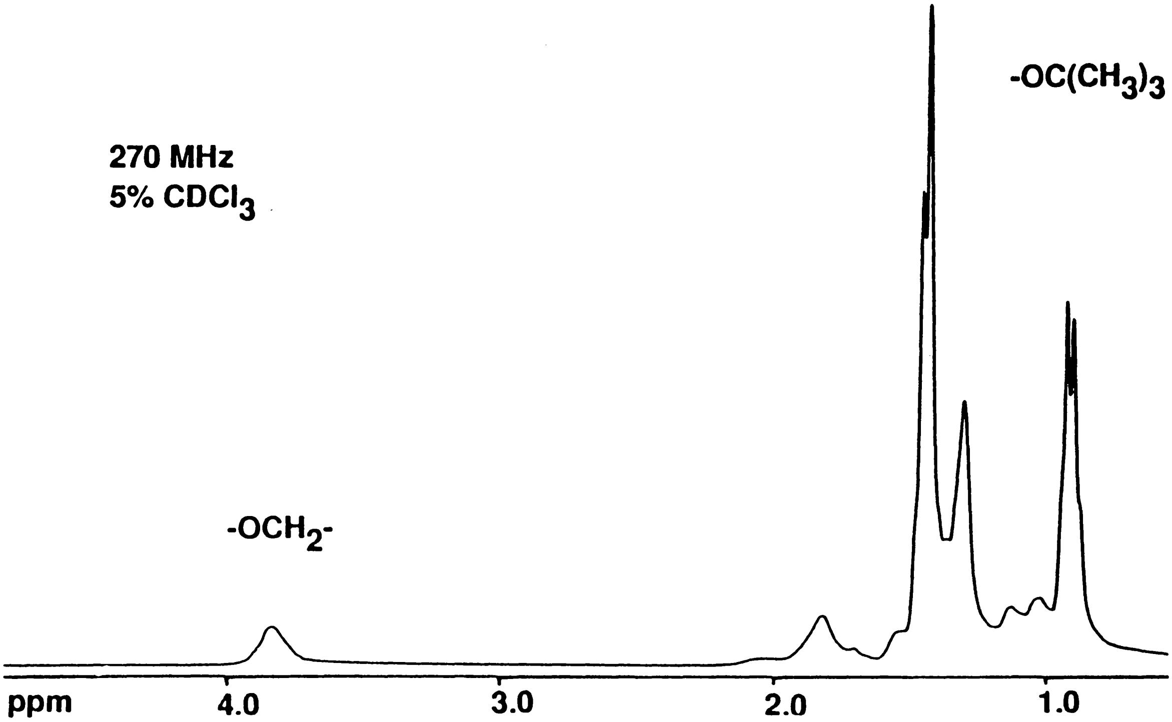


Figure 46: ^1H NMR Spectrum of P(EHMA-b-TBMA) (50:50 by wt.)

complication of overlapping chemical shifts for a P(EHMA-b-TBMA) copolymer (50:50 by weight). The t-butyl resonance reproducibly appears at 1.36ppm. At lower levels of PTBMA, the signal may appear as a shoulder. In any case, quantification is difficult and accurate measurements of the composition are impossible. Consequently, ^{13}C NMR was utilized to verify composition without the problem of overlapping chemical shifts. Table 44 indicates excellent control of composition for a series of P(EHMA-b-TBMA) copolymer samples. The methyl carbons in the t-butyl group were ratioed to various PEHMA resonances. It is important to note that controlled compositions were obtained independent of the order of monomer addition i.e. P(EHMA-b-TBMA) vs. P(TBMA-b-EHMA).

The thermal analysis (DSC) of the block copolymers was performed in order to witness phase mixing or phase separation of the blocks. The main purpose of the all-methacrylic block copolymer synthesis was to introduce an easily hydrolyzable, i.e., TBMA ester into the copolymer. The concentration of TBMA generally ranged from 2%-20% in order to control the ultimate acid and ion content in this range. Thus, phase separation was not expected due to the low PTBMA block molecular weight. Table 45 depicts the glass transition temperatures for various P(EHMA-b-TBMA) copolymers of various compositions. All samples demonstrated only one glass transition temperature which was

Table 44

Compositional Verification of P(EHMA-b-TBMA) Copolymers by ^{13}C NMR

Sample	% TBMA(Th)[a]	% TBMA(^{13}C NMR)[b]
P(EHMA-b-TBMA)	58	58
P(EHMA-b-TBMA)	58	59
P(TBMA-b-EHMA)	13	11
P(TBMA-b-EHMA)	7	undetectable

[a] Mole percent

[b] 67.9 MHz, $CDCl_3$ 5% wt./vol., 0.04M $Cr(AcAc)_3$

Table 45

Glass Transition Temperatures of P(EHMA-b-TBMA) Copolymers

Sample	mole % PTBMA[a]	Tg(°C)[b]
P(EHMA-b-TBMA)	58	64
P(TBMA-b-EHMA)	11	-27
P(TBMA-b-EHMA)	7	-27
PEHMA	0	-27
PTBMA	100	118

[a] Determined by ^{13}C NMR (See Table 44)

[b] Determined by DSC at transition midpoint; Heating Rate 10°C/min.

indicative of a phase mixed system. Both 50:50 by weight samples had block molecular weights of 30,000 g/mole for both PTBMA and PEHMA. The PEHMA transition was very broad (>70°C) compared to most other poly(alkyl methacrylates) (30-35°C). In fact, the transition is often difficult to locate and it is recommended that large sample weights be used (>12mg). This phenomenon has not been investigated in detail and it would be interesting to investigate the relaxations of longer ester poly(alkyl methacrylates) which have controlled stereochemistry.

In addition to the preparation of block copolymers by sequential addition techniques, random copolymers can also be synthesized by simultaneously charging monomers. This approach relies on the fact that the anion of each polymer is capable of initiating the other monomer. The technique has been termed the "two syringe approach". One can imagine that controlled, shorter sequence lengths can also be generated by adding partial charges of monomers in a sequential fashion. At first, random copolymer synthesis by tedious, anionic techniques does not seem feasible compared to relatively simple free radical polymerizations. However, several advantages exist which justify the investigation. First, narrower molecular weight distributions (<1.25) and predictable molecular weights are obtained more easily by anionic techniques. Free radical polymerizations generally result in materials with distributions greater than 1.8.

Second, some alkyl methacrylate monomers which are not amenable to free radical polymerization such as allyl methacrylate (AMA) can be synthesized cleanly by anionic initiation. Allyl methacrylate has been shown to undergo extensive cyclization during free radical polymerization due to the presence of the reactive, pendant double bond [294].

Figure 47 is a gel permeation chromatogram of a P(TBMA-co-AMA) sample ($\bar{M}w/\bar{M}n$ = 1.12, 58,400g/mole) that was prepared by the "two syringe technique". Good molecular weight control was observed ($\bar{M}n$(th) = 50,000 g/mole) and the composition agreed within 1% of the theoretical value (90:10 by weight). Figure 48 is the ^1H NMR spectrum of the copolymer. The t-butyl resonance is cleanly resolved at 1.36ppm and can be compared to either the PAMA vinyl protons (5.0-6.0ppm) or the protons adjacent to the ester oxygen (ca. 4.4ppm). The polymer was stabilized with Irganox 1010 Inhibitor and stored in the refrigerator. This study proved that allyl methacrylate can be polymerized by anionic techniques without side reactions involving the pendant double bond.

The thermal properties of poly(allyl methacrylate) were investigated in order to ascertain the reactivity of the pendant double bond. Figure 49 illustrates the Tg (99°C) of a PAMA homopolymer and the crosslinking exotherm onset at 143°C. The thermal stability which was determined by TGA of the copolymer is intermediate between PTBMA and PAMA and

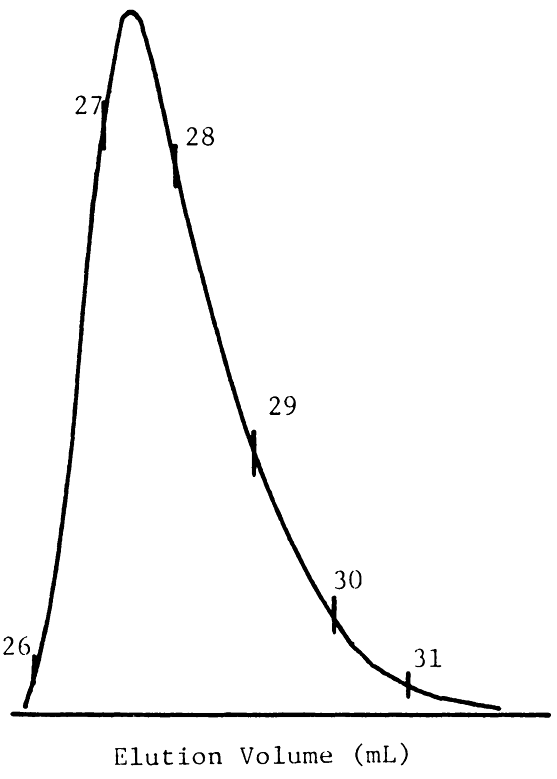


Figure 47: GPC of Poly(t-butyl methacrylate-co-allyl methacrylate) Prepared by the Two Syringe Technique

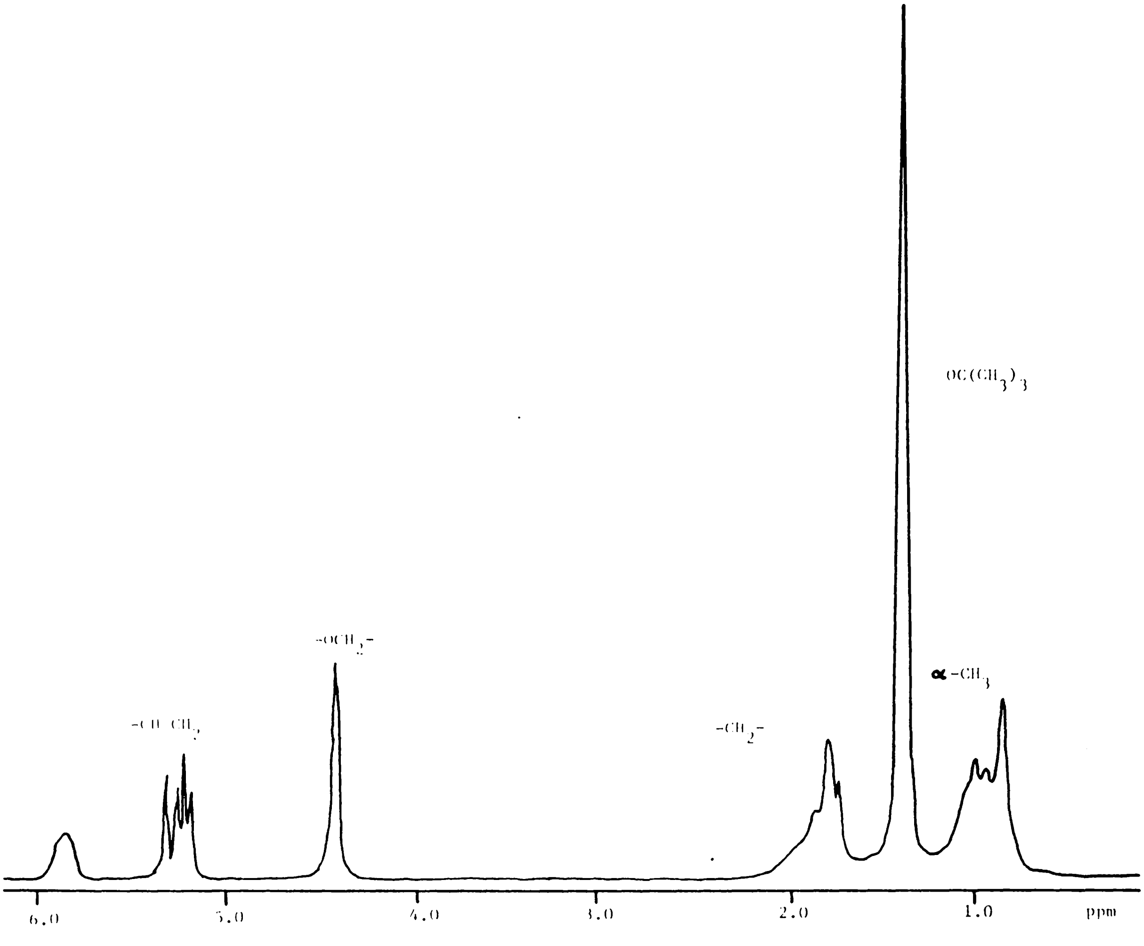


Figure 48: ^{1}H NMR Spectrum of P(TBMA-co-AMA)

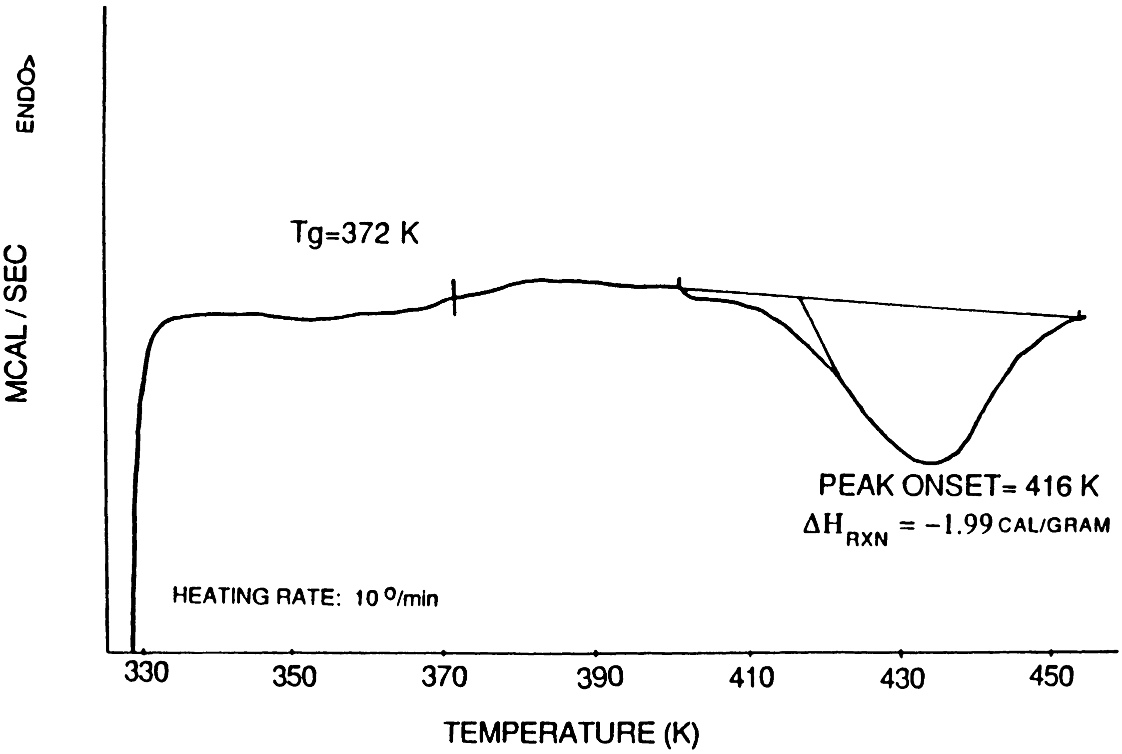


Figure 49: DSC Thermogram of Poly(allyl methacrylate)

degradation begins at 220°C in nitrogen.

3) Poly(diene-b-alkyl methacrylate)

The synthesis of diene-methacrylate block copolymers is complex, especially when one desires to maintain a high level of 1,4-addition in the polydiene and the corresponding low Tg. The complexity develops as a result of the selection of the polymerization solvent. High 1,4-microstructure (>90%) is possible if organolithium initiators are used in hydrocarbon solvents such as cyclohexane or toluene, but alkyl methacrylates generally do not undergo living polymerizations in hydrocarbons. Initial studies took advantage of the unique stability of the TBMA lithium enolate in both polar and nonpolar solvents. In addition, the "protected" carbonyl may facilitate the crossover reaction and polymerization in a fashion similar to styrene-methacrylate block copolymer syntheses.

Diene-methacrylate diblock copolymers can be prepared by sequential addition of the alkyl methacrylate monomer to the living poly(dienyl) anion. However, the alkyl methacrylate lithium enolate is not sufficiently basic to initiate a diene monomer. Thus, triblock structures such as P(TBMA-b-isoprene-b-TBMA) can only be prepared by employing a difunctional initiator. Broske and McGrath have outlined in detail the preparation of a hydrocarbon soluble, difunctional initiator [272]. The preparation and structure of the initiator were shown earlier in Scheme XXV. The solubility of the initiator in cyclohexane or toluene arises due to the meta substitution.

After complete conversion of the isoprene in cyclohexane, t-butyl methacrylate monomer was added directly to the poly(isoprenyl) dilithium anion at room temperature. A viscosity increase was evident after only 15-20 minutes. The gel permeation chromatogram of the final product was bimodal and significant homopolymer was present. In fact, films cast from either cyclohexane or tetrahydrofuran were cloudy. A representative GPC trace for a poly(isoprene-b-t-butyl methacrylate) diblock copolymer which was initiated with sec-butyllithium is shown in Figure 50. The peak at lower elution volume is twice the molecular weight of the later peak. This suggests a possible coupling mechanism involving the methacrylate monomer. It is important to note that the diblock and triblock attempts led to similar observations. Despite the inefficient crossover reaction in cyclohexane, 100% of the TBMA monomer was incorporated. This observation was confirmed by ^1H NMR and the spectrum is shown in Figure 51. Once again, the t-butyl resonance at 1.36ppm was compared to the protons attached to the unsaturated site in the poly(isoprene) block (4.5-5.5ppm) in order to confirm composition. The presence of only one α-methyl resonance at ca. 1.25 ppm indicates that purely isotactic PTBMA is formed in cyclohexane. This behavior was observed earlier in toluene. The results for the triblock

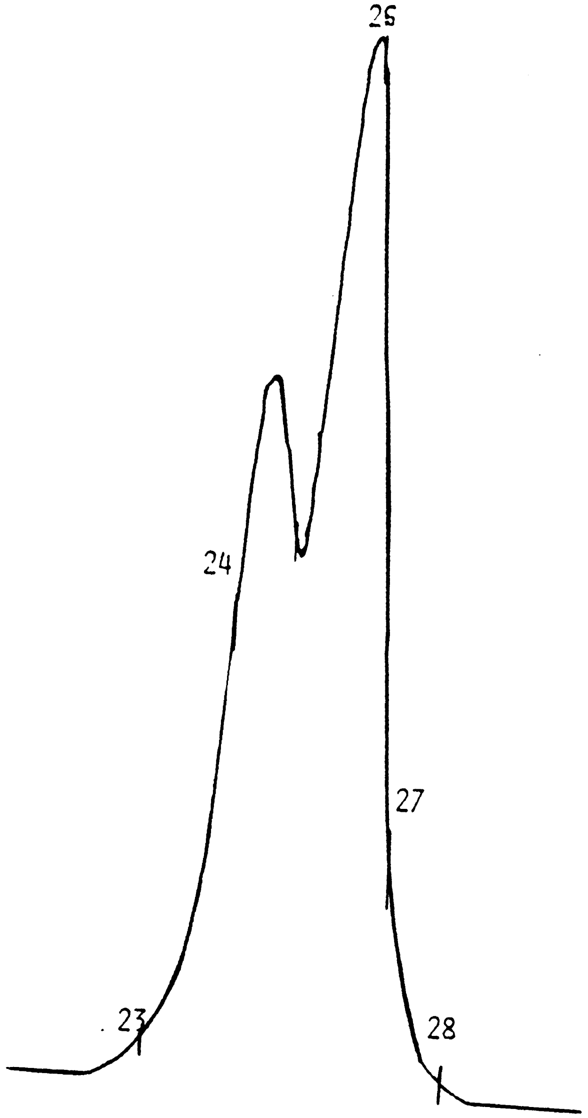


Figure 50: GPC of Poly(isoprene-b-t-butyl methacrylate) Prepared with s-Butyllithium in Cyclohexane at 25°C

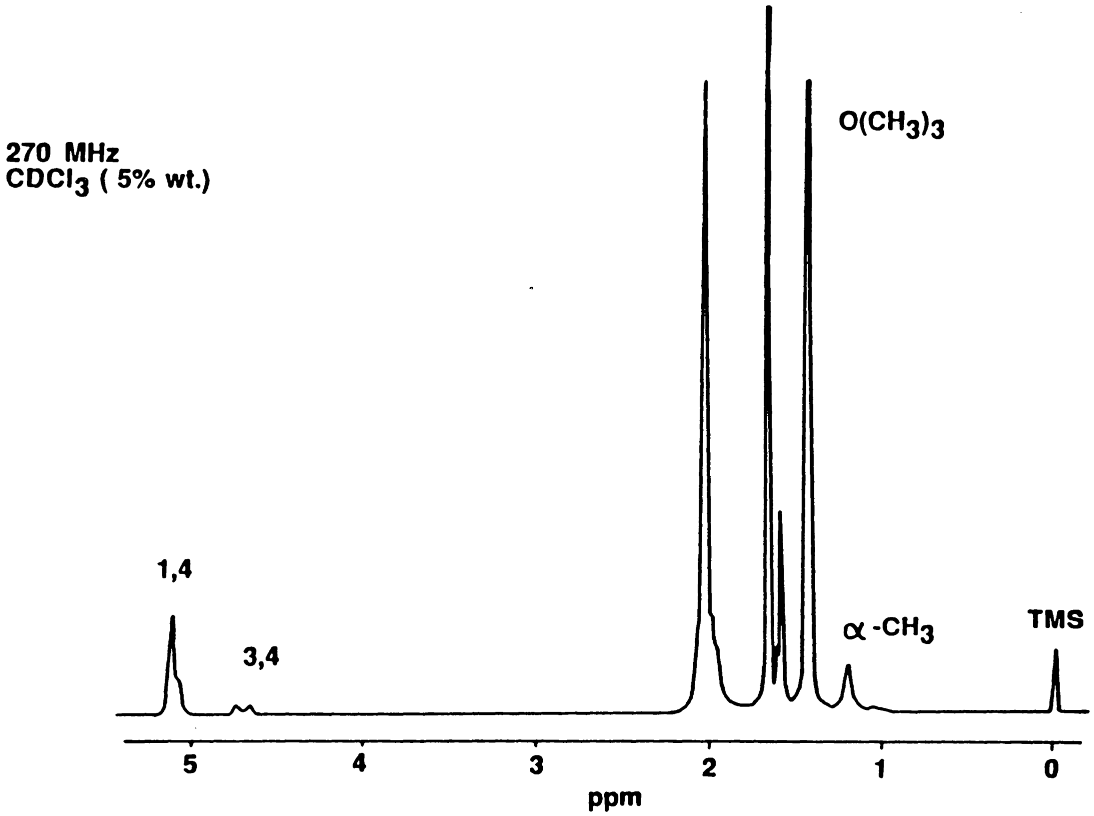


Figure 51: ^{1}H NMR Spectrum of P(TBMA-b-I-b-TBMA) Copolymer Prepared in Cyclohexane

copolymer synthesis in cyclohexane are summarized in Table 46. The molecular weight of the PI center block is 79,400 g/mole in each case. The inability to prepare monomodal diene-methacrylate block copolymers in cyclohexane was not surprising. One can recall that t-butyl methacrylate homopolymer syntheses in toluene yielded materials with uncontrolled molecular weight. The possibility of an inefficient initiation reaction was postulated to account for this behavior. Thus, one can consider the poly(isoprenyl) anion as a macromolecular initiator. However, the result in block copolymer synthesis is homopolymer contamination as opposed to a low molecular weight initiator fragment in homopolymer synthesis.

Another important factor is the polymerization temperature during crossover and subsequent polymerization of the alkyl methacrylate block. Homopolymer studies in polar solvents indicated that the TBMA lithium enolate was stable over a wide thermal range i.e. -78°C to +37°C. However, similar behavior was not found for the lithium enolate in hydrocarbon polymerization solvents. In fact, the TBMA lithium enolate undergoes side reactions at room temperature in toluene which leads to broader molecular weight distributions. Due to the high freezing point of cyclohexane (6.5°C), low temperature polymerizations are impossible. Based on the above considerations, it was believed that the crossover and subsequent polymerization

Table 46

Molecular Weight, Distribution and Composition of Poly(isoprene-b-t-butyl methacrylate) Triblock Copolymers

Sample	TBMA Polymerization Solvent[a]	mole% PTBMA[b]	$\bar{M}w/\bar{M}n$[c]
Poly(isoprene) ($\bar{M}$n(th)=80K)	---	---	1.10 ($\bar{M}$n= 79.4K)
P(TBMA-b-I-b-TBMA)	Cyclohexane	29	Bimodal[d]
P(TBMA-b-S-b-I-b-S-b-TBMA)	Cyclohexane	29	Bimodal[d]
P(TBMA-b-I-b-TBMA)	Cyclohexane/ THF (50:50)	29	1.10[e]
P(TBMA-b-S-b-I-b-S-b-TBMA)	Cyclohexane/ THF (50:50)	29	1.25[e]

[a] Diene phase prepared in cyclohexane in each case.
[b] Determined by ^{1}H NMR, 270MHz, ratio t-butyl protons to protons attached to unsaturated sites
[c] Poly(styrene) standards
[d] Films cast from cyclohexane and THF are cloudy
[e] Films cast from cyclohexane and THF are clear

should be modified with a polar solvent. It should be noted that the entire polymerization cannot be conducted in a polar solvent because high vinyl contents would result in the poly(diene) phase. High vinyl contents drastically increase the glass transition temperature and the desirable elastomeric properties of the poly(diene) would be lost.

The purity of the polar modifier is critical because it is added directly to the living poly(diene) anions. In addition, polar solvents tend to be hydrophilic and efficient purification methodologies are required. Tetrahydrofuran (THF) was selected as the polar modifier due to its availability and established purification procedures. However, initial attempts led to termination of the first block. It was concluded that distillation from the sodium/benzophenone ketyl under nitrogen atmosphere was not adequate. In addition to the distillation under inert atmosphere, a vacuum distillation immediately prior to use resulted in sufficiently pure THF. The twice distilled THF did not terminate the poly(isopropenyl) anions prior to the polymerization of the alkyl methacrylate. A facile check of solvent purity would be to add THF to a known concentration of poly(styryl) lithium and observe any loss in the orange color of the anion. The purity could be calculated by noting the amount of solvent that was necessary to lead to total termination.

Modifier concentrations in anionic polymerizations are generally quite low, i.e., 5-10 moles compared to 1 mole of living chain end. Such small amounts are adequate because the polar modifier preferentially solvates the ion pair. Initial attempts using 10/1 THF/lithium resulted in observations similar to the unmodified materials. It appears that the polarity of the entire medium is important rather than only the nature of the ion pair. Consequently, large amounts (50:50 cyclohexane:THF, 8000 moles THF to 1 mole lithium) of modifier were investigated. In principle, the THF should be considered a cosolvent rather than a polar modifier at these concentrations. The preliminary investigations involved cooling the reactor to -78°C as the THF was added via a cannula to the living first block. It is believed that if the alkyl methacrylate is added immediately after THF addition, then cooling may not be required and the second block can be formed at room temperature.

Table 46 also describes the effect of adding large amounts of THF on the crossover reaction and subsequent polymerization of t-butyl methacrylate. Narrow molecular weight distributions (<1.25) and predictable compositions are possible for the diene-methacrylate triblock copolymers. A typical GPC trace for a diene-methacrylate triblock copolymer is shown in Figure 52. Films of the triblocks cast from THF or cyclohexane are optically clear; this indicates the absence of homopolymer contamination.

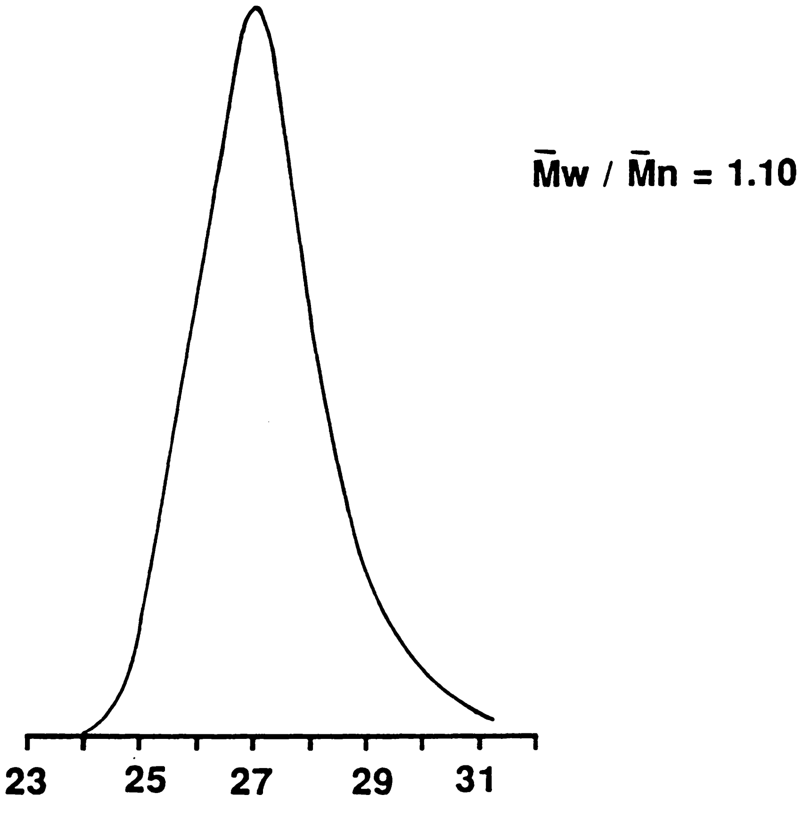


Figure 52: Typical GPC of P(TBMA-b-I-b-TBMA)
Modified Polymerization with THF

Attempts at capping the poly(isoprenyl) lithium with styrene (5% by weight) did not appreciably affect the outcome of the polymerization. This proves that the poly(isoprenyl) lithium chain end is sufficiently hindered to avoid attack on the methacrylate carbonyl during crossover. This is in contrast to sec-butyllithium initiated TBMA which led to small amounts of termination (MWD = 1.30).

The stereochemistry of the poly(alkyl methacrylate) block is determined by the polarity of the medium. The addition of THF to cyclohexane increases the polarity and the tactic composition is altered. Table 47 illustrates the effect of polymerization solvent on the stereochemistry of the methacrylate block. As expected, the addition of THF results in an increase in the syndiotacticity (52%) at the expense of the isotacticity. The stereochemistry of the poly(isoprene) block is 92% 1,4 for all samples because the THF was added after complete conversion of the first block.

Preliminary thermal mechanical analysis (TMA) of the triblock copolymers is depicted in Figure 53. Typical microphase separated behavior is seen for both the P(TBMA-b-I-b-TBMA) and P(TBMA-b-S-b-I-b-S-b-TBMA) samples. A rubbery plateau extends from the lower PI Tg to the Tg of the methacrylate phase. The glass transition temperature of PI is slightly elevated and the Tg of the PTBMA block is slightly depressed. This indicates limited solubility of the PTBMA phase in the PI phase. It is also clear that a

Table 47

Effect of Polymerization Solvent on Diene-Methacrylate Stereochemistry

Sample	Polymerization Solvent[a]	Microstructure/ Tacticity[b]
Poly(isoprene)	Cyclohexane	92% 1,4
P(TBMA-*b*-I-*b*-TBMA)	Cyclohexane	92% 1,4 99% isotactic
P(TBMA-*b*-I-*b*-TBMA)	Cyclohexane/ THF	92% 1,4 52% syndio
P(TBMA-*b*-S-*b*-I-*b*-S-*b*-TBMA)	Cyclohexane/ THF	92% 1,4 52% syndio

[a] THF present only during TBMA polymerization

[b] Values determined by ^{1}H NMR 270 MHz (± 2%); 5% $CDCl_3$

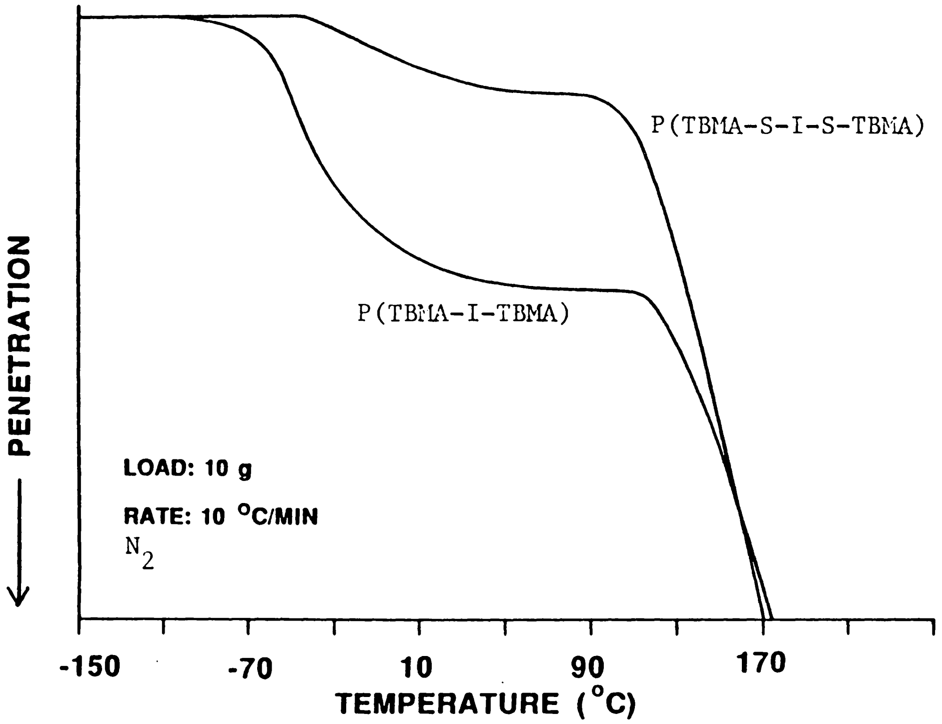


Figure 53: Thermomechanical Analysis of Diene-Methacrylate Triblock Copolymers (Nitrogen Atmosphere)

higher modulus for the rubbery plateau exists for the styrene capped (5% by weight) triblock copolymer. It is presumed that poly(styrene) is miscible in the poly(isoprene) phase and a higher modulus results.

The phase separated behavior was unexpected due to the small difference in solubility parameters between PI (8.0 $(cal/cm^3)^{1/2}$)) and PTBMA (8.3 $(cal/cm^3)^{1/2}$). However, the two phase morphology can be explained by noting the solubility characteristics of each block. The PTBMA block is soluble in methanol presumably due to hydrogen bonding with the electron rich carbonyl. On the other hand, poly(isoprene) is insoluble in methanol. Transmission Electron Microscopy (TEM) analysis of the diene-methacrylate block copolymers would be interesting.

C. Synthesis and Characterization of Acid and Ion Containing Block Copolymers

1) Solid State Hydrolysis of Poly(t-Butyl methacrylate)

In addition to the many synthetic advantages of t-butyl methacrylate monomer, poly(t-butyl methacrylate) (PTBMA) is easily converted to poly(methacrylic acid) (PMAA) by acid catalyzed hydrolysis [295,296]. However, the use of TBMA to generate acid-containing block copolymers has remained relatively unexplored. An understanding of the homopolymer hydrolysis reaction was desired before applying the technique to block copolymers.

Two criteria must be met for the polymer hydrolysis reaction to be advantageous. First, the hydrolysis reagents must not affect the hydrocarbon block or result in any chain cleavage. The absence of degradation can be verified by gel permeation chromatography of the modified polymer coupled with explainable spectroscopic changes. Second, the extent of hydrolysis should be controlled. It would be most desirable for the hydrolysis reaction to be quantitative since the final acid content could be dictated by the weight percent of alkyl methacrylate in the copolymer.

As discussed earlier, thermogravimetric analysis indicated that the t-butyl ester could be quantitatively cleaved in the bulk by heating at approximately 220°C. The effect of acid on the bulk hydrolysis can be investigated by adding a catalytic amount of acid to the TGA sample. Figure 54 illustrates the enhanced degradation of PTBMA in the presence of para-toluenesulfonic acid (PTSA) (5% by weight). The mechanism is believed to involve the initial protonation of the ester carbonyl followed by the generation of the t-butyl carbonium ion (A_{AL1}). Deprotonation of the tertiary carbonium ion yields isobutylene and regenerates the acid catalyst. The mechanism is depicted in Scheme XXXII. The liberation of a volatile byproduct, i.e., isobutylene, drives the reaction to high conversion. A PTBMA film can be converted into a rigid foam due to the generation of isobutylene gas by heating in a convection oven at

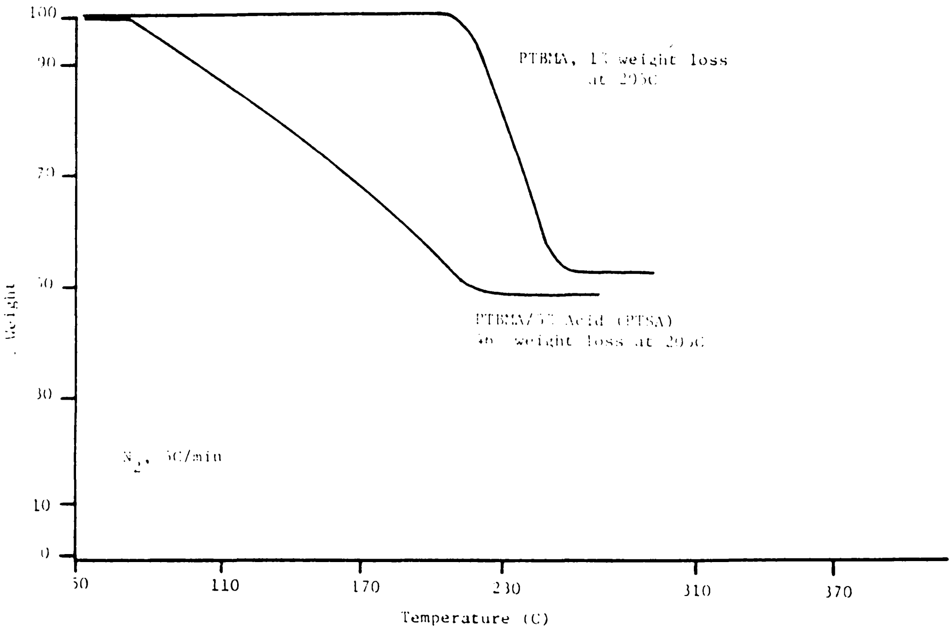
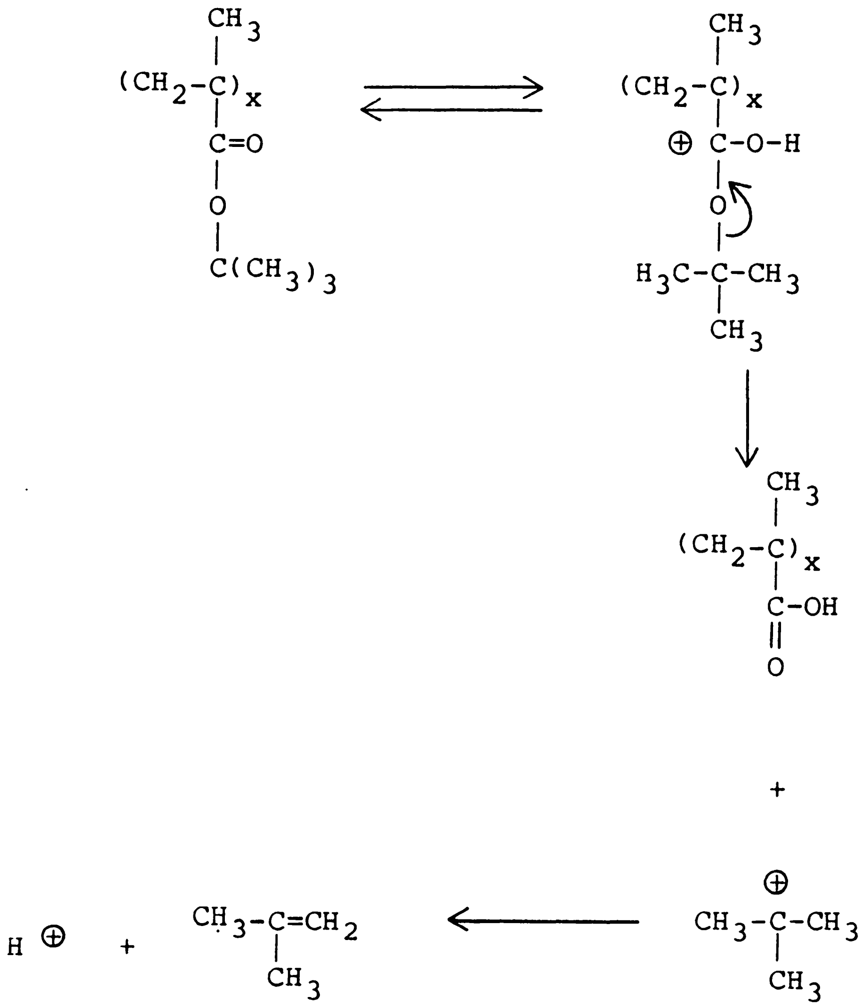


Figure 54: Effect of Acid on the Thermal Stability of PTBMA

Scheme XXXII

Mechanism of Acid Catalyzed PTBMA Deprotection



approximately 220°C for 5-10 minutes.

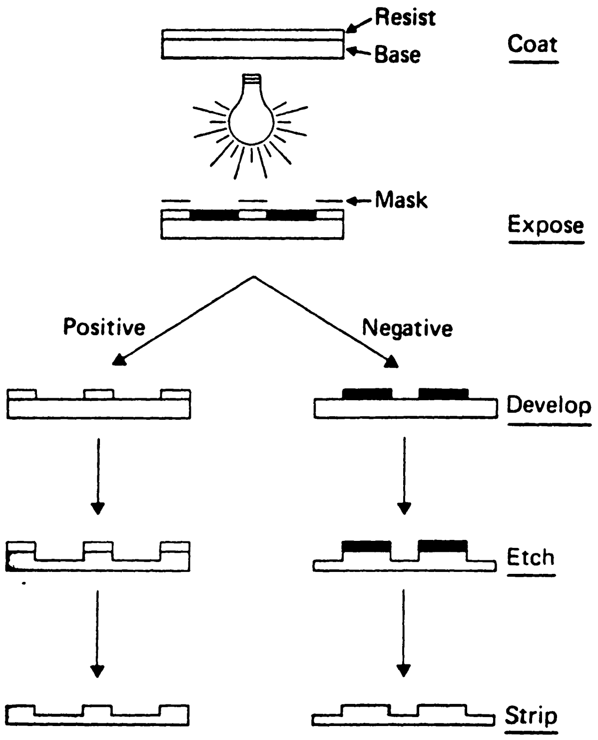
The solid state hydrolysis of PTBMA has been utilized recently to generate images with micron dimensions [297,298]. It was desired to compliment these earlier findings by investigating a variety of fundamental variables such as stereochemistry, molecular weight distribution, and molecular weight. This was accomplished by doping various stereoregular PTBMA samples with 5-10 weight percent of an onium salt such as triphenylsulfonium hexafluoroantiminate (Figure 55). The polymer and onium salt were dissolved in an appropriate solvent and a film was spun cast onto a silicon wafer. The wafer was baked at 120°C for 10-12 minutes to remove any excess solvent. A mask was placed over the film to dictate the areas that would receive radiation at 254nm. Upon irradiation at 254nm, the onium salt is converted to an acid in specific locations on the polymer film. Postbaking the exposed film at 120°C for 10 minutes led to quantitative deprotection of the t-butyl ester and poly(methacrylic acid) (PMAA) was formed in the regions that were specified by the mask design. The unexposed PTBMA regions were selectively removed by dissolution in acetone and the PMAA regions which were insoluble in acetone remained on the silicon wafer. A schematic representation of the entire photolithographic process sequence is summarized in Scheme XXXIII. The process described above for PTBMA utilizes a negative

$\phi_3S^{\oplus}\ SbF_6^{\ominus}$

Figure 55: Triphenylsulfonium Hexafluoroantiminate

Scheme XXXIII

Photolithographic Process [297]



development because the unirradiated regions were removed. The corresponding positive images can be formed by development in aqueous base which dissolves the PMAA, but does not dissolve PTBMA. The positive development was not investigated in detail.

FTIR characterization was typically performed on irradiated samples that had been cast on quartz wafers. Figure 56 is the FTIR spectrum of isotactic PTBMA after 2 mj of irradiation at 254nm. The broad COOH stretch is evident from 3300cm-1 to 2300cm-1. In addition, the ester band (1723cm-1) has been shifted to 1702cm-1, which is a characteristic frequency for the acid dimer. Another routine analysis was the observation of film thickness for the exposed regions as a function of dose. In fact, the normalized film thickness was plotted versus log (dose) (mj) and the slope defines the sensitivity. A typical plot for 60% syndiotactic PTBMA is shown in Figure 57.

The ultimate evaluation of microlithographic success is accomplished by inspecting the patterns under a microscope. Various patterns are depicted in Figures 58-60 for 60% syndiotactic PTBMA which required 25 mj of radiation. Lower amounts of irradiation resulted in inefficient imaging. Figure 61 is 60% syndio PTBMA after 6 mj (50X) and Figure 62 is another image after 15mj of energy. Thus, it appeared that the 60% syndiotactic material required approximately 25 mj of energy to generate respectable images. The 100%

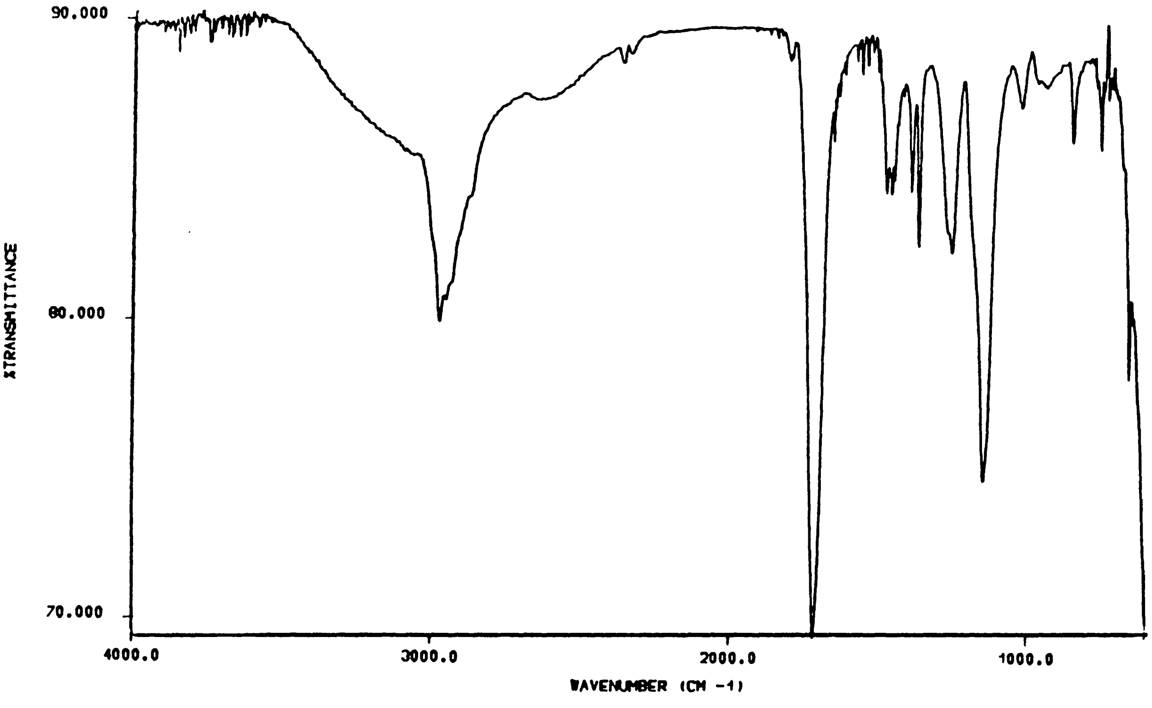


Figure 56: FTIR Spectrum after Solid State Hydrolysis of Isotactic PTBMA Using Onium Salts

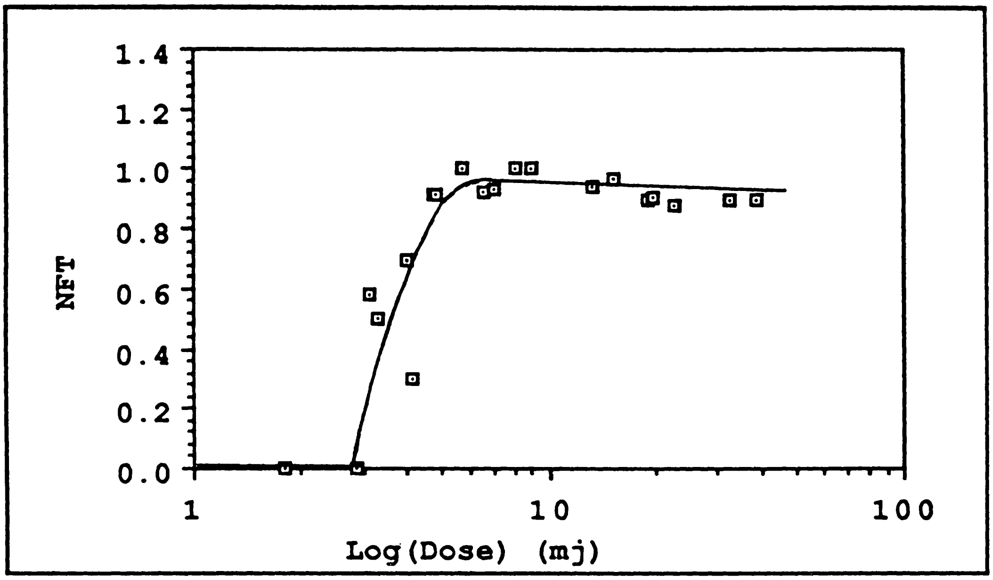


Figure 57: Normalized Film Thickness Versus Log(Dose) for 60% Syndiotactic PTBMA

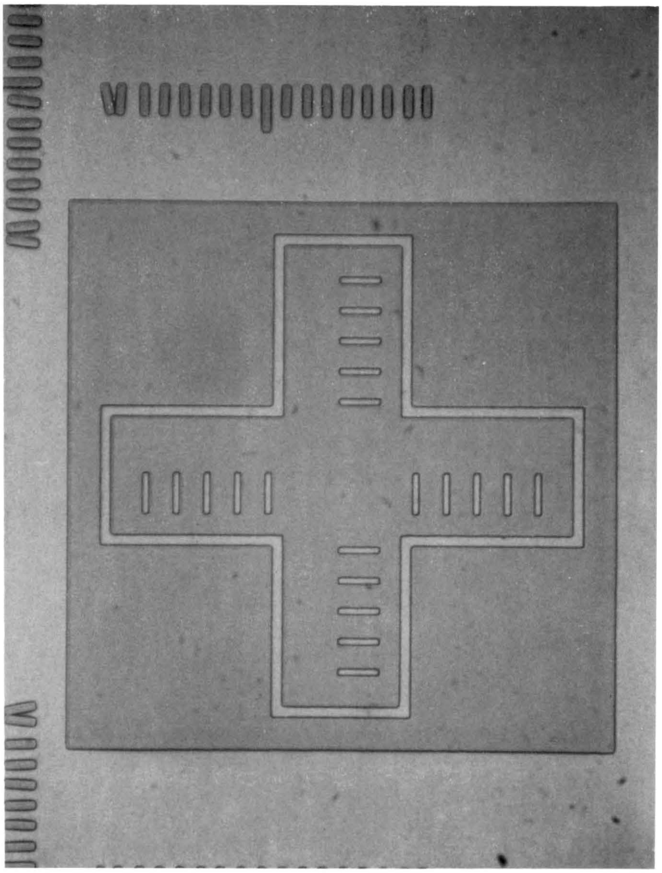


Figure 58: Imaged 60% s-PTBMA (gaps = 1 micron)
25 mj Negative (500X)

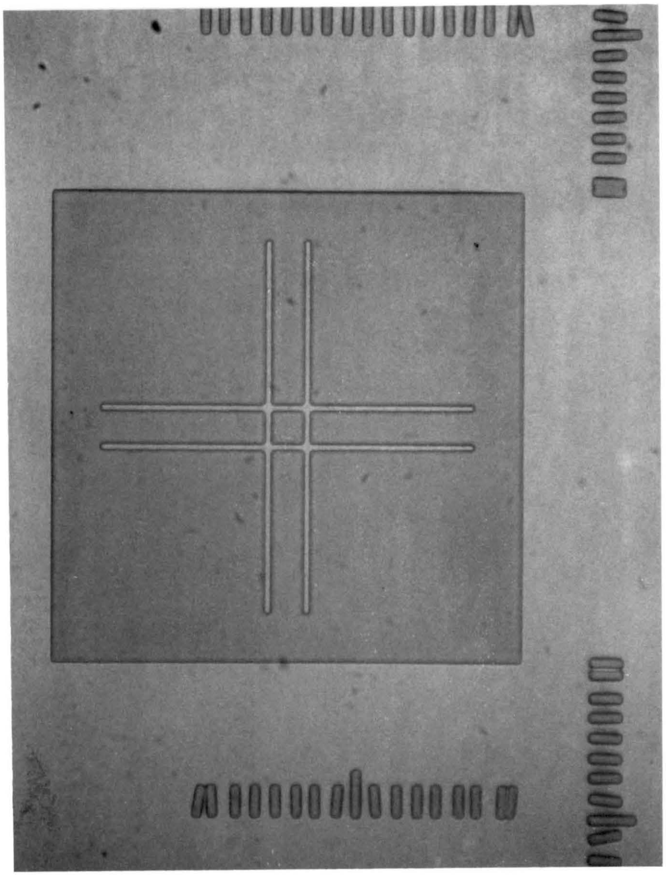


Figure 59: Imaged 60% s-PTBMA (gaps = 1 micron)
25 mj Negative (500X)

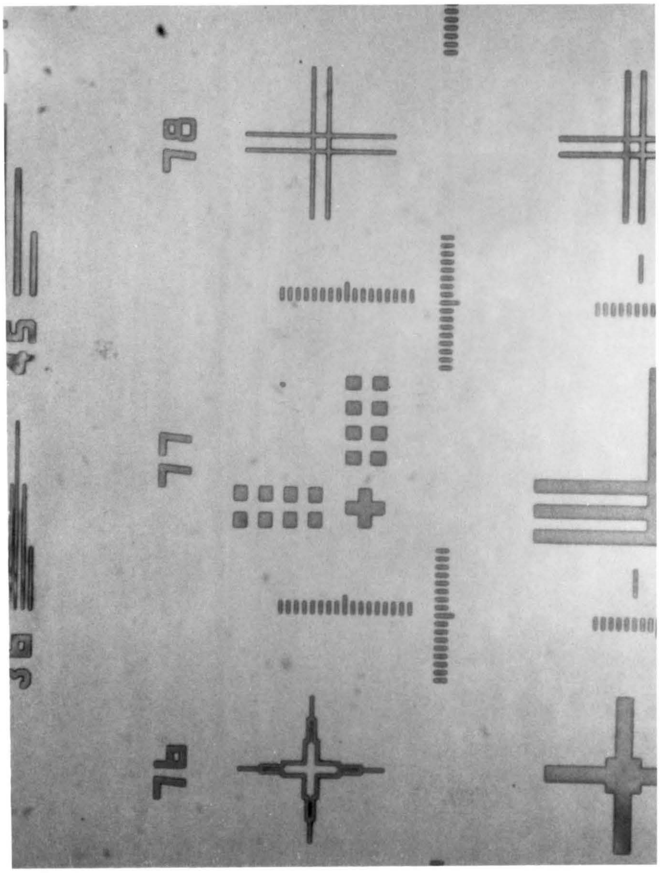


Figure 60: Imaged 60% s-PTBMA (gaps = 1 micron)
25 mj Negative (200X)

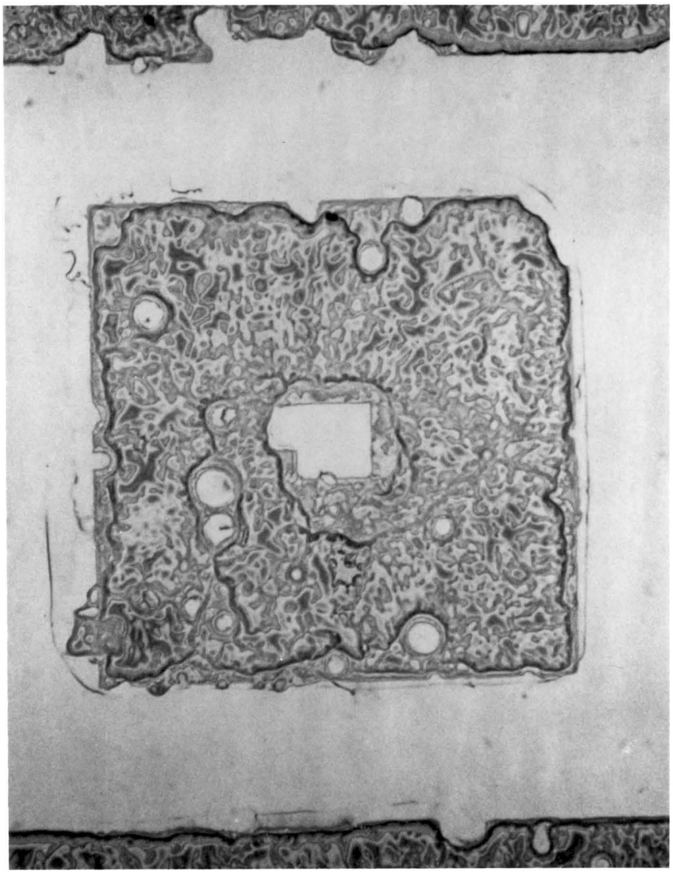


Figure 61: Imaged 60% s-PTBMA (gaps = 1 micron)
6 mj Negative (50X) Only Feature

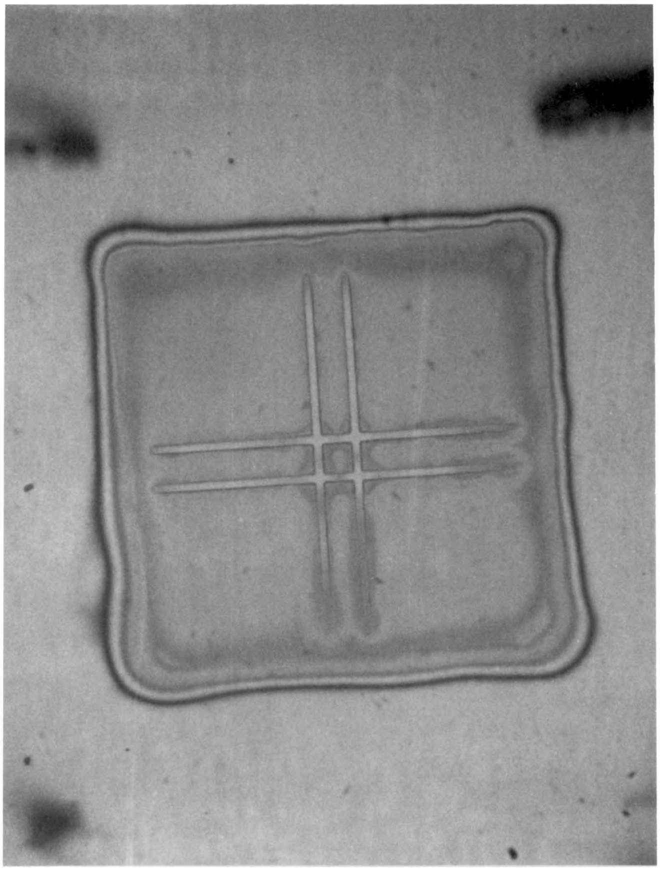


Figure 62: Imaged 60% s-PTBMA (gaps = 1 micron)
15 mj Negative (500X)

isotactic PTBMA samples were also evaluated in a similar fashion. Figures 63-65 are images that were generated by exposure with 2 mj of energy. Fine lines were resolved despite the low dose in energy. If the isotactic sample were subjected to the doses required for 60% syndiotactic PTBMA, i.e. 25mj, a phenomenon which is termed "burning" is observed. The sample has essentially been overexposed.

These preliminary observations seem to indicate that the 100% isotactic material is more sensitive than the corresponding 60% syndiotactic polymer, i.e., lower energies are required to generate the same images. At first, it was postulated that the isotactic material underwent faster hydrolysis due to the orientation of the polar side group. Further consideration led to the possibility that the stereochemistry controlled the solubility and influenced the development process. Also, the molecular weights and molecular weight distributions are different. Thus, it was concluded that there was definitely a difference in the sensitivity between the two stereoregular polymers; however, further controlled experimentation was required in order to substantiate a explanation.

2) Solution Hydrolysis of Poly(t-butyl methacrylate)

Poly(t-butyl methacrylate) (PTBMA) was easily hydrolyzed in refluxing methanol (bpt.= 65°C) which contained 5-10 weight percent para-toluenesulfonic acid

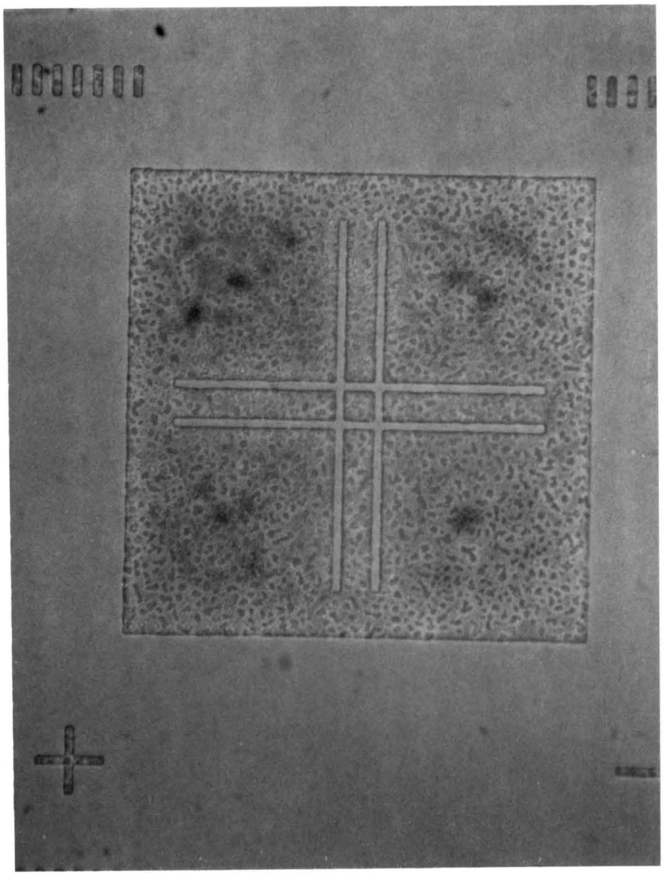


Figure 63: Imaged 100% i-PTBMA (gaps = 1 micron)
2 mj Negative (500X)

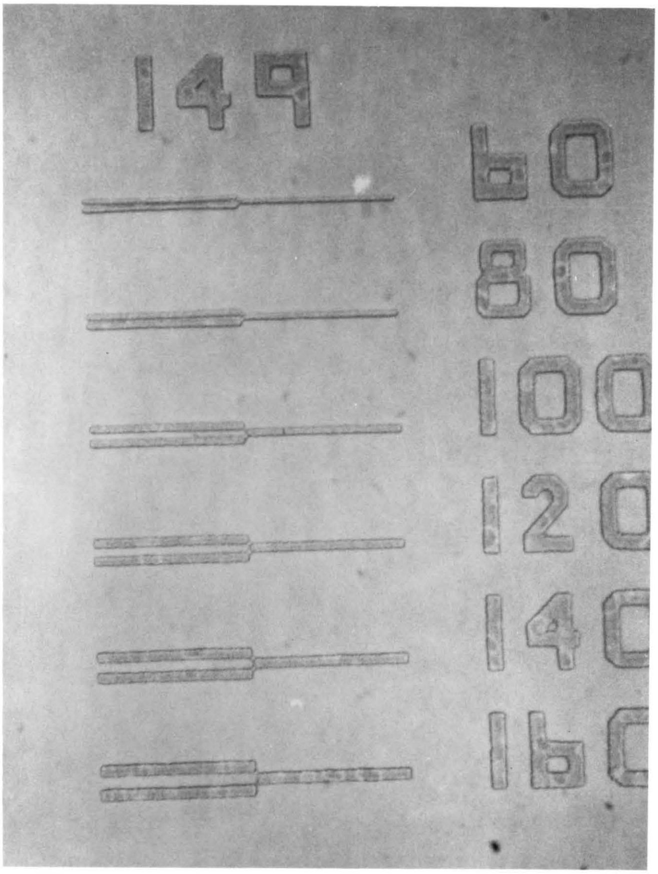


Figure 64: Imaged 100% i-PTBMA (gaps = 1 micron)
2 mj Negative (500X)

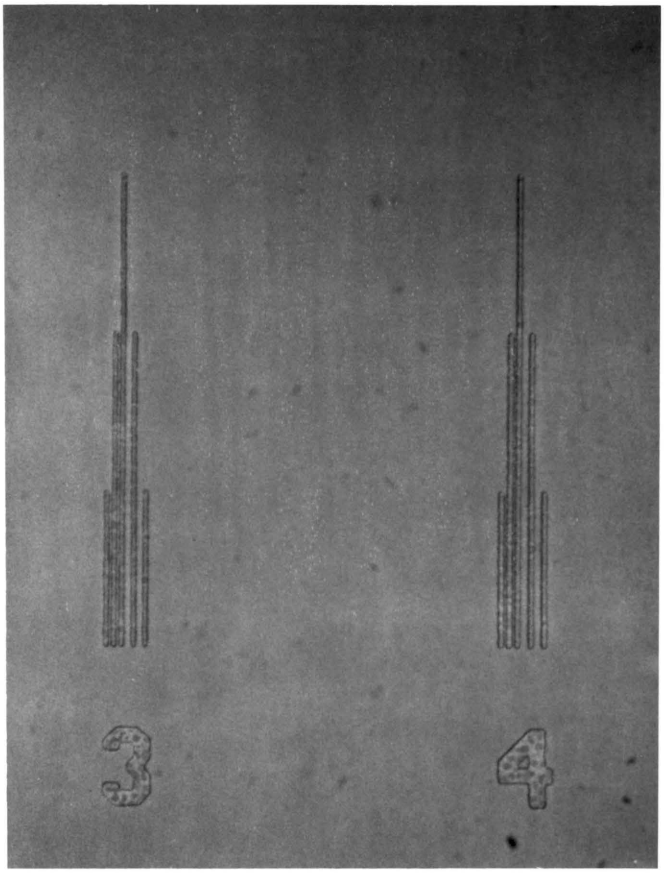


Figure 65: Imaged 100% i-PTBMA (gaps = 1 micron)
2 mj Negative (500X)

(PTSA). FTIR analysis of the product indicated typical poly(methacrylic acid) absorbances. Despite the drastic increase in the polarity of the PTBMA homopolymer upon hydrolysis, the reaction was homogeneous and precipitation did not occur. However, the ultimate goal was to hydrolyze PTBMA containing block copolymers and these materials are generally not soluble in methanol. Thus, toluene was considered as a reaction solvent due to its fairly high boiling point (110°C) and acid stability. It was also presumed that PTSA would be soluble in toluene.

Poly(t-butyl methacrylate) was readily soluble in toluene at 25°C and the reactor was warmed to 80°C. PTSA was added at 80°C and was immediately soluble. After approximately 10 minutes, precipitation occurred due to the enhanced polarity that develops as the acid units are formed. ^{1}H NMR analysis in dimethylsulfoxide-d_6 indicated that 50% conversion occurred. This was achieved by monitoring the disappearance of the t-butyl resonance at 1.36ppm relative to the acidic proton resonance at approximately 12.2ppm. Only an alcohol such as methanol would restore solubility and the reaction was allowed to proceed until complete conversion (8 hrs.).

Thermal analysis of the poly(methacrylic acid) product indicated a large endotherm which begins at 170°C and has a maximum at 200°C. The differential scanning calorimetry thermogram is depicted in Figure 66. Many workers have

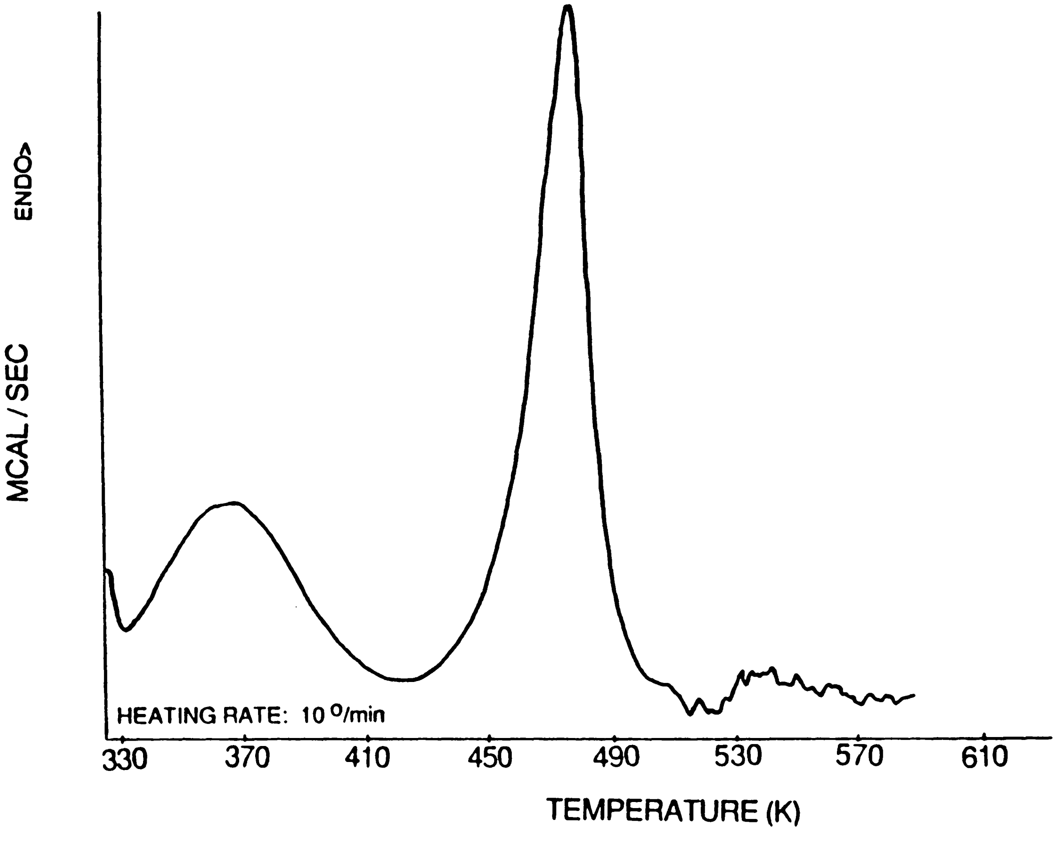


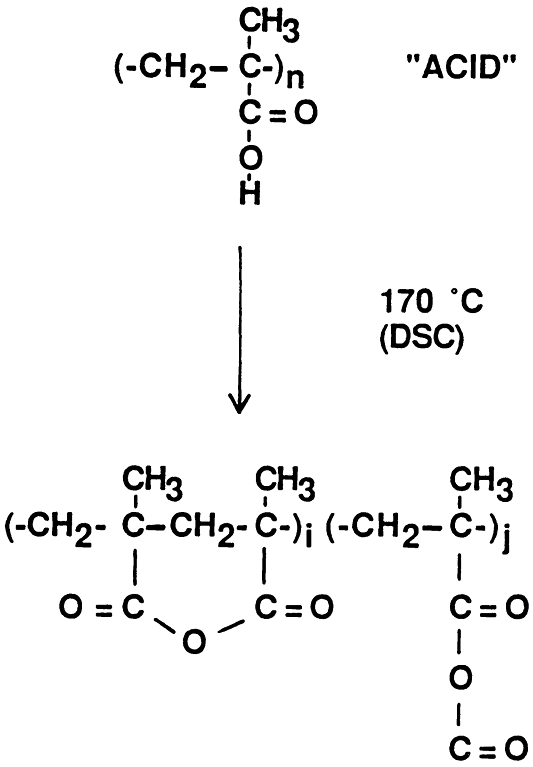
Figure 66: DSC Thermogram of Poly(methacrylic acid) (PMAA) First Run

assigned this endotherm to the glass transition temperature or a crystalline melting point. However, FTIR analysis attributes this behavior to the formation of anhydride linkages as illustrated in Scheme XXXIV. A Tg (159°C) is observed on the second run which agrees with the literature value for poly(methacrylic anhydride). It is presumed that the literature value is for the linear polymer. A cast film of the poly(methacrylic acid) product was placed in a convection oven at 200°C for 10 minutes. Figure 67 shows the FTIR spectrum of the thermally treated film. The COOH and COOR stretches have virtually disappeared and two characteristic anhydride carbonyl stretches appear at approximately 1812 cm-1 and 1760cm-1. It should be noted that the film was rendered insoluble due to the presence of the intermolecular anhydride crosslinks. However, by stirring the film in aqueous THF, a majority of the sample became soluble. FTIR analysis of the soluble material indicated the presence of anhydride and acid functionalities. It is presumed that the intermolecular anhydride linkages were hydrolyzed during the aqueous THF treatment. It is believed that the 6-membered ring, intramolecular anhydride linkages are more thermodynamically stable than the linear crosslinks.

3) Solution Hydrolysis of Block Copolymers Containing Poly(t-butyl methacrylate)

Scheme XXXIV

Anhydride Formation



POLY (METHACRYLIC ANHYDRIDE)

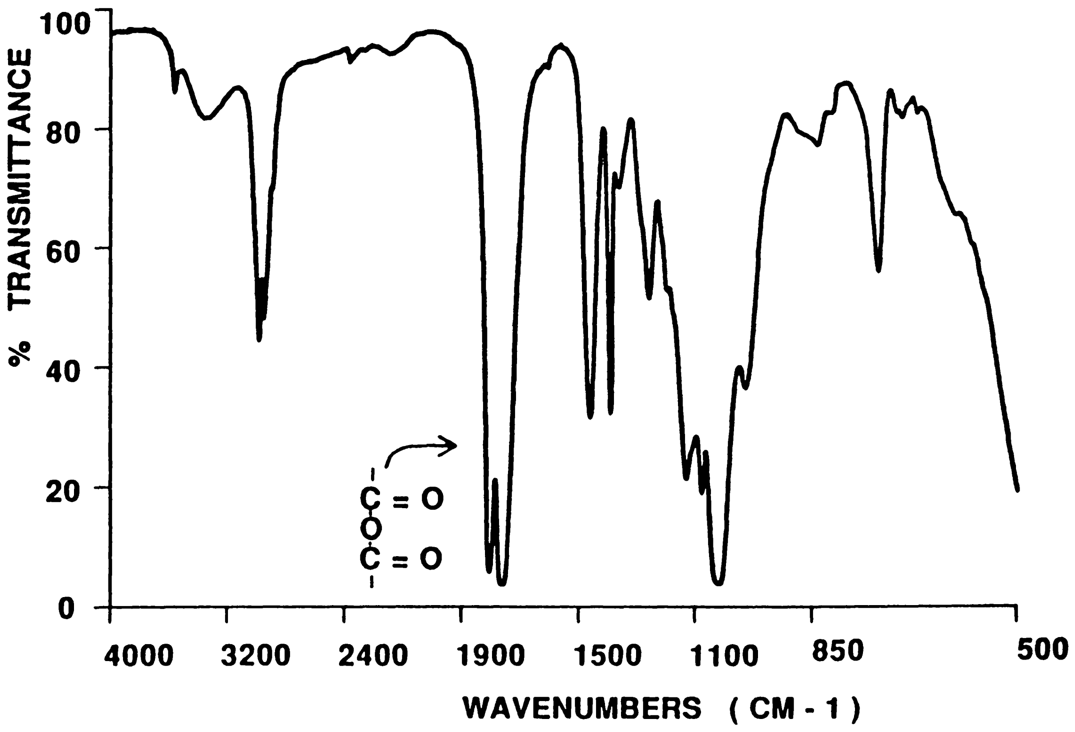


Figure 67: FTIR Spectrum of PMAA Heated at 200°C for 10 Minutes

In most cases, the amount of PTBMA in the copolymer ranged from 2-20% by weight. Most acid- and ion-containing random copolymers that have been discussed in the literature generally contain a maximum of 10-12 mole % of the acidic or ionic functionalities. In addition to remaining consistent with previous investigations by other workers, the selection of this compositional range also eliminated the possibility of precipitation during hydrolysis. The propensity of the polymer to precipitate is a result of the enhanced polarity that develops as the acid units are formed. Consequently, the selection of the hydrolysis solvent is critical because maintaining solubility throughout the hydrolysis reaction leads to higher yields of the corresponding carboxylic acid. However, for this compositional range, toluene was an excellent solvent for all block copolymer hydrolysis reactions.

A variety of substituted styrene and alkyl methacrylate hydrocarbon first blocks have been utilized. t-Butyl styrene (TBS) is particularly interesting due to its high glass transition temperature (145°C) and its low solubility parameter (8.0 $(cal/cm^3)^{1/2}$). This second attribute provides for excellent solubility of the acid-containing polymer in hydrocarbon solvents and for a unique surfactant-like macromolecule. Figure 68 is an FTIR spectrum of a poly(t-butylstyrene-b-methacrylic acid) film obtained after only 90 minutes of hydrolysis at 80°C. The carbonyl band

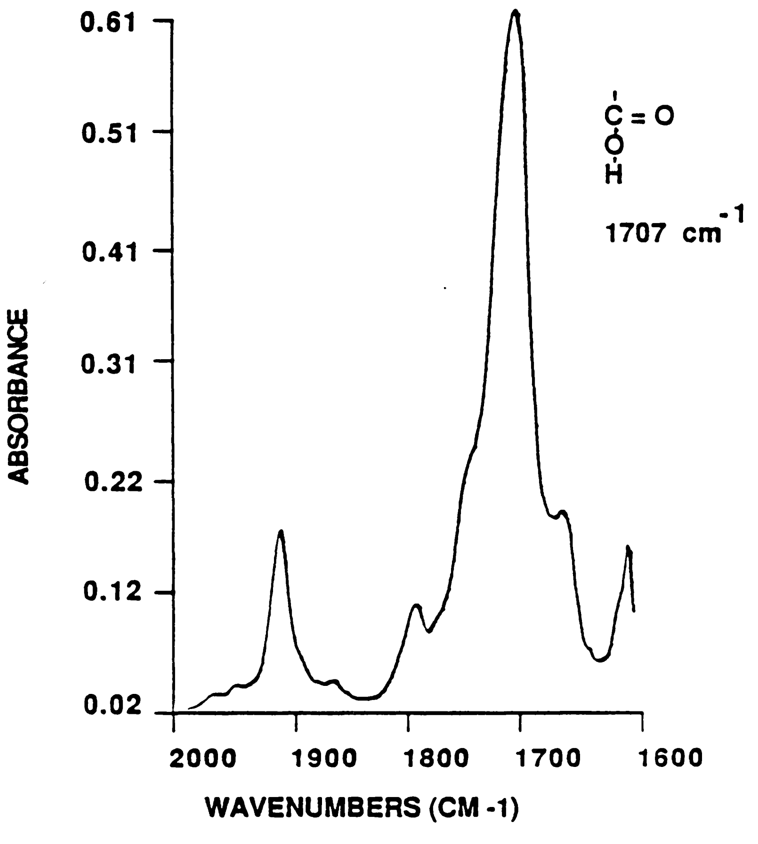


Figure 68: FTIR Spectrum of P(TBS-b-TBMA) Film After Hydrolysis for 90 Minutes (Carbonyl Region)

associated with the TBMA ester (1723cm-1) has nearly disappeared and the corresponding dimeric methacrylic acid carbonyl band has appeared at 1707cm-1. In addition, the broad COOH stretch is also quite evident in the 3200cm-1-2700cm-1 range. Despite this rapid conversion, the reaction is allowed to proceed for 6-8 hours to ensure complete conversion. Conversion versus time studies are necessary to ascertain the required reaction times. The structural integrity of the block copolymers has also been verified by ^{1}H and ^{13}C NMR. In particular, ^{1}H NMR can successfully be used to follow the transformation of poly(methyl methacrylate-b-t-butyl methacrylate) into the corresponding acid containing polymer by following the disappearance of the t-butyl chemical shift at 1.36 ppm (Figure 69). Also, the simultaneous appearance of the acid proton at (approx. 12ppm) can be used to verify conversion. In all cases, conversions are greater than 95% providing for a distinct hydrophobic-hydrophilic molecule.

GPC suggests that the reaction proceeds without degradation of the polymer backbone or simultaneous increase in the molecular weight distribution. Figure 70 illustrates the chromatogram of a P(MMA-b-TBMA) precursor and the final hydrolyzed product. The molecular weight of the product is lower than the precursor, but the difference does not correspond to the loss of each t-butyl group. This is probably due to the simultaneous change in the hydrodynamic

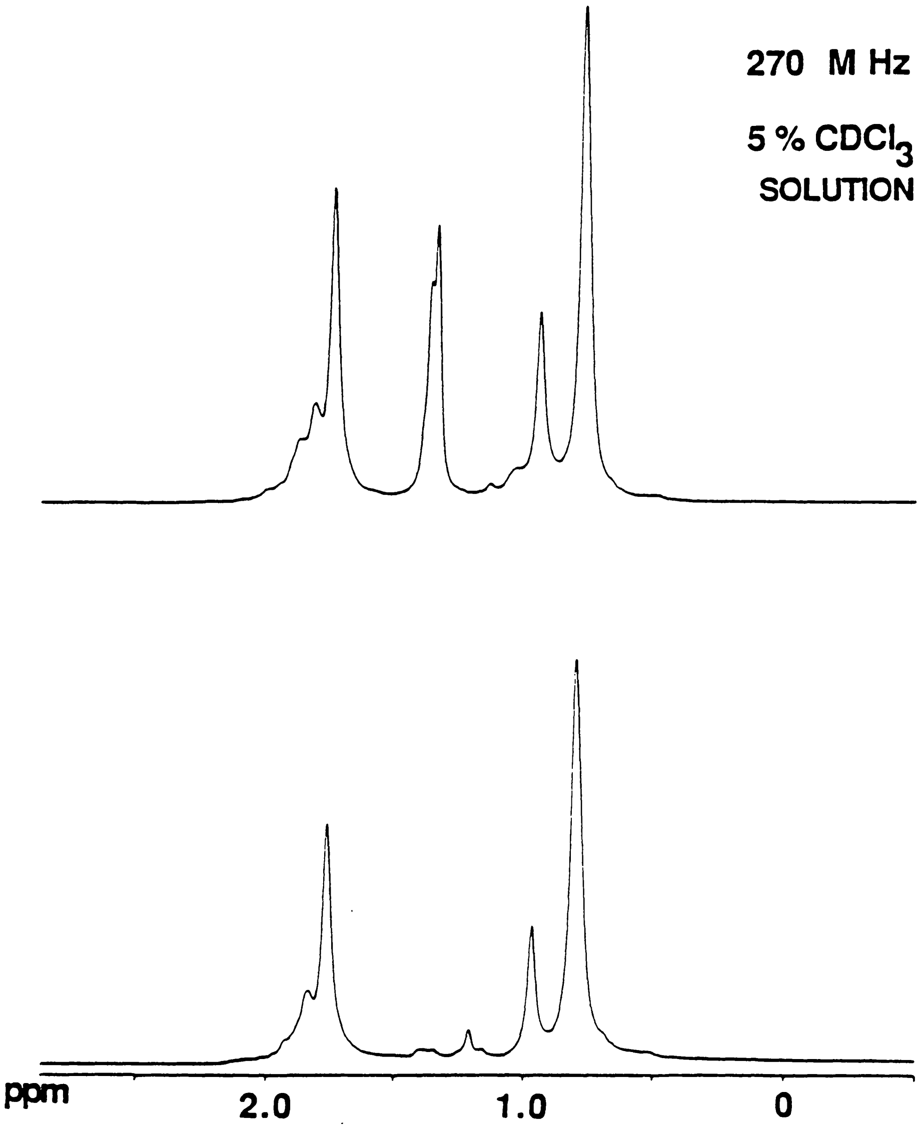


Figure 69: ^1H NMR Spectra of P(MMA-b-TBMA) Precursor (Top) and Hydrolyzed Product (Bottom)

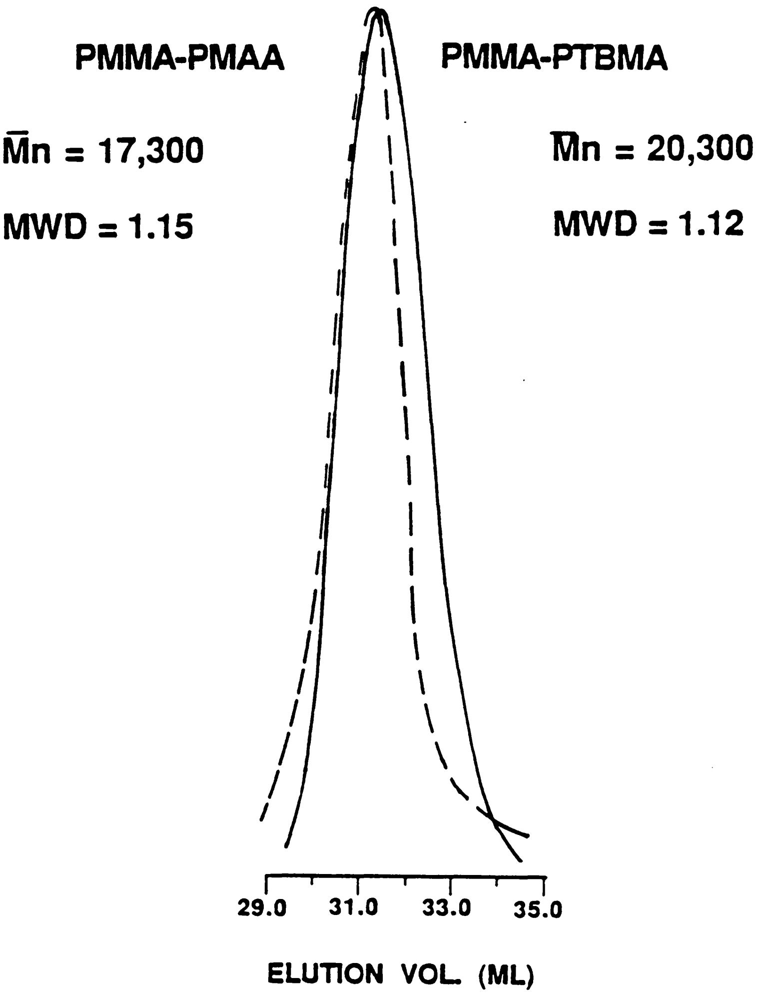


Figure 70: GPC Behavior of P(MMA-b-TBMA) Precursor (dashed) and Hydrolyzed Product (solid)

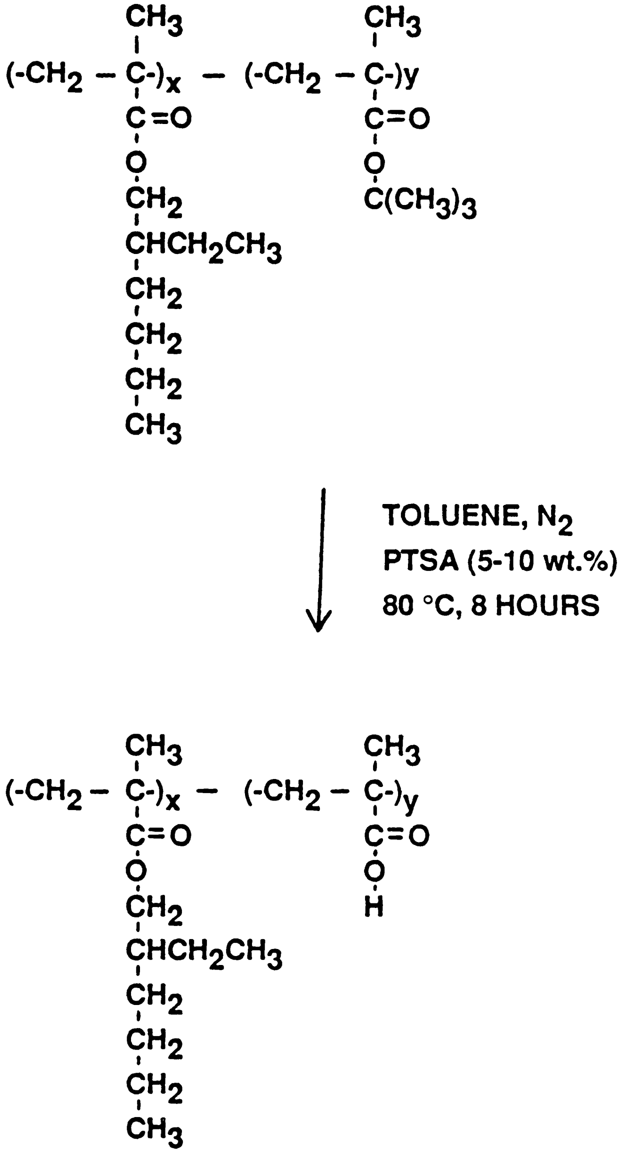
volume of the polymer upon hydrolysis. Osmometry may be a better analytical tool to characterize the shift in molecular weight.

In addition to the use of glassy, unhydrolyzed blocks such as PTBS and PMMA, blocks with lower glass transition temperature have also been investigated. Poly(2-ethylhexyl methacrylate) has a low Tg (-27°C) and is resistent to ester hydrolysis in a fashion similar to PMMA. Thus, the poly(2-ethylhexyl methacrylate-b-t-butyl methacrylate) copolymers (P(EHMA-b-TBMA)) that have been described earlier were hydrolyzed in toluene at 80°C using PTSA (5-10 wt. % compared to PTBMA). Scheme XXXV depicts the chemical structures and chemistry that are involved. For PTBMA compositions less than 13 mole%, the hydrolysis reaction proceeds in a manner similar to the styrene based systems. However, for PTBMA compositions greater than 13 mole%, gelation occurs in toluene even at solids concentrations less than 8 wt./vol. percent. The gelled reaction media can be rendered homogeneous by adding several drops of an alcohol such as methanol.

This phenomenon has been observed for ion-containing polymers with similar ionic concentrations, but gelation due to the introduction of acid groups has not been reported. It is believed that by placing the acid groups in blocks, intermolecular hydrogen bonding and gelation are facilitated. The addition of methanol disturbs the

Scheme XXXV

Hydrolysis of P(EHMA-*b*-TBMA) Copolymers



polymeric hydrogen bonding. However, this behavior was not observed in either the PMMA or PTBS based systems of equal compositions. Thus, it is believed that the 2-ethylhexyl methacrylate block is more soluble in the hydrocarbon medium and results in better aggregation of the insoluble acidic blocks. It is also postulated that alignment of the methacrylate dipoles in the unhydrolyzed block will facilitate aggregation in solution. Viscosity measurements as a function of concentration and temperature would be very interesting and provide for a more indepth understanding of this phenomenon.

Structural characterization of the poly(2-ethylhexyl methacrylate-b-methacrylic acid) copolymers revealed results similar to other systems. High conversions (>95%) of the t-butyl ester to the carboxylic acid were observed by ^{13}C NMR. FTIR techniques could be used to observe the conversion of the ester to the acid for 50:50 diblocks. Figure 71 shows the FTIR spectra of the precursor and the hydrolyzed product. The t-butyl ester at 1723cm-1 shifts to 1702cm-1. In addition, molecular weight distributions remained the same as the precursor and the molecular weight of the hydrolyzed product was lower than the precursor (Table 47).

Thermal analysis of the styrene and PMMA based block acid-containing polymers has shown an endotherm near 200°C which has been associated with anhydride formation. The DSC thermogram for a P(TBS-b-MAA) (10 mole % PMAA) sample is

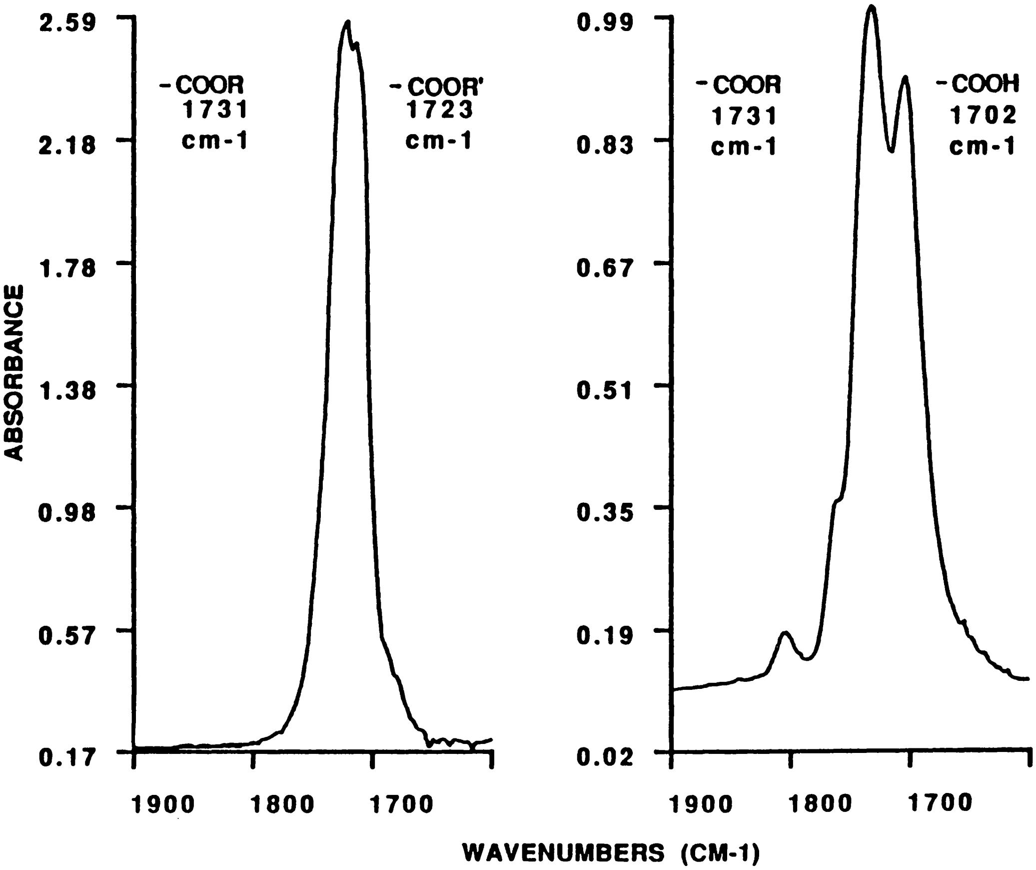


Figure 71: FTIR Carbonyl Region of P(EHMA-b-TBMA) (50:50) Precursor (Left) and Hydrolyzed Product (Right)

shown in Figure 72. The magnitude of the endotherm depends on the mole percentage of poly(methacrylic acid) in the block copolymer. The Tg that was determined on the second run after anhydride formation was unchanged. This may be due to the fact that the crosslinks are located only at the chain end and the mobility of the unhydrolyzed block is unrestricted.

Thermal analysis of the P(EHMA-b-MAA) samples similarly suggests anhydride formation. However, preliminary experiments indicate that the reaction begins to occur at lower temperatures i.e. 145°C compared to 170°C for the block copolymers with glassy, unhydrolyzed blocks. This may be due to the more flexible PEHMA block which facilitates alignment of the acid units to form both inter- and intramolecular anhydride units. Despite anhydride formation in the acid block, the Tg of the system remains the same on the second run.

Surface analysis of the acid-containing block copolymers exhibited behavior different from the precursors. For example, the advancing, water contact angle for a P(MMA-b-MAA) copolymer was 74°, which is the same as the PMMA homopolymer control. However, by withdrawing the water from the surface, the receding contact angle can be measured. This is often called "contact angle hysteresis" and describes any changes in the surface after contact with the dropping liquid. The receding contact angle for the P(MMA-

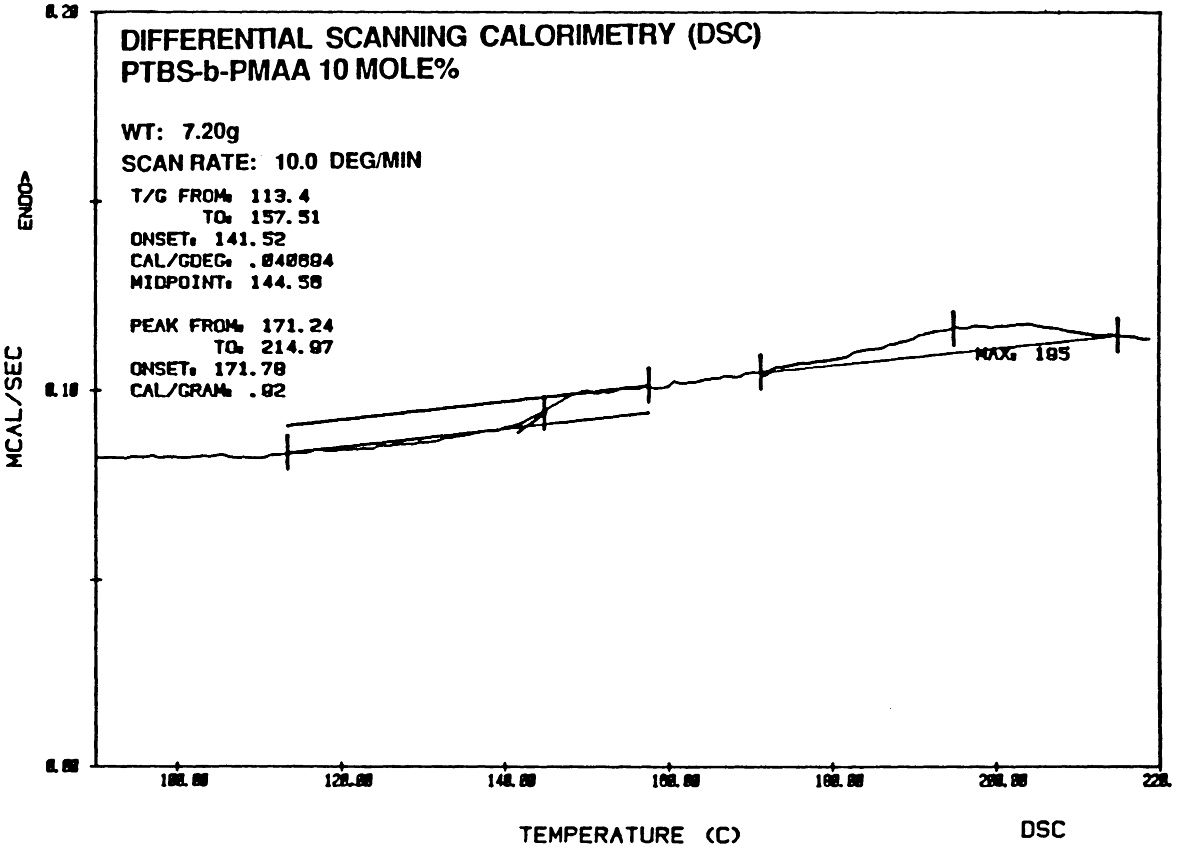


Figure 72: DSC Thermogram of P(TBS-b-MAA) Copolymer
(First Run)

b-MAA) copolymer was 0°; this indicates complete spreading of the water. A possible explanation for this behavior is that the water induces a surface migration of the acid groups in order to maximize hydrogen bonding. Further studies in this area would be interesting. For example, it would be enlightening to see if random acid-containing copolymers exhibit the same behavior.

X-ray Photoelectron Spectroscopy (XPS) was also utilized to observe any influence of casting surface on the surface properties on the acid-containing block copolymers. It was expected that the glass side would have a more hydrophilic surface due to hydrogen bonding of the glass hydroxyl groups with the acid units. Despite this confident postulation, both sides were found to have similar atomic concentrations.

Hydrolysis of poly(isoprene-b-t-butyl methacrylate) block copolymers is not straightforward due to the instability of poly(isoprene) (PI) in an acidic media. Table 48 illustrates the effect of acid on the molecular weight and molecular weight distribution of a PI sample. One can see that the molecular weight is significantly reduced and the distribution broadens with time. Despite the degradation of the PI block in a copolymer, FTIR analysis indicates that hydrolysis of the PTBMA block still occurs. However, in order to prepare well defined acid- and ion-containing polymers, further experimentation is

Table 48

Poly(isoprene) Stability in Hydrolysis (Acidic) Environment

Time (hrs.)	$\bar{M}n$ (GPC)	$\bar{M}w/\bar{M}n$[a]
0	209,000	1.11
0.5	83,700	1.73
1.5	72,900	1.74
3.0	65,700	1.68
6.0	66,300	1.91

[a] Poly(styrene) Standards; all peaks monomodal

required.

Future studies should involve the replacement of PI with poly(butadiene) (PBD). It is believed that PI degrades by protonation of the polymer backbone to form a tertiary carbonium ion which quickly cyclizes. Protonation of PBD to form a secondary carbonium ion would not be as favorable and the stability may be better. Another possibility may be the hydrogenation of the PI blocks prior to hydrolysis. This approach would result in ethylene-propylene blocks rather than poly(diene). The absence of the unsaturated site may eliminate the possibility of backbone protonation. Another approach to circumvent the problem of diene degradation may be to "short-stop" the hydrolysis before degradation occurs. This later idea assumes that the hydrolysis occurs faster than the degradation. Finally, reduced acid catalyst concentrations and lower temperatures may eliminate the problem.

4) Neutralization of Acid-Containing Block Copolymers

The conversion of the poly(methacrylic acid) blocks to metal carboxylates is accomplished by acid-base titration using an appropriate base such as potassium hydroxide. Depending on the acid composition, turbidity may develop. However, the addition of methanol to the neutralization solvent enhances solubility of the ionomer. Phenolphthalein is an excellent indicator for the neutralization in order to avoid excess neutralization reagent in the block ionomer.

The neutralization solvent can be removed by rotoevaporation and the ionomer contains residual phenolphthalein. Generally speaking, the ionomers are not readily soluble in any solvents after removal of the neutralization solvent. Thus, subsequent films must be prepared by compression molding at approximately 50°C above the Tg. However, the styrene based ionomers can be precipitated in a nonsolvent such as methanol/water and filtered.

FTIR is the most convenient method for verifying complete formation of the metal carboxylate. Figure 73 is the FTIR spectrum of poly(t-butylstyrene-b-potassium methacrylate). Residual poly(methacrylic acid) and poly(t-butyl methacrylate) can not be present because the acid carbonyl (1707cm-1) and the ester carbonyl (1723cm-1) are absent. This indirectly indicates that the hydrolysis and neutralization reactions are quantitative. In addition, the metal carboxylate absorbance appears at 1555-1570cm-1. This region is generally void of absorbances and is useful for verification of metal carboxylates. Similar behavior is noted for the all-methacrylic systems. Figure 74 depicts the FTIR spectra of the P(EHMA-b-potassium methacrylate). The ester carbonyl appears at 1731cm-1 and the carboxylate absorbance is present at 1559cm-1. There is no indication of residual poly(methacrylic acid) carbonyl at 1701cm-1.

Thermomechanical analysis of the diblock ion-containing copolymers indicated the formation of a slight rubbery

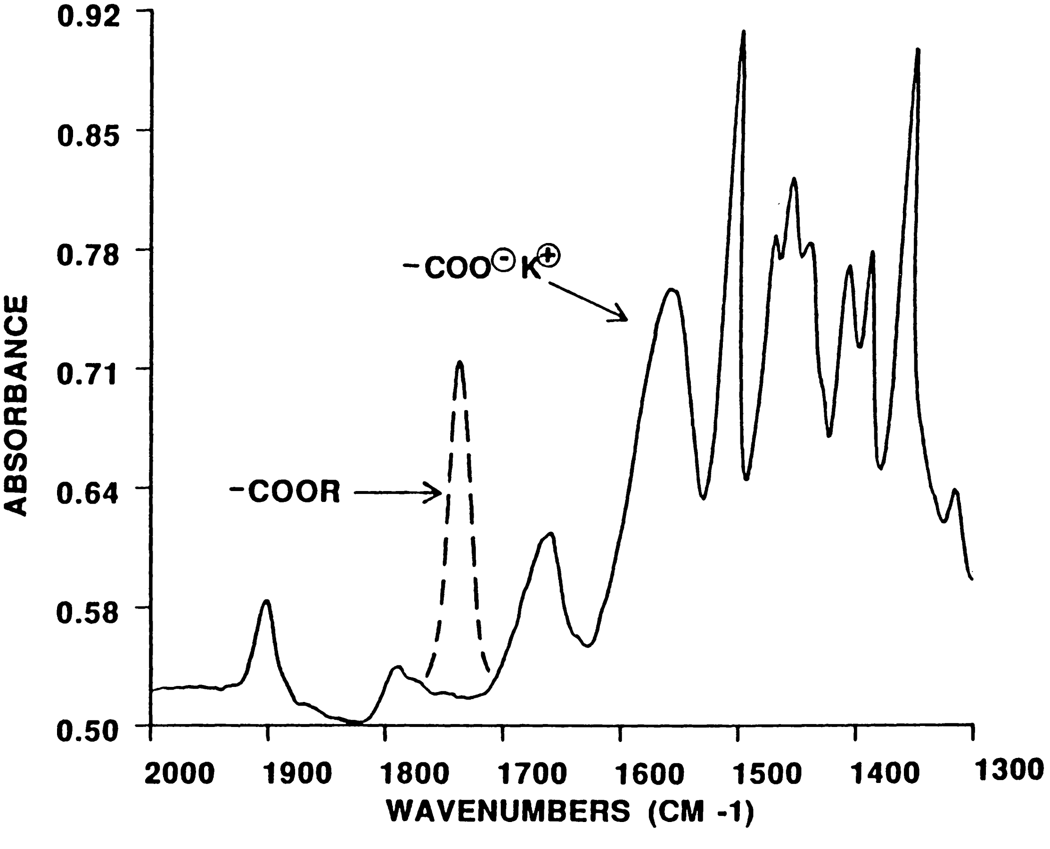


Figure 73: FTIR Spectrum of Poly(t-butylstyrene-b-potassium methacrylate)

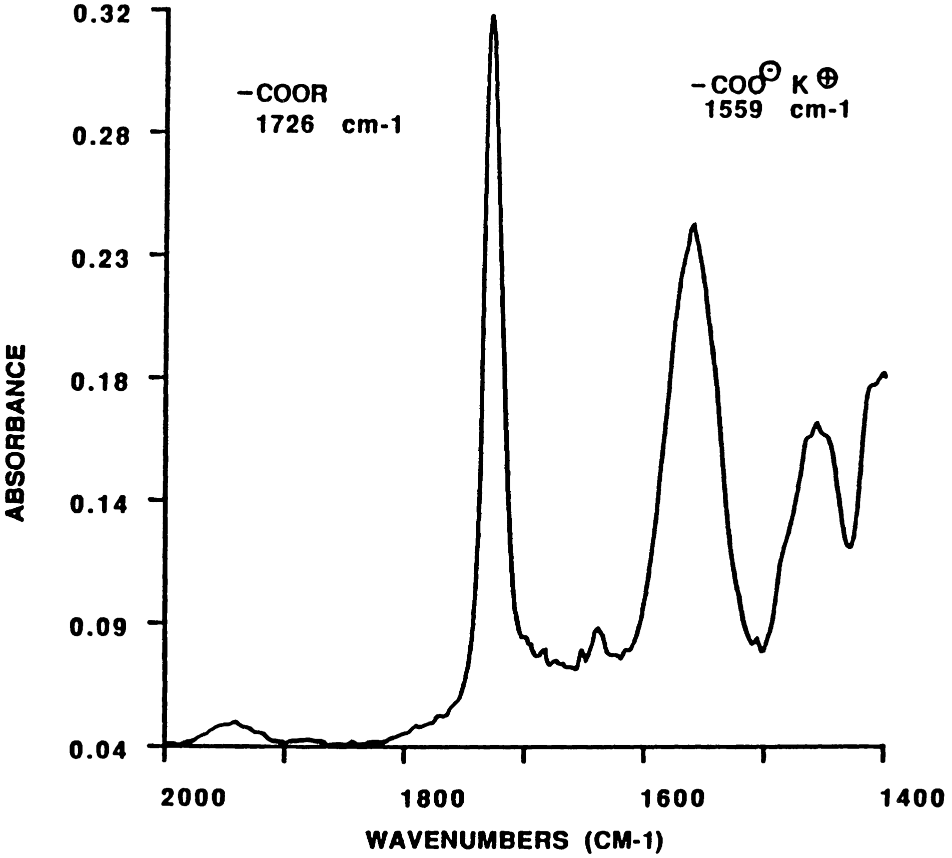


Figure 74: FTIR Spectrum of P(EHMA-b-potassium methacrylate)

plateau which was not present in the precursor. Figure 75 illustrates the TMA behavior for a poly(t-butylstyrene-b-potassium methacrylate) copolymer. This behavior is very similar to random sulfonated ionomers that have been described in the literature previously [299]. It should be noted that these materials are very difficult to dry and the Tg of PTBS is depressed compared to the precursor. Poly(methyl methacrylate-b-potassium methacrylate) copolymers exhibited the formation of a similar rubbery plateau. It is believed that a highly extended (>250°C) plateau should not be formed because the ionic crosslinks are located only at one chain end. Since the PTBMA blocks are quantitatively converted to the metal carboxylate, intervening neutral units are not present. If the hydrolysis and neutralization had been less than quantitative, then random ionomer behavior would be expected. Wilkes and coworkers have observed only short rubbery plateaus for the monofunctional telechelic sulfonated polyisobutylene [300]. The corresponding triblock structures are expected to demonstrate superior mechanical properties. Also, the ion-containing elastomers based on poly(2-ethylhexyl methacrylate) would be more interesting than the brittle, styrene based systems.

In a fashion similar to the acid-containing diblock copolymers, the Tg of the neutral block was not influenced by the presence of the ionic groups in a block. This is

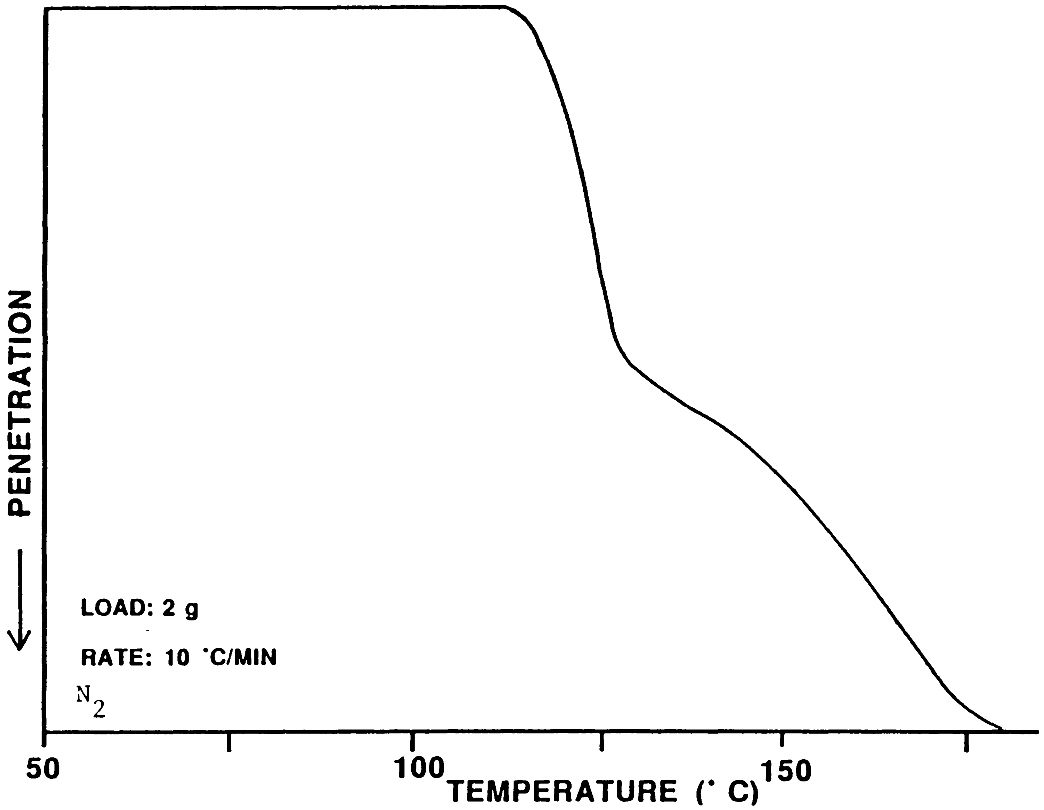


Figure 75: TMA Behavior for Poly(t-butylstyrene -b-potassium methacrylate) Ionomer

similar to the thermal properties that were witnessed for the corresponding acid diblocks. Eisenberg has also reported recently that the Tg of quaternized styrene-vinyl pyridine block ionomers was relatively unaffected by the composition of the sample [301]. The behavior of the block ionomers is different than corresponding random materials. Eisenberg has also mentioned that the block ionomers exhibit very different aggregation morphologies and a domain which is intermediate between a cluster and a multiplet has been proposed [302]. This new domain has been termed a "supermultiplet" by Eisenberg.

5) Esterification of Acid-Containing Block Copolymers

The acid-containing block copolymers are readily soluble in long chain alcohols such as dodecanol and high yields of esterification are possible. Figure 76 depicts the FTIR spectrum of the partially esterified PTBS-b-PMAA (10 mole % acid) copolymer. The new ester carbonyl is evident at 1731 cm-1 and residual acid carbonyl (1702cm-1) remains in the copolymer. These preliminary studies indicate that a wide range of alkyl methacrylate block copolymers could be prepared by esterification. It should be noted that the water resulting from esterification was removed by distillation. Future efforts should involve the development of efficient techniques to remove the water that results from esterification. This may be accomplished by azeotroping the water with toluene or conducting the

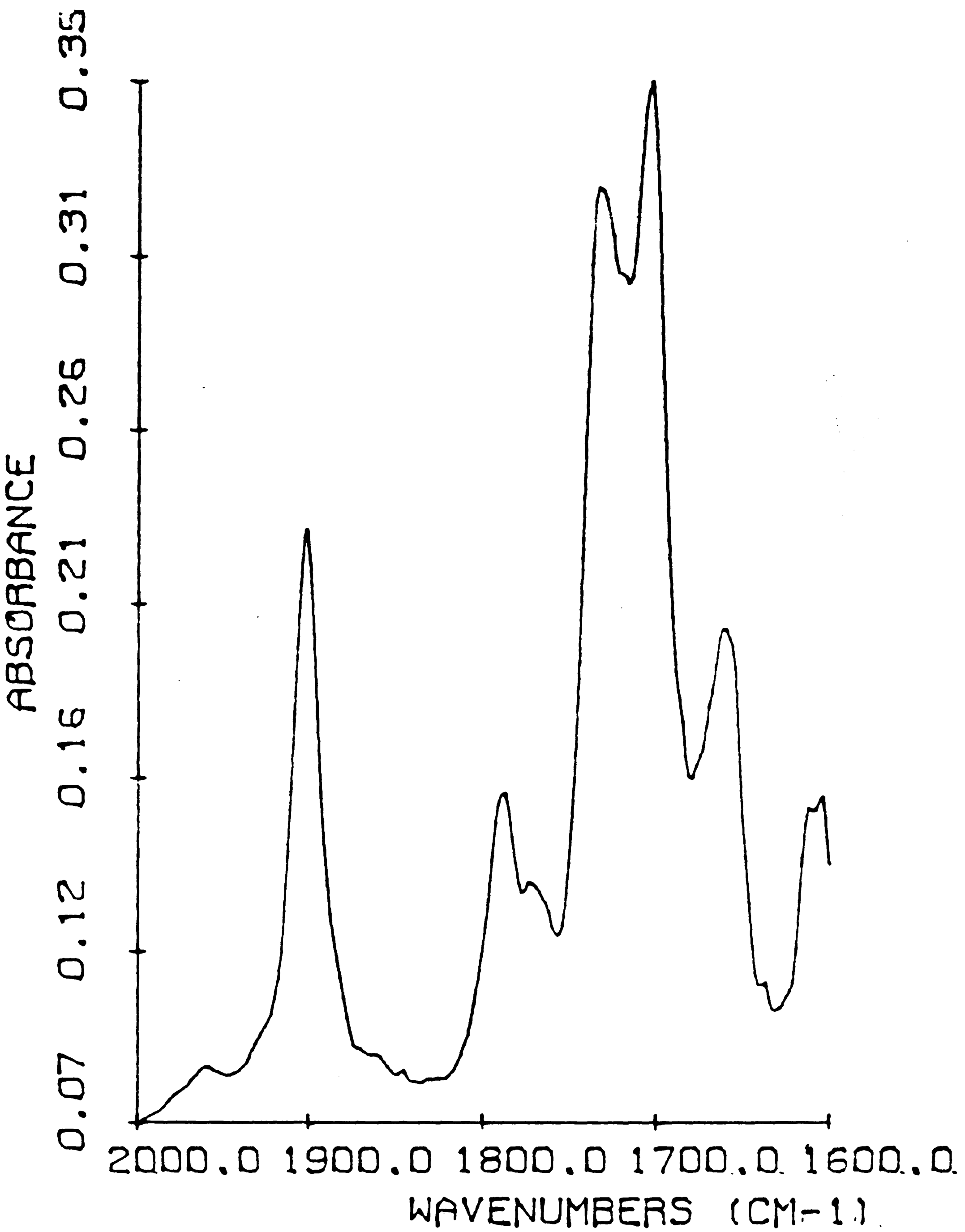


Figure 76: FTIR Spectrum of P(TBS-b-MAA) Esterified with Dodecanol

reaction in the presence of molecular sieves.

V. CONCLUSIONS

The two major obstacles which have impeded the synthetic development of poly(alkyl methacrylates) by anionic techniques are the presence of protic impurities in most commercial grades of monomer and inherent side reactions associated with the ester carbonyl. However, by utilizing trialkyl aluminum/dialkyl aluminum hydride purification reagents, poly(alkyl methacrylates) have been prepared with narrow molecular weight distributions (<1.25) and predictable molecular weights (>10^5 g/mole). The availability of ultrapure, anionic-grade monomers also permits the investigation of polymerization solvent polarity, polymerization temperature, initiator structure, and ester alkyl group size. Any subtle changes in the polymer properties were safely attributed to the polymerization chemistry and not to side reactions associated with monomer impurities.

Classical anionic polymerizations of methyl methacrylate have required low temperatures (-78°C), polar solvents, and hindered initiators in order to obtain "living" mechanisms. However, these synthetic constraints were eliminated by employing branched alkyl methacrylates such as t-butyl and isopropyl methacrylate. Deactivation of the ester carbonyl by steric and electronic factors increases the stability of the propagating lithium enolate and permits facile polymerizations at room temperature. In addition, termination-free polymerizations in nonpolar solvents were also achieved. Thus, the ester alkyl group defines the ease of polymerization of alkyl methacrylates with anionic initiators.

A wide variety of homopolymer properties were obtained by the alteration of several synthetic variables. In particular, thermoplastic, semi-crystalline and elastomeric poly(alkyl methacrylates) have been prepared by variations of the polymerization solvent and ester alkyl group. For example, the Tg of poly(ethyl methacrylate) ranged from 6°C to 86°C by changing the polymerization solvent polarity. Thermal stabilities of the homopolymers were also dictated by the mode of polymerization, e.g. PMMA which was prepared in polar solvents with anionic initiators at -78°C has a thermal stability 140°C greater than PMMA prepared by free radical initiators. Consequently, the anionic polymerization of alkyl methacrylates results in very different thermal and mechanical properties than the corresponding free radically prepared materials.

Anionic techniques also provide for the synthesis of well defined block copolymers. Styrene-methacrylic, diene-methacrylic and all-methacrylic block copolymers were prepared in a controlled manner. Diene-methacrylate block copolymers are especially intriguing due to the combination of a very nonpolar phase (polydiene) and a moderately polar (poly(alkyl methacrylate)) phase. In fact, two phase morphologies were observed for these systems. All-methacrylic block copolymers are novel materials and softer blocks such as poly(2-ethylhexyl methacrylate) were combined with glassy poly(t-butyl methacrylate) blocks. All-methacrylic thermoplastic elastomers may have many unique advantages over classical diene-styrene based systems.

In addition to the interesting properties of the block copolymers, these materials also served as polymers for subsequent modification reactions. A facile hydrolysis route involving poly(t-butyl methacrylate) was demonstrated. In addition to observing the potential morphology change upon hydrolysis, the resulting acid containing block copolymers have unique solution properties due to their surfactant-like architecture. The placement of acid groups in blocks allows for interesting comparisons to classical random copolymers that have been extensively discussed in the literature. For example, chemical reactions on block copolymers proceeded at different rates than the corresponding random copolymers. One can also imagine that the stereochemistry of the polymer will influence the kinetics of subsequent polymer modification reactions. The modified diblocks may have significant potential for such applications as surfactants, elastomers, viscosity enhancement reagents or adhesives.

Similar investigations have been conducted on the ion containing block copolymers that were prepared by complete neutralization of the acidic blocks. The effects of ion placement on the polymer properties were also ascertained using these model systems. Significant differences were noted for the block ionomers compared to the random systems. The preparation of triblock ion containing block polymers will compliment the telechelic sulfonate and carboxylate ionomers previously described in the literature. The preparation of block anionic ionomers is a fruitful area of research and will contribute significantly to the understanding of ionomer morphology and physical properties.

VI. SUGGESTED FUTURE STUDIES

An attempt has been made throughout the text to indicate the future direction of the various aspects of this research project. Detailed descriptions of future experiments have been described based on previous findings, awareness of the literature and chemical intuition. The major areas of research that deserve significant attention are listed below:

(1) Continued studies of the effects of ester alkyl group size on the ease of anionic polymerization of alkyl methacrylates. In particular, creative preparation of monomers with disubstitution at the carbon adjacent to the ester oxygen.

(2) Longer ester ($>C_6$) alkyl methacrylate monomer polymerizations may lead to novel physical properties. Indepth studies of the effect of the long ester alkyl group on the thermal, stereochemical, and mechanical properties of the homopolymers should be conducted.

(3) Development of a practical column technique employing aluminum reagents would eliminate monomer distillation.

(4) All-methacrylic thermoplastic elastomers would be novel and possess interesting physical properties. Special attention should be placed on introducing ionic groups via t-butyl methacrylate hydrolysis in the terminal blocks.

(5) Scattering and rheological analysis of the acid and ion containing block copolymers. Interesting comparisons could be made with the corresponding random systems.

(6) Continued diene-methacrylate synthesis is important especially the preparation of triblock copolymers. In addition, by employing TBMA hydrolysis ion-containing elastomers could be synthesized.

(7) Blending of elastomeric poly(alkyl methacrylates) with more brittle materials such as PMMA. Compatibilization may be required by the incorporation of the corresponding block copolymer.

(8) Study the effects of polymer stereochemistry on hydrolysis and esterification reactions. In addition, the role of polymer architecture, i.e., block versus random on the reaction kinetics should be investigated.

(9) Membrane applications of various tactic poly(alkyl methacrylates) and block copolymers especially PTBMA.

The anionic polymerization of alkyl methacrylates is a very fruitful area of research. The preparation of novel alkyl methacrylate block copolymers has remained relatively unexplored.

VII. REFERENCES

1. Chemical Purchasing, 13, November 2, 1983.
2. B. B. Kine and R. W. Novak, Encyclopedia of Poly. Sci. and Tech., 3rd Edition, 1, 235(1985).
3. E. H. Riddle, "Monomeric Acrylic Esters," Reinhold Pub. Co., New York, 1954.
4. A. S. Wood, Mod. Plast., 52, 40(1975).
5. R. Martino, Mod. Plast., 51, 62(1974).
6. Encycl. Chem. Tech., 3rd Edition, Wiley and Sons, New York, 15, 358(1981).
7. Chem. Week, 63, October 14, 1981.
8. Chem. and Eng. News, 25, February 4, 1985.
9. Chem. and Eng. News, 24, March 5, 1984.
10. "Storage and Handling of Acrylic and Methacrylic Esters and Acids," Bulletin CM-17, Rohm and Hass Co., 1975.
11. Modern Plastics, October, 92, 1985.
12. M. J. Ballard, D. H. Napper, R. G. Gilbert and D. F. Sangster, J. Poly. Sci.: Polymer Chem., 24, 1027(1986).
13. K. Hatada, T. Kitayama and E. Masuda, Polymer J., 18(5), 395(1986).
14. E. Giannetti, R. Mazzocchi, L. Fiore and F. Visani, J. Poly. Sci.: Polymer Chem., 24, 2517(1986).
15. P. Cacioli, G. Moad, E. Rizzardo, A. K. Serelis and D. H. Solomon, Polymer Bulletin, 11, 325(1984).
16. T. Kashiwagi, A. Inaba J. E. Brown, E. Masuda, T. Kitayama and K. Hatada, Macromolecules, 19, 2160(1986).
17. E. Calahorra, M. Cortazar and G. M. Guzman, J. Poly. Sci.: Poly. Letters Ed., 23, 257(1985).
18. K. Hatada, Y. Okamoto, K. Ohta and H. Yuki, J. Poly. Sci.: Poly. Lett. Ed., 14, 51(1976).

19. K. Hatada, Y. Okamoto, T. Kitayama, K. Ohta, Y. Umemura and H. Yuke, Makromol. Chem., 178, 617(1977).

20. J. L. Koenig, "Chemical Microstructure of Polymer Chains," John Wiley and Sons, New York, 1980.

21. R. C. Ferguson and D. W. Ovenall, Macromolecules, 20(6), 1245(1987).

22. F. A. Bovey, J. Polym. Sci., 46, 59(1960).

23. H. Yuki and K. Hatada, Advances in Polym. Sci., 31, 1(1979).

24. T. Tsuruta, T. Makimoto and H. Kanai, J. Macromol. Sci., 1, 31(1966).

25. F. E. Karasz and W. J. MacKnight, Macromolecules, 1, 537(1968).

26. Encyclo. Chem. Tech., 379 .

27. Ibid, 380 .

28. K. Matsuzaki, T. Kanai, C. Ichijo and M. Yuzawa, Makromol. Chem., 185, 2291(1984).

29. R. Buter, Y. Y. Tan and G. Challa, J. Polym. Sci., Polym. Chem. Ed., 11, 1003(1973).

30. T. Tsuruta, T. Makimoto and H. Kanai, J. Macromol. Sci., 1, 36(1966).

31. W. J. Copper, P. D. Krasicky and F. Rodriquez, J. Applied Polym. Sci., 31, 65(1986).

32. X. Zhongde, N. Hadjichristidis and L. J. Fetters, Macromolecules, 17, 2303(1984).

33. I. Katime and M. T. Garay, Polymer Comm., 27, 74(1986).

34. F. D. Blum, B. Durairaj and A. S. Padmanabhan, Macromolecules, 17, 2837(1984).

35. B. C. Simionescu, S. Ioan, A. Chiriac and C. I. Simionescu, Polymer Bull., 17, 439(1987).

36. J. M. O'Reilly, D. M. Teegarden and G. D. Wignall, Macromolecules, 18, 2747(1985).

37. B. Y. Li, D. Z. Jiang, G. Fytas and C. H. Wang, Macromolecules, 19, 778(1986).

38. J. A. Shetler, J. Polym. Sci., 81, 209(1963).

39. S. Bywater and P. M. Toporowski, Polymer, 13, 94(1972).

40. J. Heijboar, Br. Polym. J., 1, 3(1969).

41. W. H. Brendley, Jr., Paint Varnish Prod., 63, 19(1973).

42. C. E. Rehberg and C. H. Fisher, Ind. Eng. Chem., 40, 1429(1948).

43. P. E. M. Allen, S. Hagias, G. P. Simon, E. H. Williams and D. R. G. Williams, Polymer Bull., 15, 359(1986).

44. G. Cowperthwaite, J. J. Foy and M. A. Malloy, "Biomedical and Dental Applications of Polymers," C. G. Gebelen and F. F. Koblitz, Plenum, New York, 379(1981).

45. G. C. Martin, R. K. Mehta and S. G. Lott, Polymer Preprints, 22(2), 319(1981).

46. C. C. Chen, J. Shen and J. A. Sauer, Polymer, 26, 89(1985).

47. E. S. Sanders and W. J. Koros, J. Poly. Sci.: Poly. Physics Ed., 24, 175(1986).

48. Encyclo. Chem. Tech., 383 .

49. H. A. Bruson, U.S. Patent, 2,091,627, Rohm and Haas Co., Aug. 31, 1937.

50. W. E. Goode, F. H. Owens and W. L. Myers, J. Polym. Sci., 47, 75(1960).

51. D. L. Glusker, E. Stiles and B. Yoncoskie, J. Polym. Sci., 49, 297(1961).

52. N. Kawabata and T. Tsuruta, Makromol. Chem., 86, 231(1965).

53. H. Ailhaud, Y. Gallot and A. Skoulios, Makromol. Chem., 140, 179(1970).

54. D. M. Wiles and S. Bywater, Trans. Faraday Soc., 61, 150(1965).

55. R. Kraft, A. H. E. Muller, H. Hocker and G. V. Schulz, Macromolecules, 11, 1093(1978).

56. F. Wenger, Chem. Ind. (London), 1094(1959).

57. W. E. Goode, F. H. Owens, R. P. Fellman, W. H. Synder and J. E. Moore, J. Polym. Sci., 46, 317(1960).

58. A. Nishioka, H. Watanabe, K. Abe and I. Sono, J. Polym. Sci., 48, 241(1960).

59. P. E. M. Allen and D. R. G. Williams, Ind. Eng. Chem. Prod. Res. Dev., 24(2), 334(1985).

60. P. Pino and U. W. Suter, Polymer, 17, 977(1976).

61. K. Ute, T. Kitayama and K. Hatada, Polymer J., 18(3), 249(1986).

62. K. Hatada, K. Ute, K. Tanaka, M. Imanari and N. Fujii, Polymer J., 19(4), 425(1987).

63. K. Hatada, K. Ute, K. Tanaka, T. Kitayama and Y. Okamoto, Polymer J., 17(8), 977(1985).

64. S. Freireich and A. Zilka, J. Macromol. Sci.: Chem, A6, 1383(1972).

65. A. H. E. Müller, V. Warzelhan, H. Hocker, G. Lohr and G. V. Schulz, IUPAC International Symp. on Macromolecules Preprints, 31, 1977.

66. J. Trevkoval, J. Polym. Sci., A-1, 9, 2575(1971).

67. W. Fowells, C. Schuerch, F. A. Bovey and F. P. Hood, J. Am. Chem. Soc., 89, 1396(1967).

68. A. H. E. Muller, H. Hocker and G. V. Schulz, Macromolecules, 10, 1086(1977).

69. H. Schreiber, Makromol. Chem., 36, 86(1960).

70. K. Hatada, T. Kitayama, K. Fumikawa, K. Ohta and H. Yuki, in "Anionic Polymerization: Kinetics, Mechanisms and Synthesis," J. E. McGrath Ed., ACS Symposium Series 166, 327, 1981.

71. B. C. Anderson, G. D. Andrews, P. Arthur, Jr., H. W. Jacobson, L. R. Melby, A. F. Playtis and W. H. Sharkey, Macromolecules, 14, 1599(1981).

72. R. Fayt, R. Forte, C. Jacobs, R. Jerome, T. Ouhadi, Ph. Teyssie, and S. K. Varshney, Macromolecules 20(6), 1442(1987).

73. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. Rajanbabu, J. Am. Chem. Soc., 105, 5706(1983).

74. R. W. Hertler, D. Y. Sogah, O. W. Webster and B. M. Trost, Macromolecules, 17, 1415(1984).

75. D. Y. Sogah, W. R. Hertler, O. W. Webster and G. M. Cohen, Macromolecules, 20, 1473(1987).

76. T. Tazaki and T. Otsu, Polymer Bull., 17, 127(1987).

77. T. Otsu, A. Matsumoto and T. Tazaki, Polymer Bull., 17, 323(1987).

78. T. Otsu and T. Tazaki, Polymer Bull., 16, 277(1986).

79. T. G. Fox, B. G. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell and J. D. Stroupe, J. Am. Chem. Soc., 80, 1768(1958).

80. A. H. E. Müller, in "Anionic Polymerization: Kinetics, Mechanisms and Synthesis," J. E. McGrath Ed., ACS Symposium Series 166, 441, 1981.

81. H. Yuki, K. Hatada, K. Ohta and Y. Okamoto, J. Macromol. Sci., Chem., A9, 983(1975).

82. J. F. Rabek, "Experimental Methods in Polymer Chemistry," Wiley and Sons, New York, 534, 1980.

83. E. V. Thompson, J. Polym. Sci., A-2, 4, 199(1966).

84. S. Bywater and P. M. Toporowski, Polymer, 13, 94(1972).

85. R. Jenkins and R. S. Porter, Polymer, 23, 105(1982).

86. P. E. M. Allen, D. M. Host, V. T. Truong and D. R. G. Williams, Eur. Polym. J., 21(7), 603(1985).

87. E. L. Feitsma, A. de Boer and G. Challa, Polymer, 16, 515(1975).

88. I. Katime, J. R. Quintana, R. Valenciano and C. Strazielle, Polymer, 27, 742(1986).

89. F. Bosscher, D. Keekstra and G. Challa, Polymer, 22, 124(1981).

90. A. M. Liquori, G. Anzuino, V. M. Corro, M. d'Alazni, P. de Santis and M. Savino, Nature(London), 206, 358(1965).

91. M. A. Doherty and T. E. Hogen-Esch, Polymer Preprints, 25(2), 5(1984).

92. G. Odian, "Principles of Polymerization," 2nd ed., John Wiley and Sons, Chapter 6, 1981.

93. B. B Kine and R. W. Novak, 269 .

94. H. Yuki, K. Hatada, K. Ohta and Y. Okamoto, J. Macromol. Sci.-Chem., A9, 995(1975).

95. M. F. Llauro-Darricades, C. Pichot, J. Guillot, L. Rios, M. A. Cruz and C. Guzman, Polymer, 27, 889(1986).

96. J. E. McGrath, Pure and Applied Chem., 55(10), 1573(1983).

97. A. Noshay and J. E. McGrath, "Block Copolymers: Overview and Critical Survey," Academic Press, 1977.

98. D. C. Allport and W. H. Janes, "Block Copolymers," Halstead Press, New York, 1972.

99. C. J. C. Edwards, R. W. Richards and R. F. T. Stepto, Polymer, 27, 643(1986).

100. H. R. Jerome and PH. Teyssie, J. Appl. Polym. Sci., 26, 343(1981).

101. M. Morton, "Anionic Polymerization: Principles and Practice," Academic Press, Chapter 9, 1983.

102. I. Goodman, Editor, "Developments in Block Copolymers," Appl. Sci. Pub., 1983.

103. S. L. Aggarwal, "Block Copolymers," Plenum Press, New York, 1970.

104. D. Freyss, P. Rempp and H. Benoit, J. Polym. Sci., Letters, 2, 217(1964).

105. A. Dondos, P. Rempp and H. Benoit, Makromol. Chem., 130, 233(1969).

106. D. E. Bugner, Polymer Preprints, 27(2), 57(1986).

107. H. Ailhaud, Y. Gallot and A. Skoulios, Makromol. Chem., 140, 179(1970).

108. P. K. Seow, J. P. Lingelser and Y. Gallot, Makromol. Chem. 178, 107(1977).

109. Y. Tsukahara, A. Izumi, T. Hashimoto and H. Kawai, Polymer J., 14(11), 887(1982).

110. B. C. Anderson, G. D. Andrews, P. Arthur, H. W. Jacobson, L. R. Melly, A. J. Playtis and W. H. Sharkey, Macromolecules, 14, 1599(1981).

111. T. Q. Nguyen and H. H. Kausch, Macromol. Chem., Rapid Commun., 6, 391(1985).

112. H. A. J Schepers, B. C. Roest and N. V. Stamicarbon, Ger. Patent, DE 2231993, 1973.

113. C. Goett and J. Journe, Rev. Gen. Caoutch. Plast., 53(558), 47(1976).

114. J. Rossi and B. Gallot, Makromol. Chem., 177(9), 2801(1976).

115. R. E. Cohen and F. S. Bates, Gov. Rep. Announce. Index (U. S.), Report TR-4, Order No. AD-A0787731, Avail. NTIS, 80(8), 1317(1980).

116. T. Suzuki, Y. Murakami, O. Yamada and Y. Takegami, J. Macromol. Sci., Chem., A18(5), 817(1982).

117. T. Suzuki, Y. Murakami and Y. Takegami, Polymer J., 12(3), 183(1980).

118. P. K. Seow, Y. Gallot and A. Skoulios, Makromol. Chem., 176(11), 3153(1975).

119. P. C. Juliano, D. E. Floryan, R. W. Hand and D. D. Karttunen, "Block Graft Copolymerization," Proc. Sagamore Army Mater. Res. Conf., 19th, 61, 1973.

120. Y. Morishima, T, Hashimoto, Y. Itoh, M. Kamachi and S. Nozakura, Makromol. Chem., Rapid Commun., 2(8), 507(1981).

121. M. Kamachi, M. Kurihara and J. K. Stille, Macromolecules, 5(2), 161(1972).

122. L. H. Tung, G. Y. S. Lo and J. A. Griggs, J. Polym. Sci., Poly. Chem., 23, 1551(1985).

123. A. Echte, F. Haaf and J. Hambrecht, Angew. Chem. Int. Ed. Eng., 20, 344(1981).

124. L. H. Sperling, Editor, "Recent Advances in Polymer Blends, Grafts and Blocks," Plenum Press, New York, 1974.

125. K. Hatada, T. Kitayama, S. Sasaki, Y. Okamoto, E. Masuda, Y. Kobayashi, A. Nakajima, H. Aritome and S. Namba, Ind. Eng. Chem. Prod. Res. Dev., 25(2), 141(19860.

126. I. Akcelrud and A. S. Gomes, J. Polym. ci., Part A: Polymer Chem. Ed., 24, 2831(1986).

127. S. Nakahama, Polymer Preprints, 27(1), 194(1986).

128. R. Milkovich, in "Anionic Polymerization: Kinetics, Mechanisms and Synthesis," J. E. McGrath, Ed., ACS Symposium Series 166, 41, 1981.

129. R. Milkovich and M. T. Chiang, U. S. Patent 3,842,050, CPC, 1974.

130. G. O. Schultz and R. Milkovich, J. Appl. Polym. Sci., 27(12), 4773(1982).

131. P. Rempp, P. Lutz, P. Masson and E. Franta, Makromol. Chem., Suppl., 8, 3(1984).

132. P. Ragunath, P. Lutz, J. Ph. Lamps, P. Masson and P. Rempp, Polymer Bull., 15, 69(1986).

133. K. Ito, H. Tsuchida and T. Kitano, Polymer Bull., 15, 425(1986).

134. S. D. Smith and J. E. McGrath, Polymer Preprints, 27(2), 31(1986).

135. Y. Yamashita, Polymer Preprints, 27(2), 27(1986).

136. Y. Yamashita, J. Appl. Polym. Sci., Appl. Symp. No., 36, 193(1981).

137. K. F. Gillman and E. Senogles, Polym. Letters, 5, 477(1967).

138. K. Ito, N. Usami and Y. Yamashita, Macromolecules, 13, 216(1980).

139. B. C. Anderson, G. D. Andrews, P. Arthur, Jr., H. W. Jacobson, L. R. Melby, A. J. Playtis and W. H. Sharkey, Macromolecules, 14, 1599(1981).

140. P. Lutz, P. Masson, G. Beinert and P. Rempp, Polymer Bull., 12, 79(1984).

141. R. N. Young, R. P. Quirk and L. J. Fetters, in Advances in Polymer Sci., 56, 70(1984).

142. R. Asami, Y. Kondo and M. Takaki, Polymer Preprints, 27(1), 186(1986).

143. M. Szwarc, M. Levy and R. Milkovich, J. Am. Chem. Soc., 78, 2656(1956).

144. E. W. Duck, in "The Stereo Rubbers," W. M. Saltman, Editor, Wiley and Sons, New York, Chapter 4, 1977.

145. A. F. Halasa, V. D. Mochel and G. Fraenkel, in "Anionic Polymerization: Kinetics, Mechanisms and Synthesis," J. E. McGrath, Editor, ACS Symposium Series No. 166, 367, 1981.

146. M. Morton, 15 .

147. H. L. Hsieh, J. Polym. Sci. Part A, 3, 163(1965).

148. J. E. L. Roovers, and S. Bywater, Macromolecules, 8, 251(1975).

149. L. J. Fetters and M. Morton, Macromolecules, 7, 552(1974).

150. M. Morton, E. E. Bostick, R. A. Livigni and L. J. Fetters, J. Polym. Sci., Part A, 1, 1735(1963).

151. M. Morton, L. J. Fetters and E. E. Bostick, J. Polym. Sci., Part C, 1, 311(1963).

152. N. Ishihara, T. Seimiya, M. Kuramoto and M. Uoi, Macromolecules, 19, 2464(1986).

153. D. H. Richards, Chem. Soc. Rev. (London), 6(2), 1977.

154. F. W. Stavely, Ind. Chem. Eng., 48, 778(1956).

155. H. Hsieh and A. V. Tobolsky, J. Polym. Sci., 25, 245(1957).

156. H. Hsieh, D. J. Kelly and A. V. Tobolsky, J. Polym. Sci., 26, 240(1957).

157. I. Kuntz and A. Gerber, J. Polym. Sci., 42, 299(1960).

158. H. Y. Chen, Anal. Chem., 34, 1134(1962).

159. R. C. Ferguson, Rubber Chem. Technol., 38(3), 532(1965).

160. E. R. Santee, Jr., R. Chang and M. Morton, Polym. Lett. Ed., 11, 449(1973).

161. K. Hatada, Y. Terawaki, H. Okuda, Y. Tanaka and H. Sato, Polym. Lett. Ed., 12, 305(1974).

162. G. Velden, C. Didden, T. Veermans and J. Beulen, Macromolecules, 20, 1252(1987).

163. I.-C. Wang, Y. Mohajer, T. C. Ward, G. L. Wilkes and J. E. McGrath, in "Anionic Polymerization: Kinetics, Mechanisms and Synthesis," ACS Symposium Series No. 166, 529, 1981; see contained references also.

164. M. Morton, 150 .

165. M. Morton, 147 .

166. J. N. Anderson, W. J. Kern, T. W. Bethea and H. E. Adams, J. Appl. Polm. Sci., 16, 3133(1972).

167. W. J. Kern, J. N. Anderson, H. E. Adams, T. C. Bouton and T. W. Bethea, J. Appl. Polym. Sci., 16, 3123(1972).

168. M. Morton, 28 .

169. P. Bres, M. Viguier, J. Sleds, F. Schue, P. E. Black, D. J. Worsfold and S. Bywater, Macromolecules, 19, 1325(1986).

170. A. Eisenberg and C. G. Bazuin, Ind. Eng. Chem. Prod. Res. Dev., 20, 271(1981).

171. R. W. Rees and D. J. Vaughan, Polymer Preprints, 6, 287(1965).

172. E. P. Otocka, J. Macromol. Sci., Chem., 5, 275(1971).

173. R. Longworth, in "Ionic Polymers," L. Holliday, Ed., Halsted-Wiley, New York, Chapter 2, 1975.

174. "Ion-Containing Polymers," A. Eisenberg and M. King, Eds., Academic Press, New York, 1977.

175. "Ions in Polymers," A. Eisenberg, Ed., American Chemical Society, Wash., D. C., Adv. Chem. Ser. 187, 1980.

176. W. J. MacKnight and T. R. Earnest, Jr., J. Polym. Sci., Macromol. Rev., 16, 41(1981).

177. "Columbic Interactions in Macromolecular Systems," A. Eisenberg and F. E. Bailey, Eds., American Chemical Society, Washington, D. C., ACS Symposium Series No. 302, 1986.

178. W. J. MacKnight and R. D. Lundberg, Rubber Chem. and Tech., 57, 652(1984).

179. Y. Kihira, H. Yamamura and I. Murakami, J. Macromol. Sci., Phys., B26(2), 201(1987).

180. R. J. Statz, Eur. Pat. Appl. EP 115190 A2, August, 1984.

181. S. Nashida, M. S. El-Aasser, A. Klein and J. W. Vanderhoff, ACS Symp. Ser., 165, 291, 1981.

182. M. King and A. Eisenberg, in "Ion-Containing Polymers: Physical Properties and Structure," Vol. 2, Academic Press, New York, 169, 1977.

183. Y. Tsujita, S. L. Hsu and W. J. MacKnight, Macromolecules, 14, 1824(1981).

184. N. L. Brockman and A. Eisenberg, J. Polym. Sci. Polym. Phys. Ed., 23, 1145(1985).

185. M. W. Mackenzie Eur. Pat. Appln. EP 203739 Al, December 1986.

186. T. Saito, T. Noma, T. Matsunage, C. Tanaka, Y. Furuta and N. Naito Brit. UK Pat. Appln. GB 2064339 A, June, 1981.

187. R. D. Lundberg, Encylc. Poly. Sci. and Tech., 3rd Edition, 8, 397(1985).

188. R. A. Weiss, S. R. Turner and R. D. Lundberg, J. Polym. Sci., Polym. Chem. Ed., 23, 525(1985).

189. R. A. Weiss and R. D. Lundberg, J. Polym. Sci., Polym. Chem. Ed., 18, 3427(1980).

190. B. Siadat, B. Oster and R. W. Lenz, J. Appl. Polym. Sci., 26(3), 1027(1981).

191. I. Yilgor, K. A. Packard, J. Eberle, E. Yilgor, R. D. Lundberg and J. E. McGrath, Polymer Preprints, 24(2), 37(1983).

192. C. G. Bazuin and A. Eisenberg, J. Polym. Sci.: Part B: Poly. Phys., 24, 1121(1986).

193. J. C. Salamone, N. A. Mahmud, M. U. Mahmud, T. Nagabhushanam and A. C. Watterson, Polymer, 23(6), 843(1982).

194. J. C. Salamone, C. C. Tsai, A. C. Watterson and A. P. Olson, J. Polym. Sci., Polym. Chem. Ed., 18(10), 2983(1980).

195. H. S. Makowski, R. D. Lundberg, L. Westerman and J. Bock, in "Ions in Polymers," A. Eisenberg, Ed., Adv. Chem. Ser. No. 187, Am. Chem. Soc., Wash., D.C., 3, 1980.

196. H. S. Makowski, R. D. Lundberg and G. Singhal, U. S. Patent 3,870,841, to Exxon, March, 1975.

197. B. C. Johnson, C. Tran, I. Yilgor, M. Iqbal, J. P. Wightman, D. R. Lloyd and J. E. McGrath, J. Polym. Sci., Polym. Chem., 22(3), 721(1984).

198. H. S. Makowski, R. D. Lundberg, L. Westerman and J. Bock, Polymer Preprints, 19(2), 292(1978).

199. J. E. McGrath, Encyclo. Chem. Tech., 3rd Edition, 8, 1979.

200. W. J. MacKnight and R. D. Lundberg, 657 .

201. K. Sanui, R. W. Lenz and W. J. MacKnight, J. Polym. Sci., Polym. Chem. Ed., 12, 1965(1974).

202. K. Sanui, W. J. MacKnight and R. W. Lenz, J. Polym. Sci., B, 11, 427(1973).

203. Z. L. Zhou and A. Eisenberg, J. Appl. Polym. Sci., 27, 657(1982).

204. R. D. Lundberg and H. S. Makowski, in "Ions in Polymers," A. Eisenberg, Ed., Adv. Chem. Ser. 187, 21, 1980.

205. Y. Huang, G. Cong and W. J. MacKnight, Macromolecules, 19, 2267(1986).

206. N. L. Brockman and A. E. Eisenberg, J. Polym. Sci., Polym. Chem. Ed., 21, 3563(1983).

207. S. D. Clas and A. Eisenberg, J. Polym. Sci., Part B: Polym. Phys., 24, 2743(1986).

208. S. D. Clas and A. Eisenberg, J. Polym. Sci., Part B: Polym. Phys., 24, 2757(1986).

209. G. Broze, R. Jerome and P. Teyssie, J. Polym. Sci. Lett. Ed., 19, 415(1981).

210. G. Broze, R. Jerome and PH. Teyssie, J. Polym. Sci.: Poly. Phys. Ed., 21, 2205(1983).

211. G. Broze, R. Jerome and P. Teyssie, Macromolecules, 15, 920(1982).

212. Ph. Teyssie, R. Jerome and G. Broze, Eur. Pat. Appln. EP 57479 A2, August, 1982.

213. J. Horrion, R. Jerome and Ph. Teyssie, J. Polym. Sci.: Part C: Polym. Lett., 24, 69(1986).

214. J. P. Kennedy and R. A. Smith, J. Polym. Sci.: Polym. Chem. Ed., 18, 1523(1980).

215. J. P. Kennedy, L. R. Ross, J. E. Lackey and O. Nuyken, Polymer Bull., 4, 67(1981).

216. S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. F. Storey and J. P. Kennedy, Polymer Bull., 9, 174(1983).

217. R. D. Allen, T. L. Huang, D. K. Mohanty, S. S. Huang, H. D. Qin and J. E. McGrath, Polymer Preprints, 24(2), 41(1983).

218. R. D. Allen, I. Yilgor and J. E. McGrath, in "Coulombic Interactions in Macromolecular Systems," A. Eisenberg and F. E. Bailey, Eds., 79, 1986.

219. S. Gauthier and A. Eisenberg, Macromolecules, 20, 760(1987).

220. A. Eisenberg, Macromolecules, 3, 147(1970).

221. S. Bonotto and C. L. Purcell, Macromolecules, 1, 510(1968).

222. R. Longworth and D. J. Vaughan, Polymer Preprints, 9, 525(1968).

223. W. J. MacKnight, W. P. Taggart and R. S. Stein, J. Polym. Sci., Polym. Symp., 45, 113(1974).

224. P. L. Taylor and K. D. Vandana, Macromolecules, 17, 1706(1984).

225. A. J. Hopfinger, IUPAC Proceedings Macro., 82, 887(1982).

226. C. L. Marx, D. F. Caufield and S. L. Cooper, Macromolecules, 6, 344(1973).

227. D. J. Yarusso and S. L. Cooper, Macromolecules, 16, 1871(1983).

228. J. A. Lefelar and R. A. Weiss, Macromolecules, 17, 1146(1984).

229. B. Dreyfus, Macromolecules, 18, 284(1985).

230. C. E. Williams, T. P. Russell, R. Jerome and J. Horrion, Macromolecules, 19, 2877(1986).

231. A. Eisenberg and M. King, in "Ion-Containing Polymers," Academic Press, New York, 2, 1977.

232. T. C. Ward and A. V. Tobolsky, J. Appl. Polym. Sci., 11, 2403(1967).

233. A. Eisenberg and M. Rigdahl, J. Polym. Sci.: Poly. Phys. Ed., 19, 1641(1981).

234. A. Eisenberg and M. Nauratil, Macromolecules, 6, 611(1973).

235. R. A. Weiss, J. Lefelar and H. Toriumi, J. Poly. Sci., Polym. Lett. Ed., 21, 661(1983).

236. A. Eisenberg and M. Nauratil, Macromolecules, 7, 90(1974).

237. M. Nauratil and A. Eisenberg, Macromolecules, 6, 606(1973).

238. D. Brenner and A. Oswald, in "Ions in Polymers," A. Eisenberg, Ed., Adv. Chem. Ser. 187, 53, 1980.

239. T. Murayamo, in "Dynamic Mechanical Analysis of Polymeric Materials," Elsevier, 1978.

240. S. Bagrodia and G. L. Wilkes, Polymer Bull., 12, 389(1984).

241. A. Eisenberg, E. Matsuura and T. Tsutui, J. Polym. Sci., Polym. Phys. Ed., 18, 479(1980).

242. G. Broze, R. Jerome and P. Teyssie, J. Polym. Sci., Polym. Phys. Ed., 18, 479(1980).

243. H. S. Makowski, R.D. Lundberg, L. Westerman and J. Bock, 18 .

244. S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. F. Storey and J. P. Kennedy, Polymer Bull., 8, 281(1982).

245. S. Bagrodia, G. L. Wilkes and J. P. Kennedy, Poly. Eng. and Sci., 26(10), 662(1986).

246. M. R. Tant, J. H. Song, G. L. Wilkes, J. Horrion and R. Jerome, Polymer, 27, 1815(1986).

247. H. S. Egboh, A. Ghaffar, M. H. George, J. A. Barrie and D. J. Walsh, Polymer, 23(8), 1167(1982).

248. H. S. Egboh, Polymer Preprints, 24(1), 260(1983).

249. D. A. Bansleban and O. Vogl, J. Polym. Sci., Chem. Ed., 23(3), 703(1985).

250. O. Vogl, J. Muggee and D. Bansleben, Polym. J., 12(9), 677(1980).

251. M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, 12, 1968.

252. R. P. Quirk, "Anionic Polymerization: Kinetics, Mechanisms and Synthesis," J. E. McGrath, Ed., ACS Symposium Series 166, 117, 1981.

253. A. D. Broske, Ph.D. Dissertation, VPI & SU, 65, 1987.

254. G. Odian, 197 .

255. M. Szwarc, 154 .

256. G. Spach, H. Monteiro, M. Levy and M. Szwarc, Trans. Faraday Soc., 58, 1809(1962).

257. H. Gilman and F. K. Cartledge, J. Organometal. Chem., 2, 447(1964).

258. R. N. Young, R. P. Quirk and L. J. Fetters, Advances in Polymer Science, 56, 9(1984).

259. L. H. Tung, G. Y.-S. Lo and D. E. Beyer, U.S. Patent, 4,172,100, Dow Chemical, 1979.

260. A. D. Broske, Ph.D. Dissertation, VPI & SU, 74, 1987.

261. R. N. Young, R. P. Quirk and L. J. Fetters, 6 .

262. T. Mole and E. A. Jeffrey, "Organoaluminum Compounds," Elsevier, Amsterdam, 211, 1972.

263. B. L. Goodall, Transition Metal Catalyzed Polymerizations: Alkenes and Dienes," R. P. Quirk Ed., MMI Press Symposium Series, Vol. 4, Part A, 355, 1982.

264. T. Mole and E. A. Jeffrey, 302 .

265. M. Morton and L. J. Fetters, Rubber Chem. and Tech., 48, 359, 1975.

266. S. C. Watson and J. F. Eastham, J. Organometal. Chem., 9, 165(1967).

267. R. T. Morrison and R. N. Boyd, "Organic Chemistry," 3rd ed., Allyn and Bacon, 876, 1973.

268. V. A. Fassel and R. N. Kniseley, Analytical Chemistry, 6(13), 1155A(1974).

269. P. E. M. Allen and B. A. Casey, Eur. Poly. J., 2, 9(1966).

270. J. M. Hoover and J. E. McGrath, Polymer Preprints, 27(2), 150(1986).

271. M. D. Glasse, Prog. Polym. Sci., 9, 133(1983).

272. A. D. Broske and J. E. McGrath, Polymer Preprints, 26(1), 241(1985).

273. Y. Kihira and H. Yamamura, The 28th Japan Congress on Materials Research, March, 213, 1985.

274. J. F. Rabek, 234 .

275. F. A. Bovey, "High Resolution NMR of Macromolecules," Academic Press, 65, 1972.

276. I. Ya. Slonim and A. N. Lyubimov, "The NMR of Polymers," Plenum, 149, 1970.

277. R. C. Ferguson and D. W. Overnall, Polymer Preprints, 26(1), 182(1985).

278. J. F. Rabek, 210 .

279. M. Haney, American Laboratory, March 1, 1985.

280. M. Haney, American Laboratory, March 1, 1985.

281. A. M. Walstrom, R. Subramanian, T. E. Long, J. E. McGrath and T. C. Ward, Polymer Preprints, 27(2), 135(1986).

282. J. Felbey and J. P. Wightman, Ph.D. Dissertation, VPI & SU 000, 1987.

283. R. D. Allen, T. E. Long and J. E. McGrath, Polymer Bull., 15(2), 127(1986).

284. R. D. Allen, T. E. Long and J. E. McGrath, in "Advances in Polymer Synthesis," B. M. Culbertson and J. E. McGrath, Eds., Plenum, 347, 1985.

285. T. Mole and E. A. Jeffrey, Chapter 2 .

286. R. D. Allen, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, March, 1985.

287. P. E. M. Allen, B. O. Bateup and B. A. Casey, J. Organometal. Chem., 29, 185(1971).

288. P. E. M. Allen, Private Communication, .

289. P. M. Wiles and S. Bywater, Trans. Fara. Soc., 61, 150(1965).

290. S. D. Smith, Ph.D. Dissertation, VPI&SU, July, 1987.

291. T. C. Ward, J. Chem. Ed., 58, 867(1981).

292. G. Lohr and G. V. Schulz, Eur. Polym. J., 10, 121(1974).

293. A. M. Walstrom, R. Subramanian, T. E. Long, J. E. McGrath and T. C. Ward, Poly. Prepr., 27(2), 135(1986).

294. R. C. Daly, M. J. Hanrahan and R. W. Blevins, SPIE, Advances in Resist Technology and Processing II, 539, 138(1985).

295. H. Yuki, K. Hatada, Y. Kikuchi, and T. Niinomi, J. Polym. Sci., Part B, 6, 753(1968).

296. Y. Okamoto, S. Nakashima, K. Ohta, K. Hatada, and H. Yuki, J. Polym. Sci., Polym. Lett. Ed., 13, 273(1975).

297. L. F. Thompson, C. G. Willson and M. J. Bowden, in "Introduction to Microlithography," ACS Symposium Series 219, 125, 1983.

298. J. M. J. Frechet, E. Eichler, H. Ito and C. G. Willson, Polymer, 24, 995(1983).

299. J. J. Fitzgerald and R. A. Weiss, Poly. Preprints, 27(2), 163(1986).

300. S. R. Bagrodia, G. L. Wilkes and J. P. Kennedy, J. Appl. Polym. Sci., 30, 2179(1985).

301. S. Gauthier and A. Eisenberg, Macromolecules, 20, 760(1987).

302. A. Eisenberg, Private communication .