SYNTHESIS OF NOVEL METHACRYLATE-CONTAINING POLYMERS BY ANIONIC POLYMERIZATION

by

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(ABSTRACT)

The advent of anionic "living" polymerization in the late 1950's lead to developments in synthetic control not yet approached by other polymerization mechanisms. Parameters such as molecular weight, molecular weight distribution, stereochemistry, chain end functional groups, polymer architecture and sequence distribution may ideally be controlled with anionic polymerization.

The vast majority of anionic syntheses have dealt with the "hydrocarbon" monomers-styrene and its derivitives, butadiene, and isoprene. This attention has been due principally to these monomer's ability to polymerize in a "living" (non-terminating or transferring) fashion over a wide range of conditions. Alkyl methacrylate monomers have received very sparce synthetic attention, however. This is presumably due to the difficulty in defining non-terminating polymerization conditions and, more importantly, the inability to arrive at anionic polymerization-grade monomers (i.e., monomers that are free from terminating impurities such as alcohols).

A method has been developed which provides ultra-pure alkyl methacrylate monomers for anionic synthesis. This method takes advantage of the chemistry of trialkyl aluminum compounds - their reactivity with alcohols and moisture, and their complex formation with

methacrylic esters which facilitates titration of impurities.

These anionic polymerization-grade monomers have lead to the synthesis of controlled molecular weight methacrylate polymers up to molecular weights of 10^5 g/mole, clean all-acrylic block copolymer systems with highly controllable phase separating properties, and styrene-methacrylate block copolymer systems which also serve as model systems for the study of phase separation of glass-glass systems. The methacrylate unit has also been controllably incorporated into copolymer systems (block copolymers) to serve as a "pre-ionic" functionality. Hydrolysis of the ester group leads to ionomers of controlled structure. These systems have properties quite different from more conventional "random" ionomers, e.g., highly extended rubbery plateau behavior and no change in Tg with ion content.

This thesis is dedicated to my parents for their confidence and encouragement throughout the downs and ups of my chemistry career.

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Many thanks are due to my friends and colleagues in Lab 120A. and , two extremely talented young graduate students whom I had the opportunity to "teach", helped greatly with many later experiments which appear in this thesis. and were constant sources of thought-provoking discussion, experimental advice and good breakfast companions on Saturday mornings.

Many thanks are also due to and for their extreme helpfulness with GPC and thermal analysis, respectively. deserves many thanks for her patience in typing this thesis.

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I. INTRODUCTION

Anionic polymerization of alkyl methacrylates, especially methyl methacrylate (MMA), has been studied extensively over the last two decades [1-5]. The vast majority of these investigations have dealt with the kinetic and mechanistic aspects of anionic methacrylate polymerization. Relatively few investigations, however, have been concerned with the synthesis of novel homo- and copolymers [6]. Two major reasons why synthetic studies of these systems have lagged behind the voluminous work done on the hydrocarbon monomers, e.g. styrene, butadiene and isoprene, are problems with methacrylate monomer purity and the inherent side reactions found in most anionic polymerizations involving polar monomers. The problem of side reactions to the methacrylate carbonyl has been well documented in the literature [7]. Methods have been developed in the past to avoid these deleterious side reactions, namely bulky initiators, low temperatures and polar solvents. We have been able to synthesize narrow distribution poly(alkyl methacrylates) by utilizing the well established route of THF at -78°C with the bulky initiator diphenyl hexyl lithium (DPHL). A much less appreciated aspect of the anionic synthesis of methacrylate polymers, however, has been the problem of monomer purification. Suitable methods are available for the scrupulous purification of hydrocarbon monomers. (For example, the organometallic reagent dibutyl magnesium (DBM) has been well documented as a highly sensitive reagent which reacts with the last traces of water, air, or other terminating impurities present in styrenic and diene monomers [8].) The presence of a bright yellow complex is a useful indicator, assuring the chemist that the monomer is highly pure. Unfortunately, DBM and most other similar compounds rapidly polymerize alkyl methacrylates.

Calcium hydride is currently the established purification agent for methacrylate monomers. This "drying agent" falls short in two respects concerning methacrylate purification. First, due to the heterogeneous nature of calcium hydride dispersed in a polar monomer such as methyl methacrylate, the hydrophilic MMA may be difficult to fully dry. More importantly, as the higher methacrylate monomers are generally synthesized via transesterification of MMA with the appropriate alcohol (which in most cases has a boiling point close to the resulting methacrylate -- not to mention azeotropes), alcoholic, terminating impurities are present in most commercially available methacrylates. Calcium hydride unfortunately does not react appreciably with these alcohols. Thus, most methacrylates cannot be used for anionic polymerization with any degree of success. This places severe limitations on the potential properties one may obtain via anionic methacrylate polymerization.

A new purification method involving trialkyl aluminum reagents has thus been developed in our laboratories for the purification of alkyl methacrylates. This novel method allows for both the synthesis of narrow distribution poly(alkyl methacrylates) of controlled and predictable molecular weights and for the utilization of a wide variety of methacrylate monomers. In addition, judicious choice of the polymerization solvent permits control of polymer stereochemistry. We have taken advantage of both variables (ester-alkyl group and polymerization solvent) and utilized our rigorously purified monomers to synthesize poly(alkyl methacrylates) with a wide range of physical properties, from glasses to semi-crystalline systems, and even elastomers. Both styrene-methacrylate and methacrylate-methacrylate block polymers have been cleanly synthesized. These systems are of interest in that the phase separating characteristics can be controlled by judicious selection of block solubility parameters. These blocks also serve in the novel synthesis of ion containing block copolymers via methacrylate hydrolysis reactions. These ion containing block systems show unique properties such as no change in Tg with ion content and highly extended rubbery plateau behavior.

II. REVIEW OF THE LITERATURE

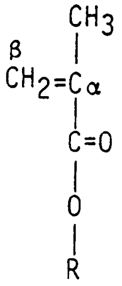
A. METHACRYLATE POLYMERS AND POLYMERIZATION

1. Introduction

Methacrylate monomers have long been valuable tools for the synthesis of polymers with a wide range of properties and applications. Due to the large number of acrylic monomers available and their propensity toward copolymerization with most other vinyl monomers, polymers with highly controllable physical properties are readily synthesized. The spectrum of properties available ranges from soft, tacky adhesives to highly stable, rigid, tough plastics.

The methacrylate story [9-11] began in 1901 with the publication of Otto Rohm's doctoral thesis. Rohm studied the preparation and properties of polymers derived from methyl methacrylate and founded a company in 1909 with Otto Haas which produced the first commerical acrylates in Germany in 1927. By 1936, MMA was being polymerized in cast sheets for safety glass applications. Several years later (1938), molding powders for injection and compression molding were made available. During the war, PMMA was utilized to make the highly aerodynamic cockpit canopy of the P-51 Mustang fighter aircraft. This important contribution lead to the war's most dominant plane and precipitated the American victory. Today, methacrylate polymers are found in plastics, constant viscosity oil additives, adhesives, sealants, floor polishes and surface coatings. Methyl methacrylate production exceeds 500,000 metric tons per year in the U.S.A., more than all other acrylic esters combined [11].

Methacrylate monomers are α,β-unsaturated esters with the structure represented by 1, where the ester-alkyl group (R) effects the physical and chemical properties of both the monomer and polymer produced.



$$\overset{\beta}{CH_2}=\overset{CH_3}{C_\alpha}-C(=O)-O-R$$

1

The momenclature of these monomers is first concerned with the ester-alkyl group, then with the methacrylate (or acrylate) skeleton. Thus, if R = methyl, structure 1 is known as methyl methacrylate (MMA). Where R is an isobutyl group, the monomer is called isobutyl methacrylate (IBMA). If the α-methyl groups is replaced by a hydrogen radical, the skeleton is known as "acrylate". Thus, when R = methyl, this compound is known as methyl acrylate. It should be noted that both acrylate and methacrylate monomers and polymers share very few similarities. In fact, the chemical and toxilogical properties of methacrylates and acrylates are quite different, while the polymers derived from these two classes of monomers are typically glasses and elastomers, respectively. The interchanging of the words "acrylate" with "methacrylate" will thus rigorously be avoided, as much confusion results when these differences are not acknowledged.

2. Monomer Preparation and Properties

A variety of routes exist for the synthesis of methacrylate monomers. These routes are most easily divided into two broad classifications. Primary routes are those in which the methacrylate monomer is synthesized (usually on an industrial scale) from common petrochemical starting materials. Secondary processes involve the conversion (usually laboratory scale) of the methacrylic skeleton into the monomer of choice. Both of these general catagories have several well known examples which will be discussed accordingly.

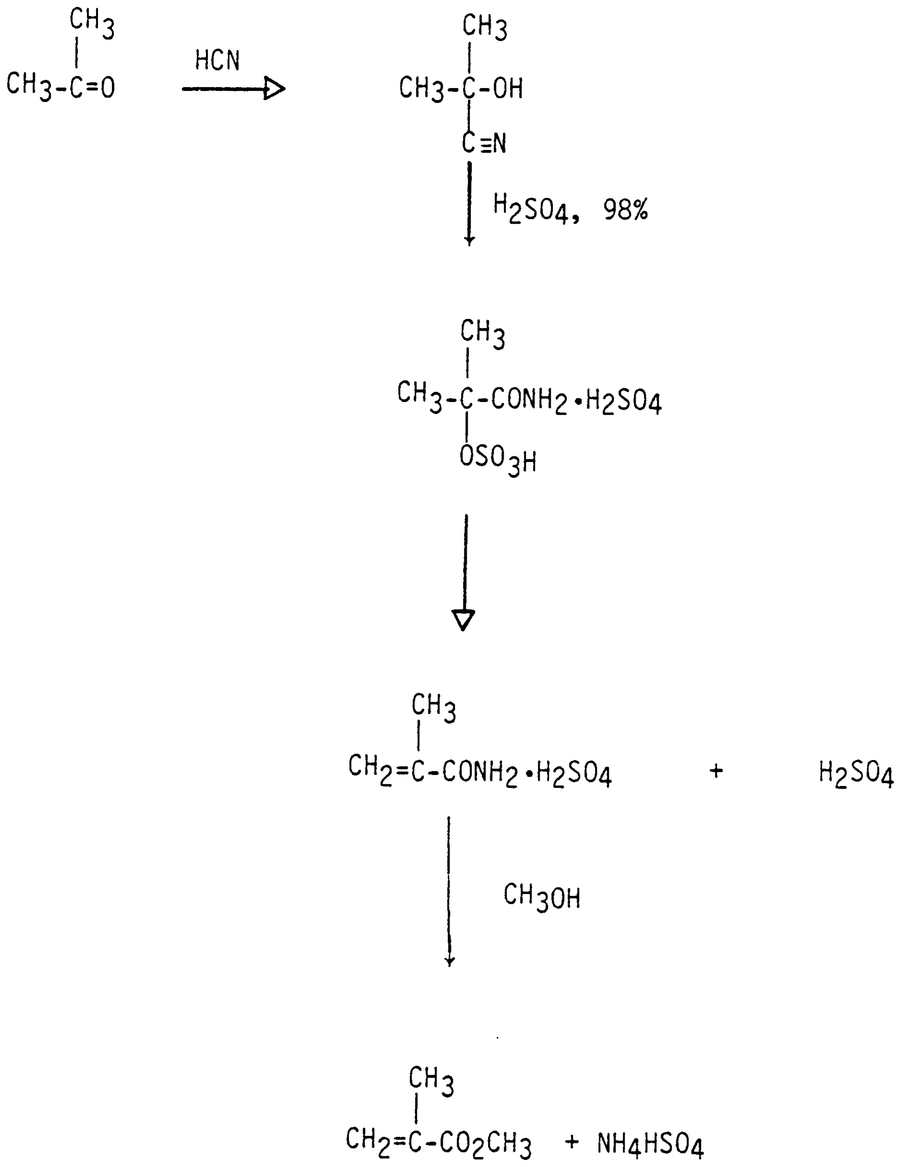
There are at present two major "primary" routes for the synthesis of methacrylates (typically MMA) [9-10]. The most widely used method for the mass production of MMA is known as the acetone cyanohydrin (ACN) process. Acetone is treated with HCN to form the cyano alcohol (Scheme 1). This product is then reacted with excess 98% sulfuric acid to give the methacrylamide sulfate salt, which is not isolated but reacted with an excess of the appropriate alcohol (methanol for MMA) to form the alkyl methacrylate. This route suffers from three serious limitations:

1) The hazardous materials employed (HCN and 98% H_2SO_4).

2) Difficult product purification.

3) Large generation of waste acid.

Byproducts from the reaction sequence depend principally an water contamination and H_2SO_4/acetone cyanohydrin ratio. These include dimethyl ether, methyl formate, acetone, α-hydroxy-butyric acid, methyl α-hydroxybutyrate, and methyl β-methoxyisobutyrate. In the last (alcoholysis) step, excess aqueous alcohol is used. The product purification involves isolation of the organic layer, flashing off the



Scheme I. The ACN Process: Commercial MMA Synthesis.

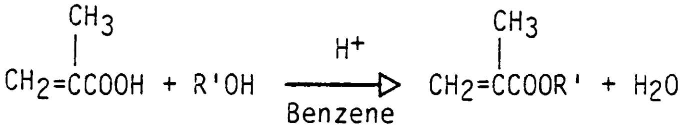
low-boilers, water washing to try to remove methanol and some methacrylic acid, followed by very careful distillation. This last distillation step removes most of the remaining water and methanol.

A second seemingly more promising but not widely utilized primary route involves the catalytic oxidation of C_4 petroleum streams, i.e., literally reacting the readily available raw material isobutylene with air to give methacrylic acid. The methacrylic acid is esterified with methanol to produce MMA [9-10]. The catalyst performance determines the yield, selectivity and overall economic feasibility of this process. The oxidation is a two stage process, first to methacrolein, then to methacrylic acid. These two stages typically demand different catalysts [10]. First stage catalyst (isobutylene → methacrolein) are complex transition metal oxides while the second stage catalysts are based on heteropolyacids of molybdenum with transition metal oxides. Formation of MMA involves acid catalyzed esterification of methacrylic acid with methanol. Find product purity is >99% with overall yield of >90% by this oxidation process.

A new process based on C_1 chemistry has been developed by Dow Chemical [12]. Methacrylate and acrylate esters are synthesized by reacting a specially constructed vinyl halide with carbon monoxide and an organic carbonate esterifying agent. This process depends on catalysis by organometallic Group VIII complexes, for example dichlorobis (triphenylphosphine)-palladium. A typical MMA synthesis using this novel C_1 catalytic chemistry would involve the reaction of 2-bromopropene with dimethyl carbonate.

Several "secondary" processes are commonly used for the synthesis of a wide variety of methacrylate monomers. These routes are based on the interconversion (following the well established chemistry of carboxylic acids and their derivitives) of basic methacrylic skeletons. The three common starting materials are methyl methacrylate (MMA), methacrylic acid (MAA) and methacroyl chloride (MACl) [9]. The two most widely utilized routes involve the direct esterification of methacrylic acid and the transesterification of methyl methacrylate.

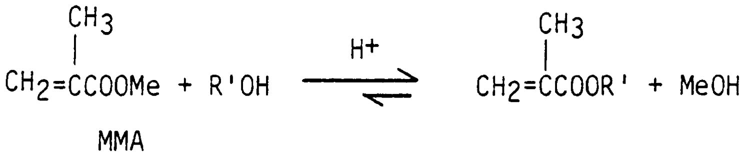
In the methacrylic acid route, the inhibited acid is refluxed with the desired alcohol in the presence of an acid catalyst (p-toluene sulfonic). The water formed as a byproduct in this reaction (Scheme II) must be removed to avoid the reverse reaction from occurring. Benzene or toluene are typically used for water removal, by virtue of their low boiling azeotrope formation. Excess alcohol is typically used, and its complete removal is quite difficult.



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}COOH + R'OH \xrightarrow[\text{Benzene}]{H^+} CH_2{=}\overset{\overset{CH_3}{|}}{C}COOR' + H_2O$$

Scheme II. Direct Esterification of MAA.

An even more widely used route to higher methacrylates involves the transesterification of MMA with appropriate alcohols. Strong acid catalysts are typically used, although certain functional alcohols may preclude these. In the transesterification or ester interchange route (Scheme III), the methanol byproduct is removed to drive the equilibrium reaction to the desired product. Due to the low boiling azeotrope methanol forms with MMA, excess MMA is used (often in several separate charges) which drives the alcohol of interest to very high conversions, assisting in product cleanup. This reaction is typically followed by monitoring the refractive index of the distillate [13-14].



$$\underset{MMA}{CH_2{=}\overset{CH_3}{\overset{|}{C}}COOMe} + R'OH \xrightleftharpoons{H+} CH_2{=}\overset{CH_3}{\overset{|}{C}}COOR' + MeOH$$

Scheme III. Ester Interchange Route to Alkyl Methacrylates.

The dehydration of tertiary alcohols by strong acid catalysts precludes the secondary routes discussed above for the synthesis of tertiary alkyl methacrylates. Monomers such as t-butyl methacrylate (TBMA) are thus often prepared by the reaction of t-butanol with the acid chloride (MACl), using a tertiary amine acid acceptor. An alternative route often employed is the addition of isobutylene to methacrylic acid [15]. Although many other routes exist for the synthesis of methacrylate monomers, the most important have been covered. The interested reader is referred to references [9-10] for a detailed discussion of a wide range of primary and secondary methacrylate monomer processes.

Methacrylate monomers are generally moderate to high boiling liquids with little or no water solubility and relatively low toxicity. Selected physical properties for a variety of methacrylates are given in Table 1.

Methacrylates are generally stabilized with phenolic inhibitors,

Table I

Physical Properties of Various Methacrylate Monomers [9-10].

Methacrylate(R)	Mol. Wt.	bp, °C	Ref. Index, n_D^{25}	Density, g/cm^3, d^{25}
methyl	100.1	100	1.4120	0.939
ethyl	114.1	119	1.4116	0.909
n-propyl	128.1	141	1.4183^{20}	0.902
i-propyl	128.1	125	1.4334	0.885
n-butyl	142.2	162-163	1.4220	0.889
i-butyl	142.2	155	1.4172	0.882
s-butyl	142.2	72-73(50mm)	1.4195	
t-butyl	142.2	52(35mm)	1.4120	0.877
n-hexyl	170.3	204-210	1.4310^{20}	0.880
n-octyl	198.4	114(14)	1.4373^{20}	
2-ethylhexyl	198.4	47(0.1)	1.4380^{20}	
isodecyl	226	120(3.0)	1.4410	0.878
lauryl	262	272-343	1.444	0.868
allyl	126.1	32(10)	1.4328	
cyclohexyl	136	44(0.3)	1.4583^{20}	0.963
phenyl	130	58-61(1.0)	1.5184^{20}	

such as hydroquinone (HQ) and the monomethyl ether of hydroquinone (MEHQ) [10]. Levels of 10-15 ppm are generally suitable for MMA and EMA, but the higher boiling methacrylates require higher concentrations. The often forgotten fact is that these phenolic inhibitors work only in the presence of oxygen. Monomers are thus not suitable for long term storage under inert atmospheres. These phenolic inhibitors are often removed from methyl methacrylate with aqueous base washing, although the higher esters form stable suspensions, precluding the use of this method. These monomers may be freed from inhibitors by passing the monomer through a column of ion-exchange resin or alumina. Distillation of the monomer will also remove these phenolic compounds.

Although methyl methacrylate has an appreciable water solubility (1.5g/100 ml soln.), the higher alkyl methacrylates are water insoluble [10]. This is not to say that these polar methacrylate monomers do not contain significant levels of molecularly dispersed water.

As mentioned in the previous section on monomer synthesis, most synthetic methods result in alcohol contamination of the alkyl methacrylate. The relatively similar boiling points of the alcohols and the parent methacrylates, as well as the azeotropic tendencies of alcohols with methacrylates make for difficult separation. For example, methyl methacrylate forms low boiling azeotropes with a variety of alcohols, including methanol (15.5% ester) and ethanol (18% ester) [16]. The azeotropic character coupled with the small differences in boiling points cause great difficulty in the final purification of methacrylate monomers.

Methacrylate monomers have low to moderate toxicities, but are much less toxic than the corresponding acrylates [9-10]. As a general rule the lower esters are more toxic, the most hazardous monomer by far being methyl acrylate, having an LD_{50} value close to that of the highly toxic ethylene oxide. An example of the toxicity differences is given in Table 2. Methyl methacrylate has been shown not to be carcinogenic towards rats and hamsters, and inhaled monomer is rapidly and extensively degraded to CO_2, being expelled from the lungs with small levels of methyl malonate [10].

3. Polymer Synthesis and Characteristics

Methyl methacrylate and other alkyl methacrylates are generally polymerized via free radical initiators. Conversions are generally very high with high molecular weight easily attainable. A wide range of copolymers are easily synthesized by copolymerizing alkyl methacrylates with other methacrylates, acrylates, methacrylic or acrylic acids, styrenics, etc. Polymerization processes employed are typically bulk polymerization to make cast sheet or molding powder, suspension polymerization to form small beads for injection molding or ion exchange, emulsion polymerization for stable latices, and solution polymerization for low molecular weight, high-solids coatings [9].

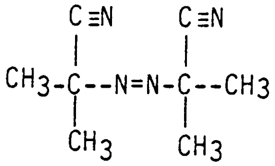
Radical initiators used are typically "azo" compounds, e.g., AIBN (1), or peroxides. Both classes of initiators are soluble in most methacrylates, thus are suitable for bulk and suspension polymerization. The use of azo compounds is more widespread due to their very high initiating efficiency [18] and non-oxidizing nature. Peroxides have lower initiating efficiencies often resulting in secondary decomposition

Table 2

Toxicity of Acrylic and Methacrylic Monomers [9]

Monomer	Acute oral LD_{50}, rats, mg/kg
methyl acrylate	300
ethyl acrylate	1,020
butyl acrylate	3,730
methyl methacrylate	7,900
ethyl methacrylate	13,300
butyl methacrylate	18,000

which can cause discoloration, crosslinking, and deterioration of the polymer with aging [9].



$$CH_3-\overset{C\equiv N}{\underset{CH_3}{C}}-N=N-\overset{C\equiv N}{\underset{CH_3}{C}}-CH_3$$

1

AIBN

The copolymerizability of alkyl methacrylates with a variety of other vinyl monomers has been investigated, and their reactivity ratios determined [17,19]. When pairs of reactivity ratios (a measure of the propensity of a growing radical to add a like monomer or a different monomer) are non-zero and similar, the copolymerization will proceed with fairly statistical monomer incorporation. Thus a ratio of the reactivity ratios ($r_{smaller}/r_{larger} \cdot 100$) should approach 100 if equal monomer reactivity is favored. This condition results in azeotropic copolymer compositions, where the feed ratio equals the composition ratio [20]. Conversely, values of this "copolymerizability ratio" approaching zero may indicate that homopolymerization of the more reactive monomer will be favored over random copolymerization. Data for the copolymerizability of several alkyl methacrylates with a spectrum of vinyl monomers is given in Table 3. Values of the "copolymerizability ratio" above 25 will indicate a tendency towards clean copolymer formation. It should be noted that continual addition of the more reactive monomer to an excess of the less reactive monomer will result in clean copolymer formation if this copolymerizability ratio is below 25, yet significant. Note while the methacrylate monomers will

Table 3

Copolymerizability Ratios ($r_{smaller}/r_{larger} \cdot 100$) [17]

	Monomer 1		
Monomer 2	MMA	EMA	BMA
acrylonitrile	12	24	19
butadiene	33	8.6	8.1
ethylacrylate	18	20	18
styrene	88	60	90
vinylchloride	<0.1	0.6	0.5
vinylidine chloride	9.5	14	16
vinylacetate	0.1	0.9	0.2

copolymerize readily with monomers which form moderately reactive radicals (styrene, butadiene, other acrylic systems), copolymerization will not occur with monomers which generate highly reactive radicals, e.g. vinyl acetate.

The properties of poly(alkyl methacrylates) are dependent on two controllable variables, ester-alkyl group and tacticity, ~~int~~ermolecular and intramolecular effects, respectively. For unbranched side chains (alkyl groups), the Tg decreases with increasing carbon number. This effect has also been seen in a number of other systems, e.g., poly-α-olefins, poly(acrylates) and (polyvinyl ethers) [18]. Very long side chains may begin to show an increase in Tg due to side chain crystallization. This Tg lowering effect is thought to involve intermolecular forces rather than intramolecular forces. Free volume arguments are generally used to explain these phenomena. Examples of the effects discussed above are shown in Table 4. It is important to note that glass transition values for methacrylate polymers are very sensitive to stereochemistry, i.e. there is no absolute Tg for a particular poly(alkyl methacrylate). The values listed in Table 4 are considered to represent "atactic" polymers, but radical polymerization often produces methacrylate polymers higher in syndiotacticity which have higher glass transition temperatures than are listed. This effect will be discussed in more detail later.

The glass temperature of a poly(alkyl methacrylate) homologous series will increase with branching, due to intramolecular factors involving the energy barriers to carbon-carbon bond rotation around the backbone. With branching, these substituents become bulkier, hindering

Table 4

Glass Transitions of Various Methacrylate Polymers with Linear Side Chains [11]

Alkyl(R) Methacrylate	T_g[a]
methyl	105
ethyl	65
n-propyl	35
n-butyl	20
n-hexyl	-5
n-octyl	-20
n-decyl	-60
lauryl[b]	-65
n-tetradecyl	-72

[a] "Atactic" polymers

[b] mostly C_{12}

this rotation from occurring due to a maximization of intramolecular forces, which raises the Tg. This effect is seen in the butyl methacrylate series, as shown in Table 5.

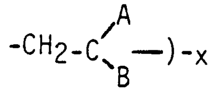
The extent of the stereochemical influence on Tg discussed above is generally not fully appreciated. Although many examples of vinyl polymers of the structure  $-CH_2-C\begin{smallmatrix}A\\ B\end{smallmatrix}-)-_x$ show Tg changes with tacticity, when A or B is hydrogen no effect has been observed [21]. For example, poly-α-methylstyrene has a Tg (atactic) of 170°C [22], while the Tg (isotactic) is 117°C [23], while polystyrene shows little or no effect on Tg of tacticity. Although the Tg sensitivity to stereochemistry of methacrylate polymers is well established, the extent of this effect is continually underestimated. The Tg of syndiotactic PMMA is commonly represented as 115-120°C [11,26], while the Tg of PMMA prepared by anionic polymerization at low temperatures in THF has a syndiotactic content of ca. 75% with a Tg of ca. 130°C. A poly(methyl methacrylate) with a syndiotactic content greater than 90% has not been prepared, but extrapolation of Tg vs. syndiotactic content (NMR) curves gives a Tg for 100% syndiotactic PMMA of 160°C [24]. It is thus quite difficult to ascertain how this 115°C value for "syndiotactic" PMMA evolved. The interested reader is referred to Fox et. al. [1] for the initial paper on this subject. Isotactic poly(alkyl methacrylates) conversly have Tg's much lower than their atactic counterparts, due to the lower energy barriers for conformational rotation. Glass transition temperatures of as low as 43°C have been reported for isotactic PMMA, synthesized by Grignard initiators in toluene [11]. Karasz and MacKnight [25] have found that for a variety of poly(alkyl methacrylates), the average

Table 5

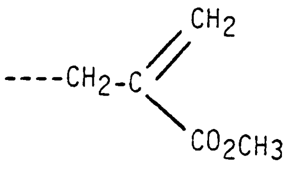
Glass Transitions of Butyl Methacrylate Polymers[a] [11]

Alkyl(R)	Tg[a]
n-butyl	20
iso-butyl	53
sec-butyl	60
tert-butyl	107

[a] Polymers are of similar stereochemistry

difference between syndiotactic and isotactic polymers, i.e., Tg (syndiotactic) - Tg (isotactic) = 112°C. They have also shown that the Tg difference between "conventional" and isotactic methacrylate polymers averages 50-60°. The extremely wide property variations which can be obtained by controlling both the ester-alkyl side chain and the stereochemistry demonstrates the synthetic capabilities of alkyl methacrylates's in the synthesis of a myriad of polymer structures.

It has been realized that PMMA rapidly depolymerizes to monomer at high temperatures, producing >95% MMA above 300°C. This "unzipping", in itself, is not extremely deleterious to the spectrum of properties of PMMA. In fact, this thermal instability has been utilized for the reclamation of polymer scrap, which is heated above these temperatures to yield crude methyl methacrylate [27]. A very recent landmark study [28] by Australian workers has shed light on the molecular understanding of this thermal decomposition. This work was based on Grassie's findings [29], which established that thermal depolymerization of PMMA takes place in two distinct stages. Approximately 50% of a "conventional" PMMA degrades at relatively low temperatures (170-250°C) while the other 50% is stable past 300°C. It was proposed that this dichotomous thermal behavior was due to end group effects. Disproportionative termination of radical polymerization produces two distinct end groups, unsaturated (1) and the other saturated (2).



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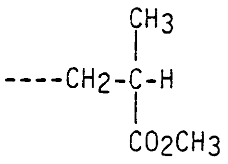
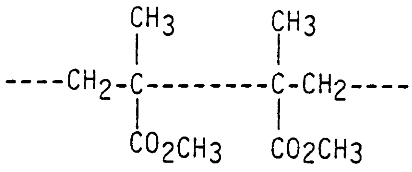


$$----CH_2-\overset{CH_3}{\underset{CO_2CH_3}{C}}-H$$

2

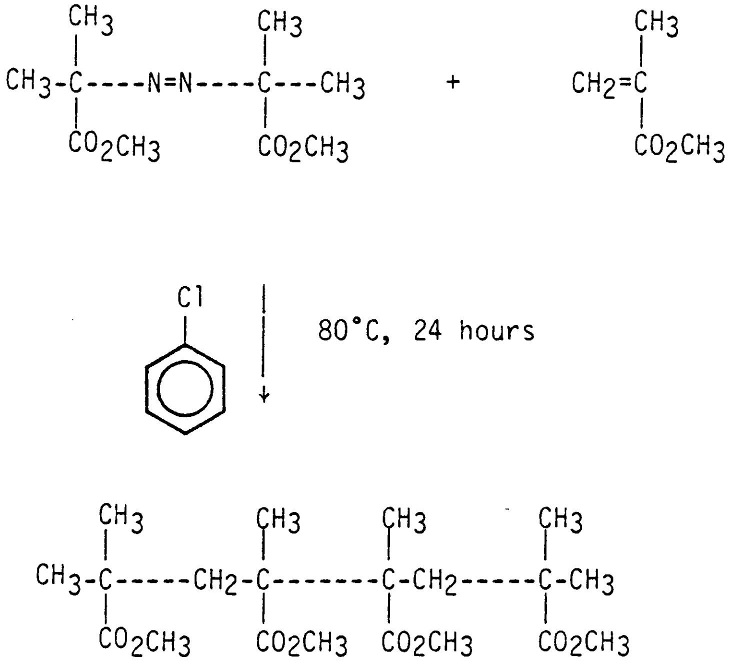
Although no direct evidence existed, it was felt that the unsaturated end group was the reactive moity which initiated the relatively low temperature depolymerization of PMMA. The Australian group [28] carefully synthesized a series of model oligomers which contained the end groups of structures (1) and (2). A mode of termination not yet discussed is radical combination. Most radical polymerizations terminate predominately by combination, e.g., styrene, butadiene, etc. [18-19]. However, the more hindered tertiary radicals produced during MMA polymerization, along with the ready availability of β-hydrogens, favor disproportionation, although combinatory termination no doubt exists at slightly depressed levels. The combination/disproportionation ratio is somewhat temperature sensitive, with disproportionation being favored at higher temperatures. This combinatory process raises the molecular weight, and more pertinant to this discussion, results in head to head (H-H) in-chain linkages of the structure (3).



$$\text{----}CH_2\text{-}\underset{CO_2CH_3}{\overset{CH_3}{C}}\text{--------}\underset{CO_2CH_3}{\overset{CH_3}{C}}\text{-}CH_2\text{----}$$

3

The Australian group carefully synthesized model oligomers which represent these three termination-induced structures. The oligomer bearing the unsaturated end group was synthesized via a cobalt tetraphenylporphyrin (CoTpp) catalyst, which yields these groups in very high yields with narrow molecular distributions [30]. As an aside, this may prove to be a facile synthesis of well defined MMA macromonomers. The saturated end groups were synthesized by hydrogenating the unsaturated oligomers with a 5% Pd/C catalyst. The oligomer containing the H-H linkage was synthesized by radical polymerization using equimolar quantities of the initiator dimethyl-2,2'-azoisobutyrate (related to AIBN only with methyl ester groups replacing the nitrile functionalities) and MMA. The reaction is represented in Scheme IV. The product of choice (tetramer H-H) was isolated by high vacuum (0.01 mmHg) Kugelrhor distillation at 110°C. What is not discussed, however, is how the disproportion products are avoided.



Scheme IV. Synthesis of H-H MMA Oligomers [28].

The three classes of oligomers were individually evaluated for thermal stability via thermogravimetry (TGA). The saturated oligomer representing polymer end group structure (2) showed onset of decomposition (depolymerization) initiating at 300°C, while the unsaturated end group oligomer representing structure (1) began decomposition at 255°C. Both these tempertures were independent of oligomer molecular weight (molecular weights of 7000, 1500, 5000, and 10,000 were employed). A very important finding was the fact that the H-H tetramer representing a combinatory termination process resulting in junction points of structure (3) showed onset of depolymerization (weight loss) at 195°C. Thus, onset of PMMA depolymerization or unzipping is first initiated, at temperatures very close to processing temperatures, by H-H linkages arising from radical termination by combination. Synthetic methods which result in only saturated end groups with no H-H linkages would thus be extremely desirable, and would result in PMMA with thermal stability up to temperatures approaching 300°C.

Methacrylates (most notably PMMA) are also found to readily depolymerize when subjected to various types of high energy radiation such as deep UV(215 nm) and electron beam. This fact has been taken advantage of in the area of microlithography in the case of PMMA as a widely used positive resist [31-32]. The advantages of PMMA as a positive (usually E-beam) resist are its very high resolution, handling ease, film forming qualities and wide availability. Its major limitation arises in its very low sensitivity ($G_{scission}$ = 1.3 vs. polyolefin sulfone G_S=10) which lowers production thoughput, and its relative instability toward dry etch environments. Attempts have been partially successful in raising the radiation sensitivity of PMMA through copolymerization [33]. Surprisingly, the end group and H-H effects are ignored in this realm. The mechanism for initiation of this radiation induced scission is elaborated on in Scheme V.

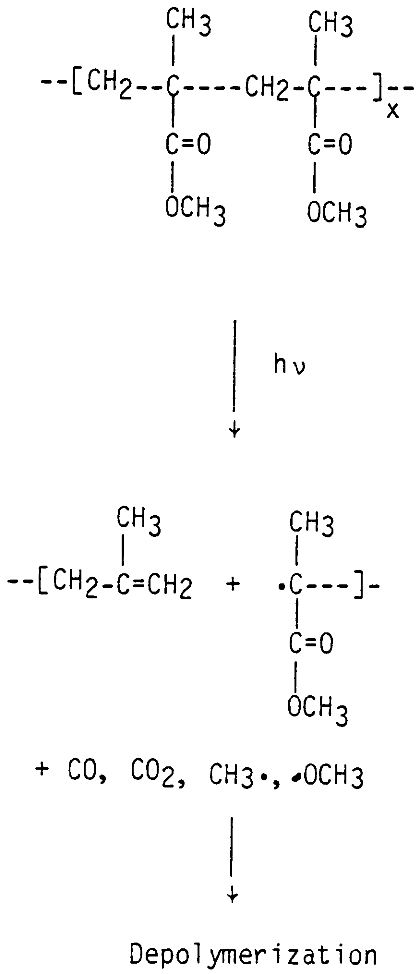
After discussion of the thermal and radiation instabilities of PMMA (and in general most other methacrylates), the chemical stability (or resistance) will now be discussed. Most ester based polymers are notoriously unstable towards acids or bases. The syndiotactic nature of conventional PMMA coupled with its sterically hindered ester group (R_3C-COOR) make it highly inert to most alkaline or acidic media [11]. These effects will be discussed in detail later in this review in the section concerning ionomer synthesis by methacrylate hydrolysis. Poly(methyl methacrylate) is highly resistant to hydrocarbon oils but is attacked readily by a wide range of more polar solvents. The combination of chemical resistance, oxidative and light stability, and relatively low cost provides a tough, transparent material far superior in many applications to other plastics. This combination of properties is represented in Table 6.

4. Controlled Synthesis of Poly(alkyl methacrylates)

Synthetic control in methacrylate polymerization involves control over the following variables:

1. Polymer molecular weight
2. Molecular weight distribution
3. Stereochemistry
4. End group functionality
5. Capability of block polymer formation

Although simultaneous control over all of these synthetic variables has



Scheme V. Radiation Induced Chain Scission of PMMA [31-32].

Table 6

Relative Outdoor Stability of PMMA [11]

Material	Initial light transmittance (%)	Light trans. 3 yrs Exposure (%)	Initial Haze (%)	Haze 3 yr Exposure (%)
PMMA	92	92	1	2
Polycarbonate	85	82	3	19
Cellulose acetate butyrate	89	68	3	70

not fully been achieved, continuing advances in the understanding of polymerization mechanisms has lead to the synthesis of methacrylate polymers where most of the criteria have been met. The development of group transfer polymerization (GTP) [34] has catalyzed interest in the synthetic utility of methacrylate monomers for controlled polymer synthesis.

Anionic "living" polymerization has traditionally been the method of choice in the controlled polymerization of a variety of monomers. Synthetic control over the five parameters listed above can be easily achieved with "hydrocarbon" monomers of the styrene and diene families. The styrene monomers employed include styrene, α-methylstyrene and a variety of alkylated styrene monomers including p-methylstyrene and p-tert-butylstyrene. Diene monomers amenable to anionic polymerization are based on the 1,3-diene skeleton. The most widely utilized diene monomers are butadiene and isoprene. The anionic polymerizations of the monomers listed above are free from termination or transfer reactions in a wide variety of (anhydrous) conditions. If the correct initiators are used, fast initiation and relatively slow propagation occur, leading to narrow molecular weight distributions with predictable molecular weights determined by the monomer/initiator ratio. The non-terminating or "living" nature of these reactive polymeric carbanions provide an opportunity for chemical reactions with a myriad of reagents [5,35] in the synthesis of telechelic (chain end functional) polymers. As an example, polystyryl anions react readily with carbon dioxide and acid to form polystyrene with a carboxylic-functional end group. Block copolymers are easily formed when a second monomer is added to a "living" polymer under the proper conditions. Stereochemistry is usually highly dependent on the solvent dielectric constant and alkali metal counterion. Especially sensitive to these factors are diene microstructures. Due to the many forms of synthetic control achieved in the anionic polymerization of hydrocarbon monomers, they have been the subject of intensive study since the discovery of "living polymerization" in 1956 [36], resulting in many reviews and monographs [5,8,35-38], and also a variety of commercial polymers.

Advances in the controlled polymerization of hydrocarbon (styrene and diene) monomers has not been mimicked by successes in the anionic polymerization of polar monomers, e.g., alkyl methacrylates. These polar monomers are subject to facile side (termination) reactions to the polar (carbonyl) substituent. These termination reactions broaden the molecular weight distribution and make prediction of molecular weight difficult. The resonance stabilized enolate anions are much less reactive toward chain end functionalization agents and less likely to initiate polymerization of a second monomer to form block polymers. And finally, from these more hydrophilic compounds are much more difficult to prepare highly purified anionic polymerization-grade monomers. These deleterious factors have lead to sproradic and retarded growth in the anionic synthesis of methacrylate polymers of controlled structure. After three decades of study, however, synthetic control over most variables has been achieved.

After Szwarc's discovery of "living"polymerization of styrene in 1956 [36] a flury of activity revolved around the polymerization of another more election deficient (and thus more readily anionically polymerizable) monomer, methyl methacrylate. The literature is awash with investigations regarding the complicated polymerization results of MMA in the five years spanning 1958-1962. An investigation of some note preceeding this era by Beamer in 1948 concerned the initiation of MMA by sodium in liquid ammonia. Although moderately high molecular weight polymer was formed ($M_v \approx 16,500$), the author found no amine terminal groups as were found in the case of styrene polymerization. It is difficult to discern if this was simply a molecular weight effect, or as the authors concluded, the initiation is a complex series of events beginning with carbonyl addition and sodium methoxide formation.

The first published work after the events of 1956 [36] (which brought anionic polymerization to the forefront of polymer chemistry) was the discovery of the Rohm and Haas group of T. G. Fox and coworkers [1] in 1958 that alkyl lithium initiation of MMA produces very different polymers in different polymerization media. These workers labelled the three polymer types I, II, and III. Type I polymer, which the coworkers incorrectly labeled isotactic (should be predominately ca. 75% syndiotactic) was synthesized by free radical initiation at low temperatures, or organolithium (9-fluorenyllithium) at -60°C in 1,2-dimethoxy ethane. This polymer had a Tg (from volume-temperature measurements) of 115°C, and a density of 1.19 g/cc. Type II polymer, which the workers called syndiotactic (actually its quite highly isotactic, ca. 90%) resulted from organolithium initiation in toluene at -60°C. The PMMA had a very low Tg (45°C) and could be crystallized by orientation, annealing at 110-130°C, or by the solvent 4-heptanone [39]. The melting point of this material was reported to be 160°C. Type III polymer which is synthesized by organolithium in a non polar solvent with low levels of polar modifier, e.g., dioxane, produced a polymer with intermediate properties and was thought to be a stereoblock, i.e., short alternating sequences of isotactic and syndiotactic isomers.

In 1959, Wenger [40] polymerized MMA in polar solvents (THF) with both sodium napthalene and butyl lithium. Monomer was added in several charges, each time producing higher molecular weight, but not as cleanly (without termination) as Szwarc's "living" polystyrene [36]. Rempp and Schreiber [41-42] first suggested that the complications occuring during MMA anionic polymerizations were caused by terminating (or transferring) reactions to the methacrylate carbonyl, i.e., 1,2 attack, along with the desired 1,4 addition.

An important overall contribution followed, from the "three G's" at Rohm and Haas (Graham, Goode and Glusker). Graham and coworkers [43-45] in a series of investigations studied the stability and reactivity of the methacrylate anion. Graham found that the methacrylate anion:

1. Is relatively stable at -78°C.
2. Will initiate the polymerization of more MMA.
3. Will initiate the polymerization of other polarizable monomers, e.g., alkyl methacrylates, acrylonitrile.
4. Will not initiate styrene polymerization.

Goode [46] studied the Grignard (phenyl magnesium bromide) initiation of MMA in toluene, which produced very highly isotactic (>95%) PMMA. His results can be regarded as representative of MMA polymerization in hydrocarbon media for a wide variety of initiators

(Grignards and alkyl lithiums):

1. Rapid initiation.
2. Polymer formed has a very broad molecular weight distribution.
3. On a mole basis, the majority of material consists of low molecular weight products.

Goode's postulation for observation #3 was that these low molecular products were the result of intramolecular cyclization or "backbiting", although other possibilities such as ketone attack (from the product of 1,2 attack) were not disproven. A summary of Goode's results are shown in Table 7. These results show that hydrocarbon mediated anionic polymerization of MMA are subject to serious terminating side reactions which broaden the molecular weight distribution. Although a great deal of control may be gained over polymer stereochemistry by appropriately adjusting the solvent, initiator and temperature, other aspects of synthetic control were apparently lacking.

The work of Glusker et. al. [47-48] corroborated Goode's result. Glusker was concerned with MMA polymerization in toluene with fluorenllithium initiators. By using tritiated acetic acid to terminate these polymerizations, it was found that greater than 90 mole % of the "chain" have a molecular weight less than 2000 g/mole. The other 10 mole percent of the chains were extremely high molecular weight in nature. Again, Glusker proposed a "pseudo-terminated" or "dormant" cyclized species to explain these results.

A degree of synthetic control began to be realized in this very

Table 7

Molecular Weight Distributions ($\bar{M}_v/\bar{M}_n$) for PMMA [46]

Initiator	Temp.(°C)	Yield (%)	$\bar{M}_v/\bar{M}_n$
n-BuLi	-70	97	3.24
9-fluoroenyllithium	-72	81	19.8
Phenyl Magnesium bromide	0	65	23.6

complex polymerization system with the almost simultaneous realization by both Rempp [49] and Wiles and Bywater [50] that sterically hindered, resonance stabilized initiators were necessary to avoid 1,2-carbonyl attack. The initiator employed by both investigators was the adduct of butyllithium with 1,1-diphenyl ethylene to afford the sterically hindered, resonance stabilized 1,1-diphenylhexyllithium (DPHL). Rempp [49] also seemed to be more aware of the work of the "3 G's" from Rohm and Haas regarding the problems associated with polymerization in toluene [43-48]. While Wiles and Bywater studied kinetics and mechanisms of DPHL initiator in toluene [50], Rempp was studying the synthesis of Polystyrene-PMMA block copolymers in THF at -78°C. Due to problems of side reactions with the highly basic polystyryl lithium with methacrylate ester groups, clean block copolymer synthesis was lacking. Upon addition of DPE, the "capped" polystyryl lithium cleanly initiated MMA polymerization, which was found to proceed quite smoothly (without detectable side reactions) in THF at -78°C. This route to the clean synthesis of PMMA and other alkyl methacrylates is utilized widely today in the "living" synthesis of narrow distribution materials.

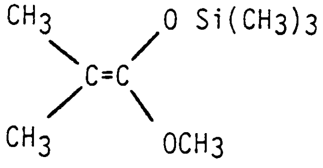
Group Transfer Polymerization

A major breakthrough in the controlled synthesis of acrylic polymers occurred recently with the development of group transfer polymerization (GTP) by Webster and coworkers at DuPont [51-54]. This new living polymerization mechanism shares the attributes of anionic methacrylate polymerization providing poly(alkyl methacrylates) with controlled (usually low) molecular weights, narrow polydispersities, and the ability to readily form block copolymers. The advantages of this new route over conventional anionic methacrylate polymerizations are as follows:

1) These polymerizations are non-terminating over a broad temperature range, from -100°C to greater than +100°C.
2) Quantitative end group functionalization is readily arrived at with GTP.
3) Acrylates may be polymerized in a non-terminating fashion with appropriate catalysts.

Advantage #1 is very important from a commercial viewpoint, where the -78°C anionic route is unsuitable for large scale commercialization. Advantage #2 has many ramifications toward coatings applications, as PMMA polyols may be readily synthesized by these methods. Polyurethane coatings based on PMMA may have many automotive applications. Advantage #3 may provide tacky adhesive coatings with superior properties.

The components of a group transfer polymerization include solvent (THF, acetonitrile, chlorinated aliphatics), monomer, initiator and catalyst. The initiators of choice in many group transfer polymerizations appear to be silyl ketene acetals, specifically trimethylsilyl dimethylketene methyl acetal (1), essentially the



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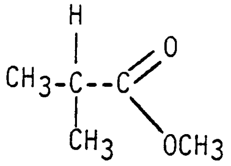
"trapped" enolate of structure (2).



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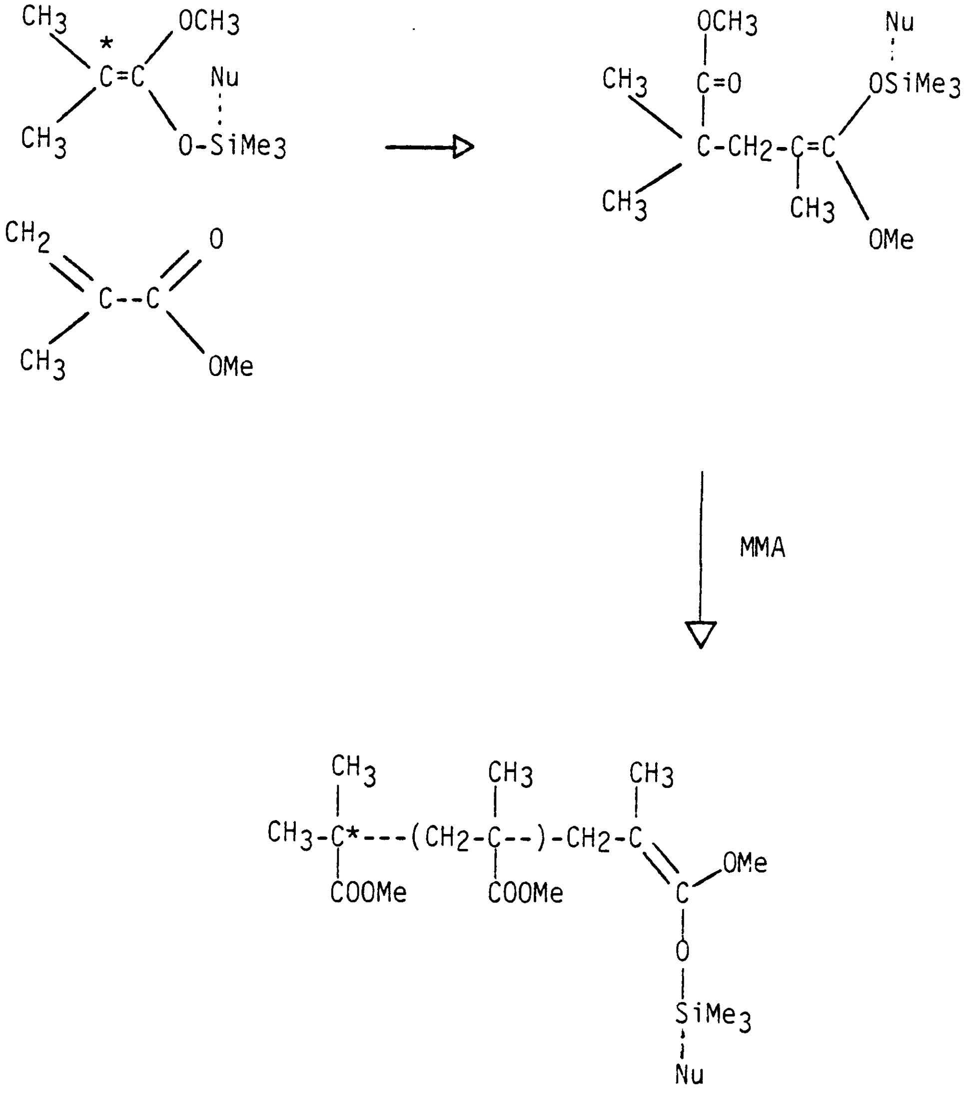
It should be noted that the enolate of (2) is the equivalent of the PMMA anionic chain-end structure.

The GTP initiator contains a group (trimethylsilyl) activated by an appropriate catalyst (bifluoride anion) which is transferred in a stepwise fashion to the carbonyl oxygen of the incoming monomer, hence group transfer. The mechanism of this transfer is elaborated upon in Scheme VI.

The polymerization procedure demands "anionic" purity, as traces of protic impurities will terminate chain ends. These polymerizations are generally conducted under dry argon by charging the initiator and catalyst to the dry solvent at room temperature, followed by slow addition of methacrylate monomer causing a controlled exothermic reaction. Temperature is generally controlled by monomer addition rate. A problem arises due to the lack of color with these initiators and chain end structures. Anionic polymerizations of MMA generally involve highly colored initiators, and thus reactor impurities are titratable, insuring relative control over molecular weights even at high monomer/initiator ratio. This titration is thus far not possible in GTP, causing large deviations of molecular weight unless high initiator charges (low MW) are employed. This expalins why the stoichiometric molecular weights in GTP work are uniformly low, as seen in Table 8.



Scheme VI

Proposed Mechanism of Group-Transfer Polymerization [53]

Table 8

Methacrylate Polymers by Group-Transfer Polymerization with Anionic Catalysts [53]

Monomer(s)	Solvent	Polymer M_N	M_W/M_N	$M_{Stoich.}$
MMA	CH_3CN	3000	1.03	3700
MMA-BMA(Random) 35% 65%	THF	22,100	1.11	20,300
MMA-ethylacrylate(Diblock) 35% 65%	THF	3400	1.92	3500

Recent advances in catalyst chemistry has lead the DuPont researchers nearer to the ability to control acrylate polymerization [54]. The anionic catalysts used in GTP methacrylate polymerization do not polymerize acrylates controllably. Lewis acid catalysts appear to be selective for acrylate polymerization, as seen in Table 9. One would expect that work is ongoing at Dupont in the development of catalysts that polymerize <u>both</u> acrylates and methacrylates controllably, so that methacrylate-acrylate block copolymers, e.g. PMMA-butylacrylate-PMMA triblocks, could be synthesized with high structural integrity. These materials would have extensive applications in pressure-sensitive adhesives, perhaps partially displacing the Kraton (S-I-S) materials.

/ In summary, the basic chemistry exists and has been quite thoroughly studied for the controlled synthesis of novel methacrylate materials. Both anionic and GTP methodologies have been shown to be suitable under very narrowly defined conditions for controlled methacrylate polymer synthesis. If suitable methods are defined for obtaining anionic polymerization grade monomers, a wide variety of new polymer structures may be reproducably synthesized. /

II. B. IONOMERS

1. Introduction

Ion containing polymers (ionomers) are receiving ever increasing attention due to the dramatic effects that small amounts of ionic groups exert as polymer properties [55-59]. Increases in tensile strength, modulus, melt and solution viscosity, glass transition temperature, and a broadening of the rubbery plateau are some of the major changes that

Table 9

Acrylate Polymerization by GTP with Lewis Acid Catalysis [54]

Monomers	Catalysts	M_N	M_W/M_N	Polymer M_{Stoich}	%Yield
ethylacrylate	ZnI	3300	1.03	3400	100
ethylacrylate	ZnBr	17,000	1.57	10,100	100
MMA	ZnBr	6020	1.20	3400	
ethylacrylate	$(i\text{-}Bu_2Al)_2O$	1330	1.19	2100	100
MMA	$i\text{-}Bu_2AlCl$	3000	2.43	1465	21
butylacrylate	$i\text{-}Bu_2AlCl$	2370	1.06	2660	100

occur when ionic groups are incorporated into polymers. These dramatic effects result from significant morphological changes which occur due to aggregation of the ionic groups, even at very low concentrations. The extent of property modification depends generally on the type, amount, and distribution of ionic groups in the polymer, although different polymer backbones are effected to very different extents by the same ions at the same concentration. Although utilization of a wide variety of ionic groups is possible, carboxylates and sulfonates have thus far received considerable attention, due to their stability, ease of incorporation, and high level of property modification at low concentration. Polymer backbones modified most widely include polyethylene (the commercial "SURLYN" materials), polystyrene, poly(acrylates), polypentenamers, ethylene-propylene-diene terpolymers, and polysulfones [58-64]. However, the major difficulty in this field is the lack of available synthetic methods that can lead to the preparation of well-defined ionomeric structures.

Ion containing polymers are prepared via two fundamentally different approaches. The first method involves a post-polymerization reaction in which the ionic group is "grafted" onto a preformed polymer [58,65,66], whereas in the second method a vinyl monomer is directly copolymerized with an unsaturated acid or salt derivative. Another possibility, which in fact is a combination of the above two approaches, is to copolymerize two covalent monomers and then derivatize one by, for example, ester hydrolysis [67]. Carboxylated ionomers are generally synthesized by the direct copolymerization of acrylic or methacrylic acid with vinyl monomers. The copolymers produced are then either partially or completely neutralized with bases to incorporate the various counterions [e.g., Na^+, K^+, Zn^{++}, etc.] into the system. Sulfonate groups are most often introduced into the polymer backbone via post-polymerization reactions using sulfonating agents such as acetyl sulfate or SO_3/triethylphosphate complex in a suitable solvent [58,65,66]. The sulfonic acid groups introduced into the polymer backbone are then neutralized. This method of sulfonation is difficult and is limited to only backbones which provide suitable sites for sulfonation. Therefore, although sulfonated ionomers reportedly exhibit association properties far superior to carboxylated systems [58], relatively limited work appears in the literature on sulfonated ionomers.

The synthetic routes discussed above usually result in random placement of ionic groups along polymer backbones often possessing high degrees of compositional heterogeneity, thus making characterization and interpretation of structure-property studies quite difficult. Although limited work on the controlled synthesis of model ionomers has recently appeared [68,69], the continued advancement of this field depends on further systematic work in this area of polymer synthesis.

2. Structure and Properties of Ionomers

The initially accepted theory for explaining the dramatic strengthening of unvulcanized elastomers upon ion incorporation was advanced in the late 1950's to explain the zinc oxide "curing" of carboxylated polybutadiene [70]. It was felt at the time that these ionic crosslinks simply consisted of the divalent zinc coordinating with two carboxylate ions as in Figure 1. Ths naive view was laid to rest in the next decade with the advent and evolution of the aggregation theories [56-57], although this early explanation continues to be held by some rubber technologists [71].

It is presently felt that the drastic change in properties a polymer undergoes with the incorporation of ionic groups is due to the preferential aggregation of these moities, i.e., a form of microphase separation. The structure of these ion-rich aggregates is a matter which seems to be open to question. Eisenberg [56,59,72] has proposed a conceptually simple but highly useful scheme involving two types of aggregates: multiplets and clusters. Multiplets are defined as small groups of ion pairs with no polymeric content which serve as simple multifunctional crosslink points. Clusters arise from further aggregation of multiplets, forming a larger, more loosely associated structure which may have an appreciable hydrocarbon (polymer) content. Clusters are thus analogous to a microphase separated "hard segment" in a conventional block or segmented copolymer. Many (quite similar) models exist for the exact structure of the clusters [57], which are based on small angle x-ray scattering (SAXS) investigations on many different ionomer systems, all of which possess an "ionic peak" at very low scattering angles ($2\Theta=4°$). Due to the model dependent nature of scattering data interpreation, it is presently difficult to discriminate between the various models proposed for these very complex systems.

As stated above, Eisenberg made a great contribution toward understanding the many complexities of ion containing polymers with his theoretical treatment and experimental verification of aggregation in

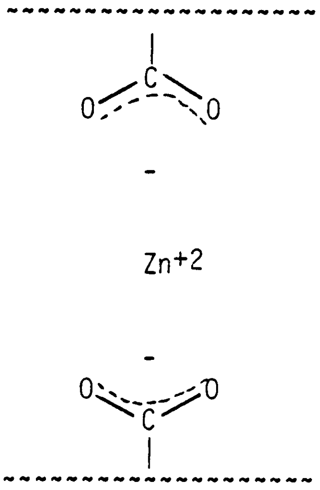


Figure 1. Early View of "Ionic Crosslinking" [70].

these systems [56,72]. A discussion of the molecular parameters effecting this aggregation or clustering in ionomers enables one to better understand the driving forces for aggregation, and thus gives one the means for controlling the aggregation and thus the morphology and physical properties of these systems. The molecular parameters effecting aggregation in ionomers are as follows:

1) ion content
2) ion type
3) counterion and percent neutralization
4) backbone dielectric constant
5) relative position of ionic groups in the polymer chain

The first four of these factors (which profoundly effect the morphology and the physical properties of ionomers) are easily controlled and have been carefully investigated. The results of these investigations will be highlighted. Little attention has been focused on control over ion location, however, due primarily to the synthetic difficulties involved, although preliminary investigations indicate that this factor may exert a profound influence on ionomer properties [98]. Recent work on the controlled synthesis of ionomers, e.g., the synthesis of telechelic (chain end functional) materials will be discussed later in this review.

The above mentioned molecular parameters have been empirically found to dramatically effect ionomer properties. They have, however, also been applied in Eisenberg's theoretical treatment [72] to influence the formation and size of clusters. An equation was derived showing the role of these controllable parameters on cluster size:

$$n = \rho N_{AV}/M_C \left[\frac{4\ell^2}{3kT_c} \frac{h^{-2}}{h_0^{-2}} \frac{M_C}{M_0} \frac{k'}{K} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} + 2 {\frac{M_0 M_C}{\rho N_{AV}}}^{2/3} \right]^{3/2}$$

where: n = cluster size (#multiplets/cluster)

M_C = molecular weight between ionic groups

K = backbone dielectric constant

r = distance between charge centers in the ion pair

e = electronic charge in an ion pair

The other parameters reflect the conformational properties of the backbone, cluster geometry, and characteristics of the basic repeat unit.

Clusters, as stated early in this section, are formed via loose associations of multiplets interspersed with polymer chains. Due to the extremetly low dielectric constant most polymers posess, the ion pairs form higher aggregates in this hydrocarbon medium. These higher aggregates (multiplets) results from dipole-dipole interactions. The interaction of two ion pairs to form a small multiplet (in this case a quartet) arises in a electrostatic, reversible, difunctional crosslink point, as seen in Figure 2. Although higher functionalities are possible, steric limitations prevent these ionic structures from becoming too large. This limitation results from the large, bulky polymer chains attached to the ionic groups which form a hydrocarbon skin around these multiplets. Eisenberg [72], assuming spherical multiplets, has calculated a maximum of eight ion pairs/multiplet for

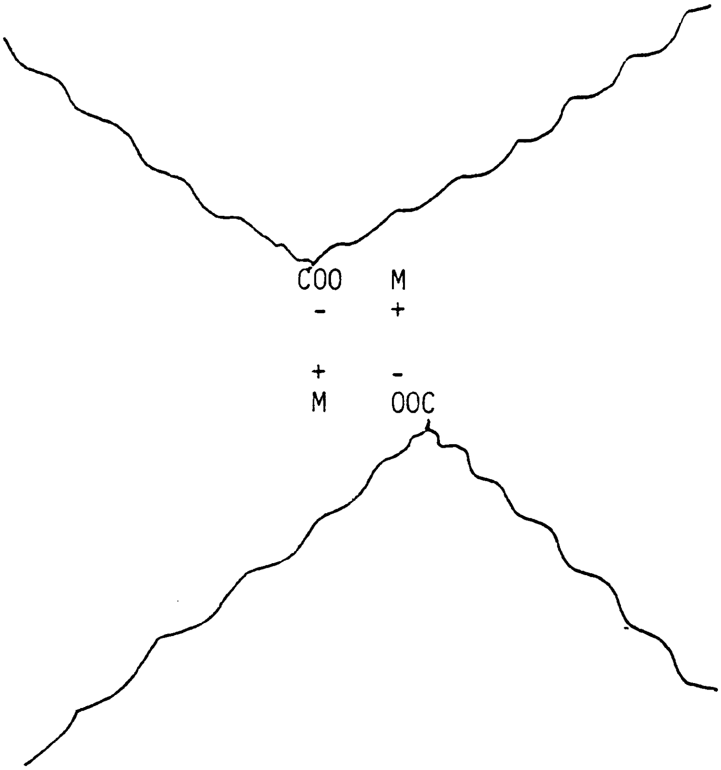


Figure 2. Multiplet Formation.

polystyrene-sodium methacrylate copolymer, although changes in both polymer and ion type, as well as multiplet geometry will surely effect this number. Cluster formation results from the electrostatic attraction of the multiplets for each other. Two opposing forces are in operation here: the electrostatic dipole-dipole attraction of multiplets for each other which favors clustering, and the chain entropic forces (or chain flexability) which impedes it. Thus, for a polymer backbone with a given dielectric constant and flexibility, containing randomly situated ionic groups of a given interactive energy, there must exist a critical ion concentration (analogous to the micellular C.M.C.) above which clustering takes place and below which only multiplets exist. Below this C.I.C., as the ionic content decreases the distance between multiplets increases, lowering the electrostatic attraction between multiplets so that the chain's elastic forces dominate preventing cluster formation. Conversly, at ion concentrations above the C.I.C. the electrostatic energy increases favors cluster formation. An important factor in this multiplet → cluster question not yet mentioned is temperature. There exists a temperature (T_C) (actually a temperature range) above which the chains elastic forces increase to a point where they overcome the ion's electrostatic forces. Thus, the critical ion concentration is a temperature dependent value.

Experimental Evidence

Needless to say, the morphological change resulting from the critical ion concentration (multiplets → clusters) should result in a dramatic change in the properties of the ionomer. The effect of ion content on the thermal, viscoelastic and rheological properties of ionomers will be briefly discussed.

Eisenberg's group [56,59] has been concerned mainly with the study of carboxylate ionomers, extensively studying three very different carboxylated polymer systems: polyethylene [56], a semicrystalline material, polystyrene [73,74], a glassy system, and poly(ethyl acrylate) [75], an amorphous rubber. The polarity or dielectric constant (ε) is quite different for each of these materials. The range of dielectric constants and physical states of these materials provides a systematic investigation of the effect of backbone characteristics on ionomer properties. These characteristics are shown in Table 10. Due to the very complex behavior of ionomers, however, wide-ranging conclusions are quite difficult to draw if more than one variable at a time is altered. Thus, a more desirable comparison of the effect of backbone dielectric constant might be the study of several backbones of the same physical state with a range of dielectric constants. A hypothetical group of interesting glassy backbones is presented in Table 11. The recent investigations of MacKnight [57,61,62,76] and Lundberg [58,63,77] have sparked a great deal of interest in sulfonated ionomers, which have achieved only limited study due primarily to difficulties in the synthesis of these materials.

Due to the young nature of the field, inconsistencies have developed which make the drawing of more than generalities from the diverse body of literature quite difficult. These inconsistencies result from several factors, including the varied systems studied, the

Table 10

Characteristics of Backbone Polymers Serving in Eisenberg's Carboxylated Ionomer Studies [59]

Polymer	State	ε
Polyethylene	Semicrystalline	2.2
Polystyrene	Glass	2.5
Poly(ethylacrylate)	Rubber	4.0

Table 11

Characteristics of Hypothetical Ionomer Backbones

Polymer	State	ε
Poly(tert-butylstyrene)	Glass Tg ≈ 145°	~2.0
Polystyrene	Glass Tg ≈ 100°	2.5
Poly(methylmethacrylate)	Glass Tg ≈ 110-130°	~4.0

number of workers involved, the very random, impure nature of the systems thus far synthesized, and the lack of care taken with synthetic aspects such as neutralization of acids to form the ionomer. At attempt will be made, however, to equate the various molecular parameters with property modifications and structure of selected ionomer systems.

The glass transition temperature (Tg) is one of the most important properties that characterizes a polymer system. The Tg generally provides information on the temperature use range of a polymeric material. It is often desirable to raise the glass transition temperature of a glassy polymer so as to increase its use temperature range. Ion incorporation has been shown to dramatically influence the Tg behavior of most polymers. The studies of Eisenberg [73,74,75] on polystyrene and poly(ethyl acrylate) carboxylate ionomers and MacKnight's studies [61,62,76] on sulfonated polypentenamers will be discussed, with particular emphasis on the effect of ion content (concentration) on the Tg of these materials.

The incorporation of carboxylate ions into polystyrene, via a free radical bulk copolymerization of styrene with methacrylic acid followed by NaOH titration, raises the glass transition temperature dramatically [74]. For example, with 9 mole % ion content the Tg increase for this system is 30°C, from 100°C (PS Tg) to 130°C (PS-NaMA Tg). This effect is seen in most ionomers. Generally, the Tg increases slightly with acid incorporation and then dramatically increases with neutralization. The system which has achieved perhaps the most study in this regard is the ethylacrylate-based carboxylate ionomers [75]. These materials were prepared via a free radical solution copolymerization of ethyl acrylate and acrylic acid, followed by neutralization via NaOH titration and very careful drying. The copolymers contained a range of acid concentrations, from 4.4 mole percent to 18.1 mole percent. While the Tg's of the acid-acrylic copolymer increased linearly with acrylic acid content as expected, a plot of Tg as a function of ion content for the neutralized materials provides a sigmoidal curve. The DSC data for these ionomers is given in Table 12. When the counterion is changed, the location of the sigmoid changes. These curves (Na^+ and Cs^+) coalesce into one sigmoidal curve when Tg is plotted against $C \cdot q/a$, where C is ion content, q is the formal charge of the counterion and a is the interatomic distance of the ion pair. Thus, a small (hard) cation will possess a larger q/a value than a larger (soft) cation. The importance of this finding is that the occurance of the sigmoid corresponds to the ion content (12 mole% for Na^+) where the time-temperature superposition principal fails, as found in viscoelastic (stress relaxation) studies of these interesting materials [78], indcating the formation of a two phase system. The time temperature superposition holds only for materials with one major relaxation mechanism, and fails when two mechanisms (as in two phase systems) appear. Thus, using Eisenberg's terminology, it seems that for ethyl acrylate-based carboxylate ionomers (with sodium counterion) the critical concentration for clustering (C.I.C.) appears to be around 12 mole % ion content. It should be noted that the time-temperature superposition holds for the PEA-Acrylic acid copolymers (before neutralization). The relatively high concentration for clustering can be rationalized from several points of view, including the high (4.0)

Table 12

Tg's for PEA Ionomers [75]

Acid Content (mole %)	Counterion	Tg(DSC)°C
0	-	-25
4.4	Na^+	-11
9.4	Na^+	3
12.0	Na^+	11
16.3	Na^+	30
16.3	Cs^+	12
18.1	Na^+	45

dielectric constant and flexability of the backbone, which favor multiplet formation. These multiplets which are present below 12 percent act as crosslinks which restrict chain mobility and thus raise the Tg. Above 12 percent sodium carboxylate ion concentration, clustering occurs and a second phase is generated, much like in a phase separated block copolymer.

When the lower dielectric constant polystyrene backbones were investigated [73,74], the sigmoidal behavior of the Tg with ion content was not as obvious due to scattering of data, although failure of the time temperature superposition principle at 6 mole percent sodium methacrylate content coincided with the formation of ion clustering by SAXS evidence [73,57,56]. Another important finding of this study was the reestablishment of the time-temperature superposition at higher temperatures (above the T_c). Thus, for essentially the same ionic moities (sodium carboxylates), the different backbones with differing flexabilities and dielectric constants have very different C.I.C.'s for clustering, twelve mole percent for the polar ethylacrylate system and six mole percent for the more hydrophobic polystyrene system. When the backbone dielectric constant is further lowered as in the polyethylene-sodium methacrylate case, evidence indicates that the critical concentration for clustering occurs at very low levels, around 1 mole percent [56].

MacKnight [79] used DSC and dynamic mechanical measurements (Rheovibron) to study the effect of various concentrations sodium sulfonate ions on the properties of unvulcanized polypentenamer. The materials studied ranged from 2 to 18 mole percent sulfonation, although complete neutralization of the sulfonic acid residue was never realized. This is not a trivial matter, since it is well known that sulfonic acids are not stable and may crosslink, particularly in the presence of highly reactive carbon-carbon double bonds.

Sulfonation reactions were carried out on a Goodyear polypentenamer containing 82% trans, 17% cis and less than 1% vinyl double bonds. The molecular weights were high with broad distributions as with all coordination polymerized material. Sulfonations were performed with a 1:1 complex of sulfur trioxide-triethyl phosphate in chloroform at room temperature. Neutralization was performed by precipitating the polymer into a basic ethanol-sodium hydroxide solution, a practice which lead to incomplete neutralization, resulting in the presence of highly reactive sulfonic acid moities. These relatively unstable polypentenamers were stablized with hydroquinone.

Five samples were prepared, and the degree of sulfonation as well as neutralization are given in Table 13. The DSC results showed that the glass transitions both broadened and increased as the degree of sulfonation increased. Table 13 also contains a summary of the DSC data. At 6.7 mole percent sulfonation, the glass transition is in a narrow range centering around -85°C while at 17.6 percent sulfonation the Tg has broadened considerably and is centered around +30°C. The glass transition temperatures seem to be increasing linearly up until ten mole percent of ion content. This seems to indicate a kind of "copolymerization" type of relationship (in combination with a crosslinking effect) which qualitatively follows the Fox or Gordon-Taylor relationships, perhaps indicated a one phase system.

Table 13

Characterization Data for Sulfonated PP's [79]

Sample	% Sulfonation	% Neutralization	Tg (°C)
$PPSO_3Na(2)$	1.9	89	-95
$PPSO_3Na(5)$	6.7	72	-85
$PPSO_3Na(10)$	10.8	73	-72
$PPSO_3Na(15)$	14.3	78	-38
$PPSO_3Na(20)$	17.6	74	+31

Above ten mole percent of sodium sulfonate groups, this linear relationship (see Figure 3) is broken. The glass transition sharply rises with ion content. This indicates some type of critical behavior, discussed earlier in this review as the multiplet to cluster transition, which occurs around ten mole percent for this polymer-ion pair combination.

The relaxation data from the dynamic spectra give much information regarding the transitions when combined with information from the DSC. Table 14 gives the temperatures (at 11Hz) at which the relaxations α, β, and γ occur.

The two percent sulfonated polypentenamer shows three relaxations, while the five percent sample shows only two relaxations, having no α relaxation. The β and γ relaxations are unchanged. As the DSC showed, the two percent sample crystallized at -65 degrees centigrade and melted below room temperature, presumably due to the high trans content and very low degree of sulfonation. All higher degrees of sulfonation showed no tendency to crystallize. Thus, the α relaxation in the two percent sulfonated sample is due to the melting of the high trans containing crystals.

The ten percent sulfonated polypentenamer shows three transitions. This time the α transition is not due to crystallinity, as DSC confirmed that none exists at this sulfonation level. This α relaxation is fairly small for the ten percent sample, but increases with increasing ion content above this level. Because of this increase, it was felt that this α relaxation peak at ten percent sulfonation levels or greater (wich also corresponds with the critical point above which the Tg arises

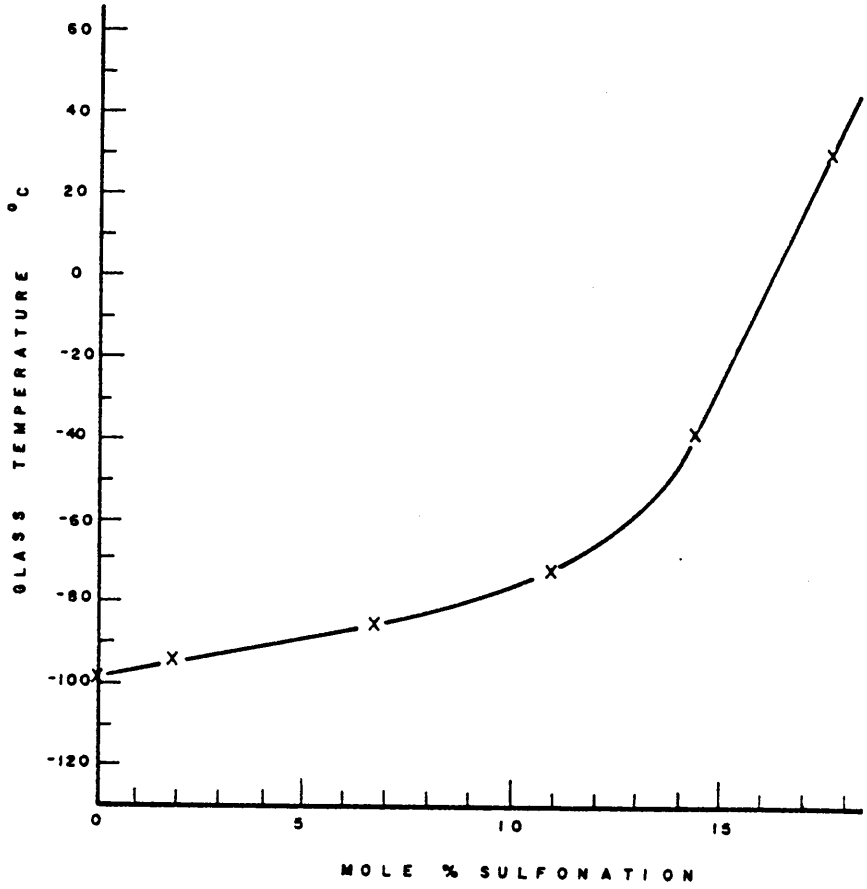


Figure 3. Tg vs. Sulfonation degree [79].

Table 14

Temperatures of Relaxations in Sulfonated PP's [79]
(°C at 11 Hz)

Sample	$\alpha(E'')$	$\beta(E'')$	$\gamma(E'')$
$PPSO_3Na(2)$	-8	-77	-130
$PPSO_3Na(5)$	-	-72	-130
$PPSO_3Na(10)$	0	-49	-120
$PPSO_3Na(15)$	25	-35	-123
$PPSO_3Na(20)$	12	-35	-120
$PPSO_3Na(15);H_2O$	-	-36	-123
$PPSO_3Na(20);H_2O$	-68	-35	-134

All temperatures have error bounds of ±3°C.

exponentially) could be due to the ionic cluster. To confirm this hypothesis, the two samples with the highest levels of sulfonation (15% and 20%) were run both "dry" and "wet", dry being exposed only to atmospheric humidity and wet being immersed in distilled water overnight. For the 15% dry sample, three relaxations were encountered, with the α relaxation more intense than that of the 10% sample and at a slightly higher temperature. The wet sample (15%) had absorbed 72% of its weight in water, which corresponds to about twenty three molecules of water per molecule of sodium sulfonate. The dynamic spectrum shows that the α relaxation has disappeared in the wet sample while the β and γ relaxations remain essentially unchanged. The behavior of the storage modulus is also changed drastically from the dry to the wet sample. Although the storage modulus decreases slightly at the β relaxation in the dry sample, it drastically drops at the α relaxation. The wet sample shows a drastic drop in modulus at the β relaxation, however.

For the 20% sulfonated polypentenamer, the α relaxation has become the dominant mechanism in the dry state. The storage modulus decreases only at the α relaxation. The sample absorbs 84% of its weight when immersed in water, which again corresponds to about 23 molecules per ionic group. The water absorption has not affected the temperature of the β and γ relaxations, but has lowered by 80 degreees centigrade the temperature at which the α relaxation occurs. This is truly a water plasticization effect of the ionic cluster. The storage modulus drops at the β relaxation in this sample.

This important study has shown that in this particular polymer-ion pair system, at a critical ion content of ten percent, clustering may occur which is evidenced by an exponential increase in the glass transition temperature with ion content above this point, and the development of a dynamic mechanical relaxation mechanism which is proportional in intensity to ion content. These ion-rich clusters are readily plasticized by water. As the dielectric constant of this backbone is quite low (~2.0), the very high C.I.C. for clustering is somewhat surprising. A portion of this effect may be due to the high flexability of the polypentenamer chain, which favors multiplet formation, but this author feels that part of the reason for this high C.I.C value is the incomplete neutralization which effectively lowers the ion content, i.e., ion content does not equal sulfonation level. This incomplete neutralization may also cause crosslinking in this system, further complicating to results.

This critical ion concentration is dependent on the type of ion pair present in the ionomer. By far the most studied ionic groups have been carboxylates and sulfonates, as discussed above. In a landmark investigation, Lundberg and Makowski [58] studied the sulfonate vs. carboxylate question by carboxylating and sulfonating identical monodisperse samples of polystyrene. Sodium ionomers of sulfonated and carboxylated polystyrenes were synthesized with a range from 0.3 to 5 mole percent ionic functionality. Sulfonation was carried out using acetyl sulfate in 1,2-dichloroethane. Carbonation of polystyrene was achieved by bubbling CO_2 gas into a solution of lithiated (BuLi/TMEDA) polystyrene in THF/cyclohexane. Thermo mechanical analysis (TMA) of both the 5 percent samples are shown in Figure 4. Both of the polystyrene ionomers show small increase in the glass transition

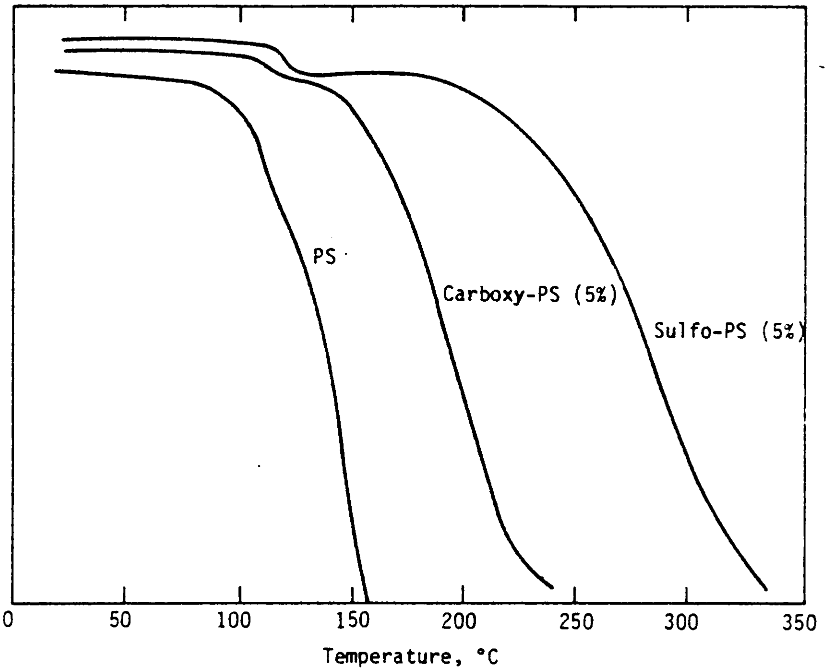


Figure 4. TMA of Polystyrene, and Ion Modified PS [58].

temperatures, but extension of the rubbery plateau is the most noteworthy feature. The carboxylated polystyrene (5 mole percent) exhibits a small plateau until just past 150°C where flow begins to occur. The sulfonated ionomer (5 mole percent) shows a rubbery plateau region well past 200°C almost 75 degrees higher than the carboxylated version and 125 degrees higher than unmodified polystyrene. This qualitatively shows the effect small amounts of ionic character may have on polymer behavior, and also demonstrates the much higher associating power of sulfonates over carboxylates. Thus, sulfonates seem to be the ions of choice for polymer modification, in that less are required (vs. carboxylates) to achieve substantial property improvement. These highly associating sulfonated ionomers suffer from a serious limitation arising from this same property (superior aggregation) that makes them so attractive from a bulk property point of view: very high melt viscosity. Figure 5 shows the melt viscosity (poise) vs. mole percent sodium salt content at 220°C for both the sulfonated and carboxylated polystyrene ionomers. Unmodified polystyrene had a melt viscosity of $4x10^3$ poise in the conditions of the test. A two percent carboxylated polystyrene has a melt viscosity of $4x10^5$ poise, while the sulfonated ionomer of comparable ion content has a melt viscosity greater than 10^8 poise. This again shows the aggregating power of sulfonates over carboxylates, even in the melt.

Eisenberg has compared the viscoelastic properties of sulfonated [80] and carboxylated [73] polystyrene ionomers. A problem with this comparison is the different molecular weights studied. The sulfonated PS had a relatively low molecular weight (30,000) while the carboxylated

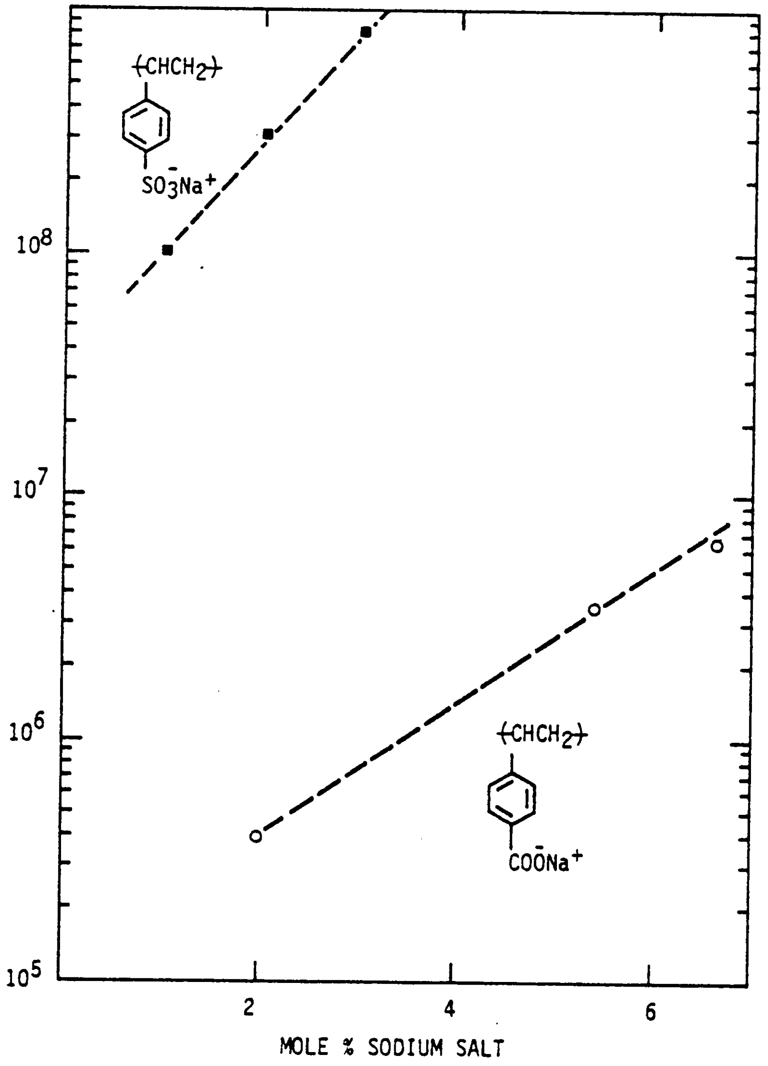


Figure 5. Melt Viscosity vs. Ion Concentration [58].

polystyrene had a very high molecular weight (>105). Quite surprisingly, the failure of the time-temperature superposition corresponded to similar ion concentration for both materials (5-6 mole percent). Not surprisingly, however, a tan δ peak corresponding to the cluster Tg found at 9.9 percent sulfonation occured at a higher temperature than was found for the carboxylated system. More work should be done in this area to determine the effect of ion type on the CIC.

Although only briefly alluded to earlier, the effect of counterion (or cation) on ionomer properties is often dramatic. As introduced in Eisenberg's q/a scheme, the principle differences are due to the formal charge of the cation and also the interionic distance, although recent work of Weiss [81] indicates that this q/a scheme is an oversimplification, and that the coordinating power of the cations is very important in explaining some of the complex behavior found with various cations. Sulfonated EPDM elastomers are a good example of this phenomenon. These ionomers have achieved a great deal of study [63,77,82-84], and are close to commercial reality. Although dramatic changes in properties occur at very low sulfonation levels (1-2 mole%), these ionomers are exceedingly difficult to process, due to the extreme melt viscosities. Makowski and coworkers [77] studied the effect of counterion on sulfonated EPDM's prepared from the same base sulfonated EPDM (which is very important, since changes in molecular weight, ENB (the non-conjugated diene) content and distribution, and ethylene content can greatly effect results). The degree of sulfonation is less than one mole percent. Cations studied were Hg, Mg, Ca, Co, Li, Ba, Na, Pb, and finally Zinc. The mercury cation gave the highest melt viscosity, basically showing no signs of flow. Most of the remaining cations (Mg, Ca, Co, Li, Ba, and Na) gave very high, identical melt viscosities. This extremely high degree of association is achieved in a material with one ionic group per 200 backbone carbon atoms.

Only the lead and zinc cations showed a signficiant amount of melt flow. The lowest melt viscosity was achieved with the zinc cation. This may seem surprising, since it would conventionally be thought that monovalent cations would show less aggregative tendencies than a divalent zinc cation. Adding excess zinc acetate during neutralization lowers the melt viscosity even further, since excess zinc is present which result in a higher degree of monosulfonates.

This initial study showed that elastomers with high tensile strengths easily result when sulfonate salts are incorporated into EPDM. But balancing mechanical properties with rheological considerations is a much more difficult task. By carefully choosing an EPDM backbone with an appropriately low molecular weight, sulfonate content, and a zinc counterion, good elastomers which do indeed flow can be produced. Even with the incorporation of a rubber recipe (processing oils, fillers, etc.) these sulfonated EPDM's show much higher melt viscosities than polymers which are normally extruded or injection molded. New plasticizers needed to be developed in order to make this new and movel system more economically realistic.

Makowski and Lundberg [82] developed additives which both dramatically improved melt viscosity and mechanical properties. The successful plasticizers happened to be ionic derivatives of stearic acid. Stearic acid itself appreciably lowers the melt viscosity of the zinc sulfonate EPDM, but detracts from the high temperature mechanical properties of the material. Also, "blooming" occurs if over 10 phr stearic acid is added to the ionomers.

Although many metal stearates were tested, zinc stearate has been recognized as the best candidate for the plasticization of sulfonated EPDM ionomers, especially the zinc ionomers. This is due to a number of reasons:

1) It is one of the best candidates for increasing melt flow.
2) Zinc stearate increased the tensile strength of all the metal sulfonate systems tested.
3) The best tensile properties were observed in the zinc stearate-zinc sulfonate system, at both room temperature and at higher temperatures.
4) The system could tolerate very high loadings of zinc stearate without blooming occuring. Over 60 phr zinc stearate could be tolerated.

Thus, plasticization of sulfonated EPDM has produced thermoplastic elastomers with acceptable melt flow. Surprisingly enough, in addition to dramatically decreasing melt viscosity, zinc stearate also increased the tensile strength of sulfonated EPDM. It has been postulated that the plasticizer may also be acting as a filler at the use temperature, as it melts above 120°C. The ionomer may interact with this type of filler particle, thus acting as a reinforcing filler [77]. In conclusion, much knowledge about counterion effects are empirical in nature, i.e. theory has not yet caught up with experiment in this young field.

The only molecular parameter not yet mentioned is the position or architecture of ionic groups along a polymer chain, which may in fact be the single most importnat parameter effecting the properties of ionomers. As discussed earlier, almost all the systems thus far studied have resulted from post-reaction or free radical copolymerization with an acidic monomer. The resulting ionomers have a random distribution of ionic groups with a great deal of compositional heterogeneity. Molecular weights and their distribution are also not controlled. The synthesis of telechelic (chain end functional) ionomers has been the first step in controlled synthesis of well defined ionomers [68,69]. Much more work needs to be done, however, to carefully synthesize very well defined series' of ionomeric materials to be able to obtain more definite structure-property relationships. This author feels that the use of anionic polymerization is ideally suited for this task. As Prof. Eisenberg states, "In any case, the general understanding of ionomers and their structure-property relations entails a much more extensive exploration than has been undertaken to date of the effects of the various molecular parameters, in particular the effects of ion position, ion type, counterion type, and the dielectric constant of the backbone" [59].

3. Synthesis of Controlled Ionomer Structures

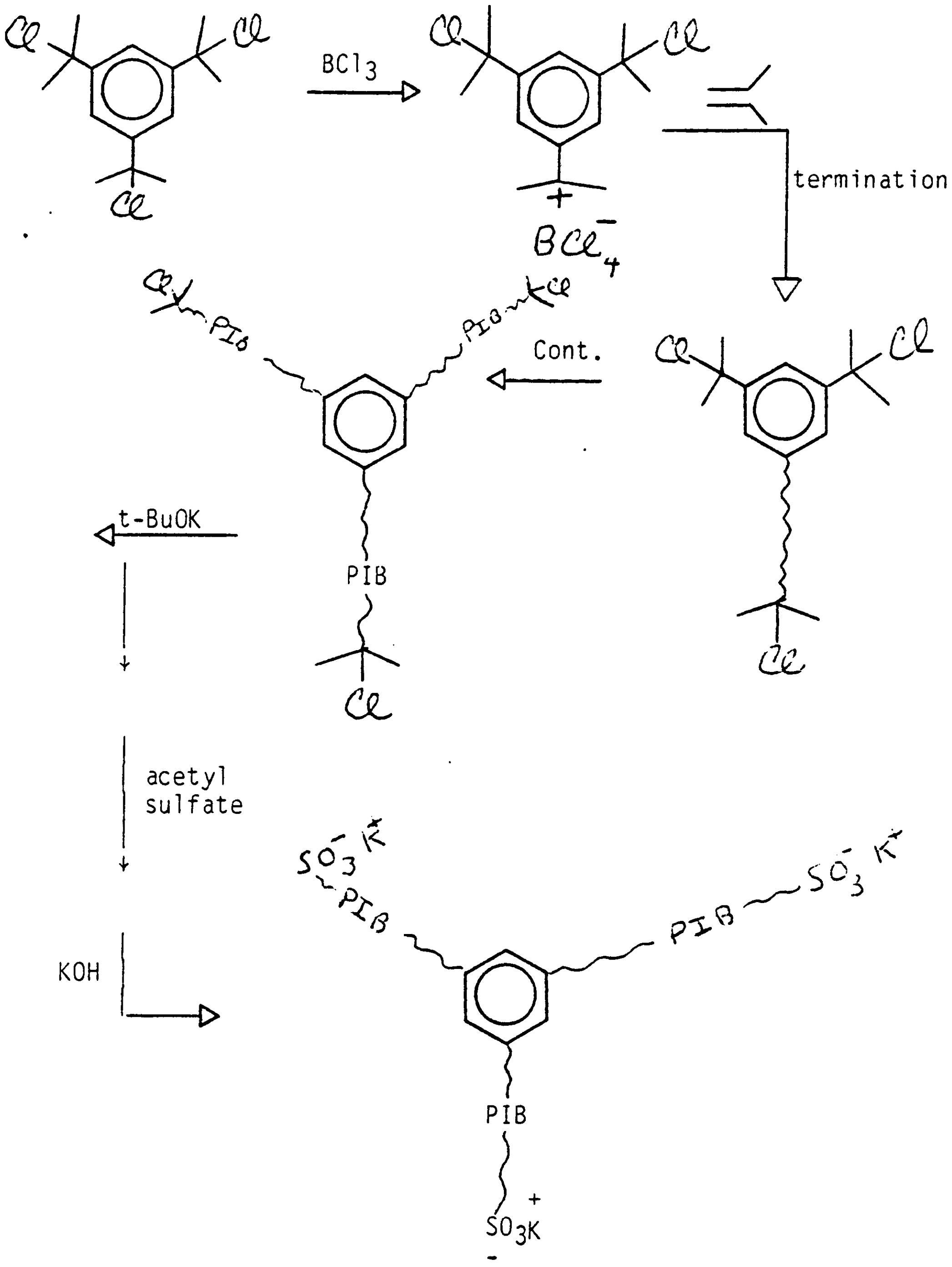
"Telechelic" polymers are defined as chain end functional materials. Thus, telechelic ionomers are quite simply ionomers with the ionic groups located only at the chain ends. This architecture simplifies the characterization task, as both the number of ions per chain and the molecular weight between ions may be obtainable. Two research groups which are instrumental in the development of this field are the groups of Teyssie and Kennedy. Teyssie has dealt with telechelic linear polybutadiene, while Kennedy has developed the synthesis of three-armed telechelic polyisobutylene. This review will cover briefly Teyssie's work, as it developed earlier, and then Kennedy's new route to novel, fairly well defined ion containing thermoplastic elastomers.

Most of Teyssie's interest has dealt with solution properties of telechelic polybutadiene carboxylated ionomers [68,85-86]. Some preliminary results regarding the properties of these telechelic ionomers have recently appeared, [87-88]. The base polymer principally utilized is HYCAR CTB (Goodrich: Mn=4600 and Mw/Mn = 1.8) made via free radical polymerization (~80% 1,4 content). Anionically polymerized difunctional polybutadiene has also been utilized, although it was synthesized in THF via electron transfer initiation and thus has a very high 1,2 content, losing its elsatomeric properties near 0°C. Recent developments in anionic difunctional polymerization initiators soluble in nonpolar solvents which may produce difunctional polybutadiene with a 90% 1,4 content may lead to telechelic polybutadiene ionomers far superior to Teyssie's materials [89-90]. In addition to the high 1,4 content (low Tg), these initiators are capable of producing polybutadiene in a highly controlled manner (narrow distributions with controlled molecular weights). Typically, carboxy terminated polybutadiene is neutralized in toluene by adding a stoichiometric amount of magnesium methoxide in methanol. No effect of neutralization on the glass transition temperature (-80°C) was found. The unneutralized materials are of course liquids, but upon neutralization elastomers exhibiting a rubbery plateau (up until room temperature) are observed. A SAXS investigation [88] has claimed a lamellar morphology exists at two percent ion content. This morphology (Bragg "d" spacing) is independent of counterion, but dependent on ion concentration or polybutadiene molecular weight.

Much more careful work on polyisobutylene-based telechelic sulfonated ionomers has recently been initiated by Kennedy and Wilkes [91-95]. A synthetic technique has been developed utilizing cationic polymerization to produce three arm star polyisobutylenes bearing terminal olefin sites. These are quite easily sulfonated to afford (ideally) a 3 armed polyisobutylene with three sulfonate groups per chain, each group located at the end of a chain. Scheme VI shows the oversimplified and idealized synthetic methodology [91].

The characteristics of the three armed polyisobutylene are not given, other than Mn (osmometry). No mention is made of characterization of arm number or molecular weight distributions, although for sulfonic acid determination a titration method was discussed.

Two counterions were originally studied, calcium and potassium. The calcium ionomer typically gives higher elongations at break along with higher stress at break. Typical values are over 1000 percent elongation and stress values of greater than 6 MPa. An upturn in the stress-strain curve at high elongations indicates that strain induced crystallization is taking place, offering an additional reinforcing mechanism. This effect was corroborated by WAXS [93-95] and given



Scheme VI. Synthesis of PIB Star Ionomers [91-92].

fairly detailed attention. It is novel that such low molecular weight materials (Mn=9000) show strain induced crystallization, as linear PIB's show this behavior only at very high molecular weights. This effect must be due to the ionic associates remaining stable at high elongations.

These ionomers have several advantages over sulfonated EPDM's and are clearly better than carboxy terminated polybutadienes. They are exceedingly easy to process (can be molded at 150 degrees centigrade) and have a lower permanent set than zinc stearate EPDM's. At 200% elongation, only 10% set was found. The strain induced crystallization behavior at higher elongations (the exact elongation depends on M.W. and cation) provides an additional strengthening mechanism, much like that of natural rubber. These materials are exceedingly interesting and will generate many new ideas in the field of ion containing elastomers.

Another route to ionomers not yet discussed is the copolymerization of vinyl monomers with ionic monomers. Although copolymerization of acrylic acid monomers for ionomer synthesis has long been utilized, very little work with ionic monomers has been attempted. Solubility problems have mainly precluded this route to ionomers. Several attempts have been made to copolymerize sulfonated styrene with vinyl or diene monomers via emulsion polymerization. Most have met with poor results [96-97], presumably due to the fact that organic soluble initiators were used. However, quite recently success has been achieved in the emulsion copolymerization of sulfonated styrene (sodium and potassium salts) with various acrylate monomers (e.g. n-butyl acrylate) using a water soluble initiating system with a nonionic emulsifier [98]. Acrylic elastomers with novel properties are produced in high yields. These elastomers are soluble in mixed solvent systems only when chain transfer agents are used. The insolubility of the acrylate ionomers produced without chain transfer agent was thought to be from the combined effects of high molecular weight and ionic association.

The sulfonated acrylate ionomers produced in this way can be compression molded at 200°C to produce transparent, strong elastomers. The behavior of these materials is extremely different from the studies of Eisenberg [75], where copolymerization of the acid with the ester was performed. As stated earlier in this review, the Tg of the ethyl acrylate ionomers rises sharply with ion content, and shows a critical ion concentration of 10-15 mole percent. The polymers synthesized by Yilgor et. al. [98] by emulsion copolymerization show no change in the glass transition with ionic content, however. At the same time, dramatic increases in the tensile properties of these materials result. The above facts lead these workers to believe that emulsion copolymerization of vinyl monomers with ionic monomers (sulfonated styrene) result in block ionomer formation. These block ionomers maintain a low Tg while developing a highly extended rubbery plateau. These two complimentary effects have important ramifications in thermoplastic elastomer synthesis. This is the first evidence that the relative location of ionic groups drastically effects ionomer properties, a molecular parameter ignored in previous studies of ionomers.

Several other miscellaneous reactions are available to aid in the controlled synthesis of ion containing polymers. These post-polymerization reactions would typically be preformed as well defined polymers bearing labile (pre-ionic) functionalities at controlled locations. The reactions discussed below have, in most cases, already been performed on polymers, but not in the controlled synthesis of well defined ionomers.

Poly(alkylmethacrylate) Hydrolysis

The hydrolysis of methacrylate and acrylate polymers (especially PMMA) has received sporadic attention for several decades. The effects on hydrolysis rate of tacticity [99], ester-alkyl group [100-101], and acid or base catalysis [99,102] have been studied. Hydrolysis of PMMA has most often been employed in the synthesis of "tactic" poly(methacrylate acid). Hydrolysis reaction has even been used for ionomer synthesis in an investigation by M. W. Williams [103-104] for ionomer synthesis. Williams synthesized, by free radical solution polymerization, butyl methacrylate-styrene copolymers containing a range of the styrene "diluent" from 0 to 39 percent. These polar starting materials were partially or fully soluble in relfuxing isopropanol, a medium which also dissolves sodium hydroxide. Williams was able to achieve very low levels of hydrolysis by this method, although no discussion is given regarding the details of this procedure, e.g., the reaction times, hydroxide concentrations, etc.

The early studies involving the hydrolysis of methacrylate polymers dealt with the effect of tacticity as the acid and base hydrolysis of PMMA [99]. Essentially three PMMA's of various tacticities were hydrolyzed using both base (aqueous NaOH in isopropanol) and acid (p-toluene sulfonic acid in acetic acid/water mixtures of 4/1) catalysts.

The characteristics of the various PMMA's are elaborated upon in Table 15. The alkaline hydrolysis of the various PMMA's is carried out in a heterogeneous medium consisting of an organic solvent (isopropanol) and aqueous base (NaOH) at 80-85°C. The hydrolysis data for the above mentioned polymers is given in Table 16. As can be seen from the data, while isotatic methacrylate polymers undergo (basic) hydrolysis at very fast rates, both of the predominantly syndiotactic materials are quite inert toward basic conditions, as would be expected for these highly hindered polymeric esters (R_3CCOOR) [105]. It should also be noted that the sterically hindered methyl esters undergo nucleophilic hydrolysis much more quickly than their higher alkyl group counterparts. Glavis [99] has also tried acid catalyzed hydrolysis reactions on these PMMA starting materials. A homogeneous medium was employed for the p-toluene sulfonic acid catalyzed hydrolysis reactions. The unusual hydrolysis medium contained 400g acetic acid and 100g water. These reactions were quite slow, involving refluxing of these mixtures at 110°C for 14 days. Even with these drastic conditions, both "conventional" PMMA and type I polymer were hydrolyzed to very low extents (6%).

The hydrolysis of esters containing alkyl groups which can stabilize carbonium ions, e.g., t-butyl-, allyl and benzyl esters, undergo under mild acid catalysis alkyl-oxygen cleavage to form carboxylic acids by a different mechanism [105]. This technique has been repeatedly employed in the synthesis of poly(methacrylic acid). One of the earliest investigations in this regard dealt with the dilute

Table 15

Characteristics of PMMA Starting Materials [99]

Type	Mv	Stereochemistry[b]
Conventional[a]	100,000	60% syndio
I	130,000	70-75% syndio
II	129,000	70-80% iso

a) Free radical bulk polymerization, AIBN, 60°C.

b) This writer's estimation.

Table 16

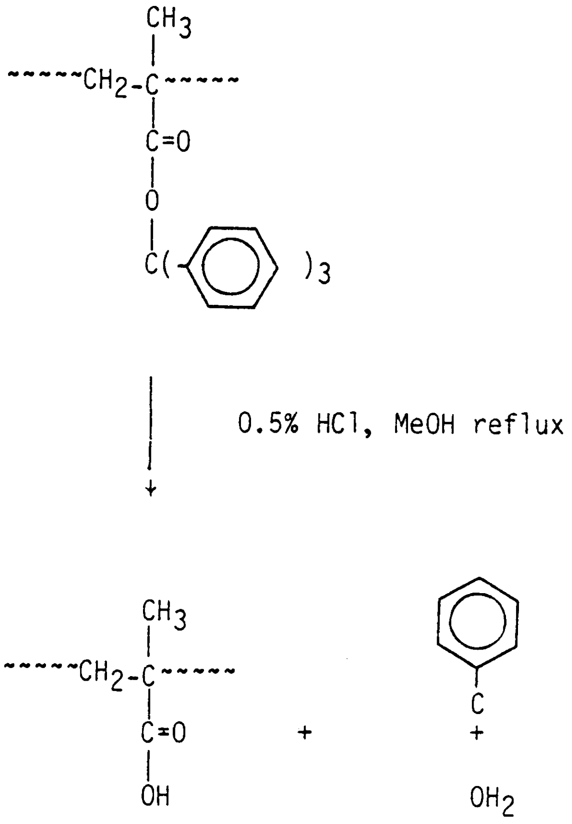
Basic Hydrolysis of Methyl Methacrylate Polymers [99]

Type	Degree of hydrolysis, (%) 1.5 hr	24 hr	140 hr
Conventional	13	39	50
I	11	33	45
II	49	75	75

HCl hydrolysis of crystalline poly(t-butyl acrylate) [102]. It was found that hydrolysis of this material lead to crystalline poly(acrylic acid) by the crystalline x-ray pattern, although it was not determined whether this crystallinity was due to the stereoregular (isotactic) structure or the very high intermolecular forces involved (strong hydrogen bonding).

This hydrolysis technique has been extensively utilized by Yuki and Hatada, [100,106-107] in the hydrolysis of bulky, tertiary alkyl esters such as poly(trityl methacrylate) (Scheme VII) in the stereochemical elucidation of anionically prepared methacrylate materials. The facile hydrolysis to poly(methacrylic acid) is typically followed by methylation with diazomethane to form PMMA, which is easily stereochemically characterized using high resolution ^{1}H NMR. The conditions employed lead to quantitative hydrolysis in three hours, partly due to the reactivity of the trityl group, but also no doubt due to the highly isotactic nature of the polymer. The major limitations of trityl methacrylate are the difficult preparations, difficult purification due to its solid nature, and low-yielding polymerization to give only highly isotactic products.

The difficulty in hydrolyzing conventional methacrylates, e.g., methyl-, ethyl-, and n-butyl- esters, has lead to the development of a novel methacrylate which is readily purified, polymerized to high yields with controlled tacticity and rapid, quantitative hydrolysis. This monomer is trimethylsilyl methacrylate (TMSM) which is prepared by three different methods. Tsuruta and Furukawa [108] prepared the monomer by reaction of silver methacrylate with trimethylsilylchloride.



Scheme VII. Hydrolysis of Poly(Trityl Methacrylate) [100].

Larger quantities were prepared by Aylward [109] by the base catalyzed route involving methacrylic acid, trimethysilyl chloride and dimethylaniline. The purification of the monomer using this route leads to high degrees of hydrolysis, however. The currently utilized preparative method has been developed by Chapman and Jenkins [110]. They utilize the active silating agent hexamethyl disilazane with methacrylic acid, in which the only reaction byproduct is ammonia, allowing for facile purification. This monomer may be polymerized to yield polymers with a variety of tacticities ranging from highly isotactic to highly syndiotactic. Hydrolysis is quantitatively performed with refluxing aqueous base for short times (1-12 hours), first forming a suspension which gradually solubilizes due to the carboxylate ion (polyelectrolyte) formation [109,111]. The soluble polyelectrolyte is typically precipated by acidification with HCl.

The hydrolysis methods discussed above have been performed on block polymers to form methacrylic acid [114-115] or polyelectrolyte [112-113] blocks. As expected, trimethylsilyl methacrylate units were typically utilized, due to the quantitative nature of their hydrolysis. Stille [112] attempted to hydrolyze various poly(alkyl methacrylates) and acrylates in addition to TMSM blocks. Table 17 summarizes his results. This clearly shows that very vigorous conditions are required to hydrolyze most methacrylates (conc. H_2SO_4 or NaOH:HMPA). This study also shows the higher reactivity of acrylate esters ($R_2CHCOOR'$) than methacrylic esters (R_3CCOOR') toward hydrolysis reactions due to steric limitations.

The synthetic control which may be achieved with methacrylate

Table 17

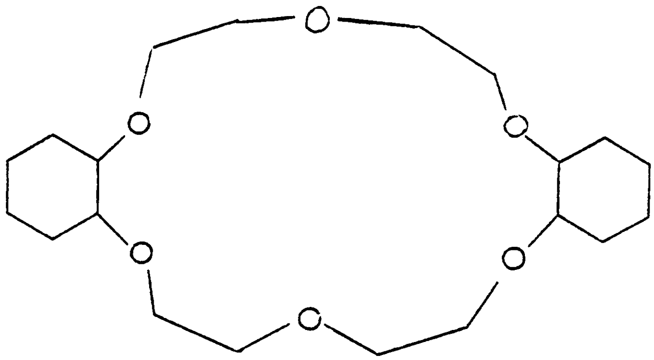
Hydrolysis of Block Copolymers [112]

Block Polymer	Hydrolysis Method	Time(hr)	Temp(°C)	% hydrolysis
(2-vinyl pyridine)-b-MMAa	Conc. H_2SO_4	72	30	90
(2VP)-b-t-butylacrylate	Conc. H_2SO_4	72	30	100
(2VP)-b-MMA	NaOH:HMPA	12	60	48
(2VP)-b-methylacrylate	NaOH:HMPA	12	60	58
(2VP)-b-t-butylacrylate	NaOH:HMPA	12	60	32
(2VP)-b-TMSM)	NaOH	12	30	100

incorporation into a polymer via a living (anionic or GTP) mechanism, coupled with the hydrolizability of certain methacrylates, provides an interesting and novel alternative route to model ionomer synthesis.

Potassium Permanganate Oxidation

Oxidations involving the permanganate anion have traditionally involved aqueous conditions due to the insolubility of $KMnO_4$ in nonpolar solvents. The water insolubility of most polymers precludes the use of aqueous $KMnO_4$ in post reactions. An alternative to this problem has recently been developed [116] which takes advantage of crown ethers to solubilize $KMnO_4$ in non-polar solvents such as benzene. Potassium permanganate was made soluble in benzene by complexation with dicyclohexyl-18-crown-6, providing an efficient oxidant, 1, for organic compounds under relatively mild conditions. When no crown ether is present, $KMnO_4$ is insoluble in benzene and no reaction with various oxidizable organic compounds takes place. The soluble reagent is formed when equimolar amounts of dicyclohexyl-18-crown-6 and potassium permanganate are added to benzene at room temperature to form "purple benzene". Concentrations as high as 0.06M remain soluble. The solution



1

is quite stable, with a half-life at 25°C of 48 hours. Alkyl benzenes are oxidized at a much lower rate than more reactive substrates such as alkenes. Toluene was completedly oxidized to potassium benzoate in 72 hours.

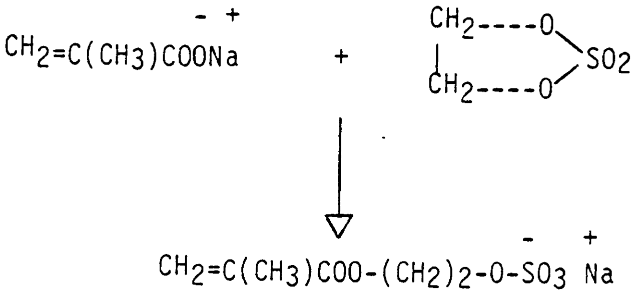
This novel route to carboxylate ions has capabilities toward the synthesis of model ionomers. Model macromolecules containing p-methyl styrene units may be cleanly oxidized by this technique in the future to produce novel carboxylate ionomers.

Sulfination of Anions

Quite recently, polymeric sulfinate anions have been produced by the reaction of lithiated polystyrene with sulfur dioxide gas [117]. The purpose was to produce new ion-exchange resins. Styrene-divinyl benzene beads were swollen in an unnamed solvent (probably hot cyclohexane) and lithiated with a complexed alkyl lithium reagent (t-BuLi+TMEDA). Treatment of this active polymer gel with sulfur dioxide afforded the polymeric lithium sulfinate, a relatively stable anion. The authors found that the anion could attack selected alkyl halides (Sn2) to afford alkyl-aryl sulfones. It is known however, that sulfinate anions may be easily oxidized with various reagents (sodium bicarbonate) to form sulfonate groups. This reaction may thus lead to a new route to sulfonated ionomers. The truly exciting aspect of this new route is the capability of reacting anionic "living" chain ends with SO_2 to afford very cleanly synthesized, well defined, telechelic ionomers.

Carboxylate-Sulfonate Conversion

A recent synthetic study by Czechoslovakian workers [118] detailed the preparation of salts of sulphoxyalkyl acrylate and methacrylate monomers from sodium methacrylate and cyclic sulphates (Scheme III). It may be anticipated that this reaction could also be used to convert a carboxylate ionomer into a sulfonate ionomer with higher clustering power and high temperature stability.



Scheme VIIA. Conversion of Carboxylates to Sulphonates via Cyclic Sulphates [118].

III. RESEARCH INTROCUTION

The overall goal of this research was to first establish polymerization conditions where the anionic methacrylate polymerization would proceed in a living, termination free manner. Once these experimental conditions had become established, it was intended to utilize the many alkyl methacrylate monomers available and the range of stereochemistry attainable to synthesize narrow distribution homopolymers and copolymers (both all acrylic and hydrocarbon-acrylic) of controlled molecular weight. Using this approach, a dramatic range of materials would be attainable. Further, controlled systems could be synthesized by taking advantage of the known reactions of ester groups (e.g., hdyrolysis) to expand the already vast range of properties.

It quickly became apparent after many months of inconsistent polymerization results that synthesis of methacrylate polymers of high enough molecular weight to discuss physical properties (above a critical molecular weight where "properties" such as Tg become relatively constant) could not be realized due to the significant levels of alcoholic, terminating impurities found in almost all methacrylate monomers. A purification method involving trialkyl aluminum reagents was thus developed to remove terminating impurities from the methacrylate monomers of interest. Resulting from the discovery of these new purification agents was the development of a facile route to a new class of high-purity, anionic polymerization monomers. Molecular weights higher than 10^5 g/mole are readily obtainable with these highly pure monomers when the synthesis is done under inert atmosphere conditions. Narrow distribution methacrylate polymers of $>10^6$ g/mole may presumably be readily synthesized under high vacuum conditions with these ultra-pure monomers.

The synthetic ramifications of this route to "anionic"-quality methacrylate monomers are many. In addition to homopolymers of controlled molecular weight and narrow polydispersity, all acrylic (methacrylate-methacrylate) copolymers were an interesting synthetic target, as very little work has appeared regarding these materials and the polymerization route employed offers the almost unique possibility of finely controlling the sequence distribution of these materials (random, segmented and block systems are quite easily synthesized). The ability the select the solubility of the various components is also desirable, especially in the all acrylic block copolymer synthesis.

Hydrocarbon-methacrylate block systems offered an even wider range of potential materials. The ability to choose both the hydrocarbon (styrene vs. diene) properties offers a further dimension of synthetic control.

Finally, the controlled synthesis of ionomers via hydrolysis of the methacrylate ester group allows the chemist to control for the first time the location of the ionic groups in the polymer chain. Using this technique, the synthesis of ion containing block copolymers was realized.

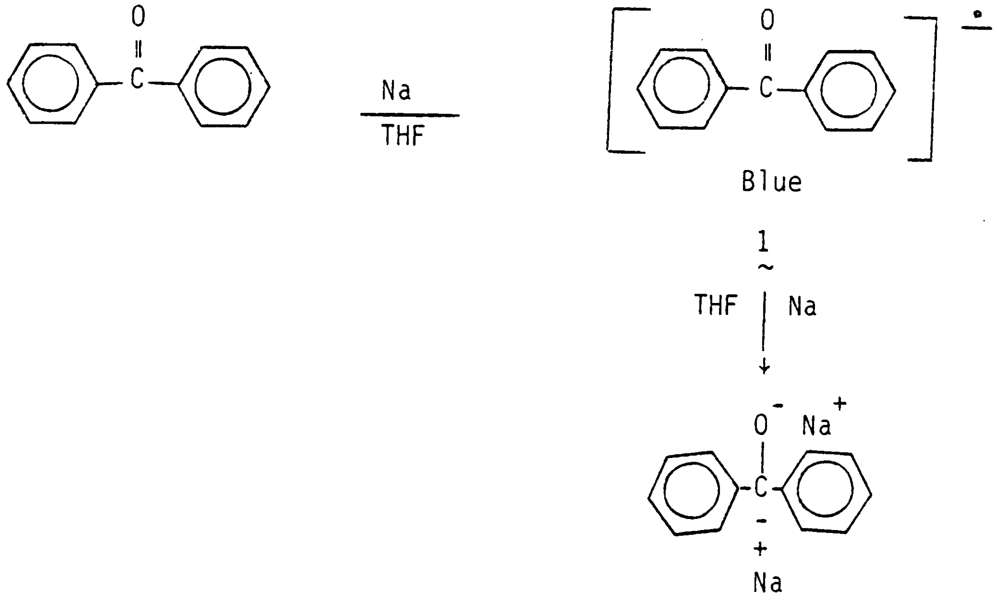
IV. EXPERIMENTAL

A. Reagents and their Purification

1) Polymerization Solvents

a) Tetrahydrofuran (THF) (Fisher, Certified Grade) was typically placed in a 1ℓ round bottom flask with a teflon-coated stir bar and degassed by bubbling a nitrogen stream via a disposable pipette through the liquid while stirring. To the partially degassed material was then added several grams of sodium, finely dispersed in paraffin wax. It should be noted that this form of sodium dispersion is preferred over sodium metal, in that a drying agent with a large surface area is readily arrived at with the wax dispersion, while other methods (short of utilizing the highly dangerous Na/K alloy) produce large lumps of drying agent with minimal surface area. To the THF/sodium mixture is then added (under nitrogen) a small amount (~0.1g) of benzophenone. Benzophenone reacts with Group 1A metals in ethereal solvents to form highly colored adducts, which will thus indicate dryness, as this reaction will only occur in anhydrous conditions [37]. The sodium/benzophenone reaction is thought to involve a series of electron transfers to form first the radical anion (1) and then the dianion (2).

In our case, the drying agent (sodium metal) is present in a very large excess, thus the color of a dry, degassed THF solution should be deep purple. It should be noted, however, that if structure (2) is allowed to oxidize, a green color will result. It is thus important to degas the THF prior to use and keep it under a nitrogen (or Argon) purge. The purple color, which denotes anionic purity, can be achieved again after oxidation simply by degassing and adding another small



Blue

1

purple

2

amount of benzophenone (as the sodium dispersion is still present in a very large excess).

The 1ℓ flask containing the degassed material (THF/Na dispersion/ benzophenone) is then placed on a nitrogen purged distillation apparatus where it is allowed to reflux for several hours prior to distillation. The THF is then distilled into a 500 ml flask which also contains excess sodium dispersion and benzophenone. After the distillation is complete and the purple complex color denoting dianion formation is achieved, the 500 ml flask is transferred to the vacuum distillation apparatus shown in Figure 6. This apparatus has been carefully cleaned and dried and flamed under a nitrogen stream.

After the attachment of flask A to the apparatus under a nitrogen stream, the apparatus is repeatedly evacuated and filled, using the

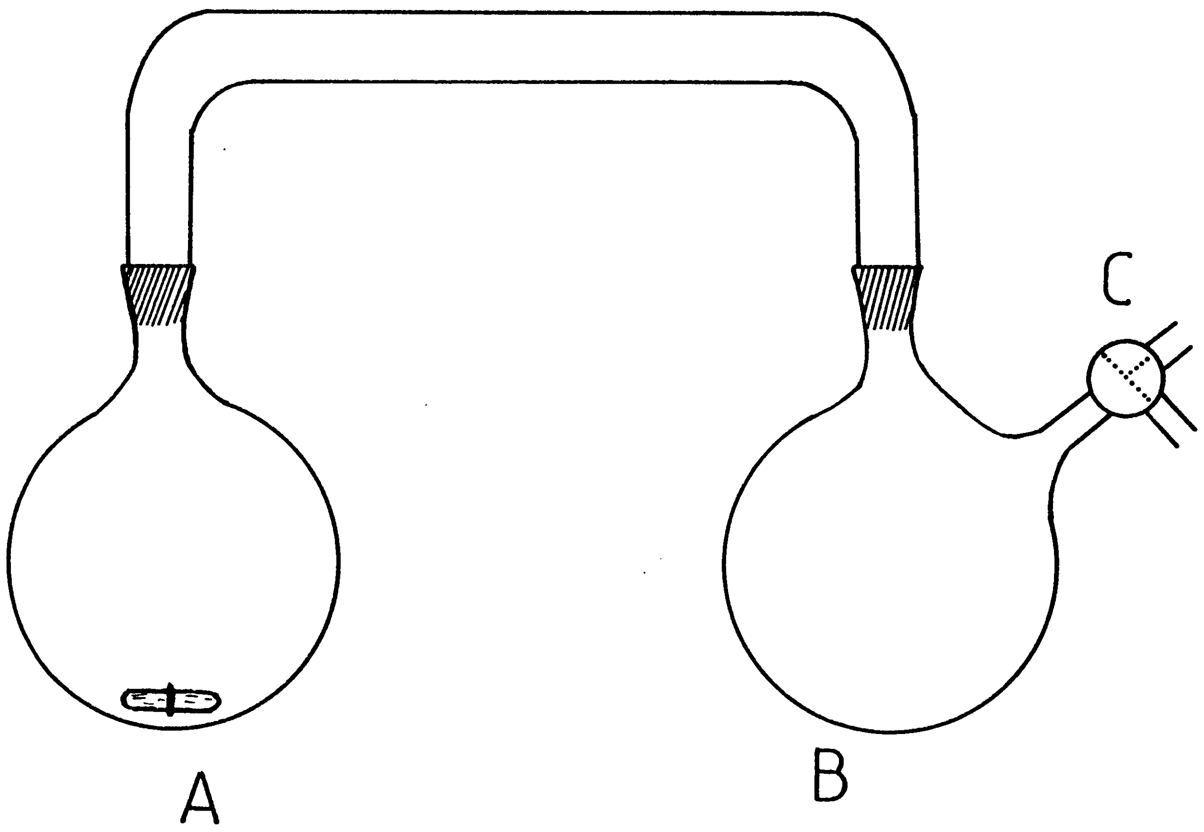


Figure 6. Vacuum Distillation Apparatus for THF Final Purification.

three-way stopcock C, while the stirring solution is being cooled to -78°C with an isopropanol/dry ice bath. After the solution reaches -40°C, more frequent evacuation is performed. Below this temperature, the vapor pressure of THF is low enough that frequent pumping will not cause bumping or foaming, but will remove dissolved gasses. The apparatus is repeatedly flamed at these low temperatures to remove any water bound to the glass surfaces. After the THF reaches -78°C, it is allowed to slowly warm. The longer pumping is maintained during this period, the greater the resulting vacuum. It should be noted, however, that this distillation is extremely difficult to control at a pressure approaching 10^{-2} torr. Bumping or foaming of the purple solution is quite difficult to avoid. It is thus recommended to stop evacuation at the beginning of the warm up phase. This will allow a quite rapid but controllable distillation at room temperature, cooling the receiver (B) with dry ice/isopropanol. Note: If the level of this ice bath is allowed to rise significantly above the level of the THF distillate, bumping will rapidly occur.

The distillation is terminated by filling the apparatus with nitrogen. The dryness and oxygen-free nature of the THF during storage is mirrored by the color of the residue in flask A. As mentioned before, oxygen or water will turn the complex color from purple to green. Experience indicates that the highly pure THF is best used within 1-2 weeks after distillation.

b) n-Hexane (Phillips High Purity Grade) is first stirred over concentrated sulfuric acid for one week to remove olefinic impurities. The color of the acid layer will darken noticably in 24 hours, indicating the formation of sulfonated material. The hexane layer is then decanted into a clean, dry 1ℓ round bottom flask with a teflon coated stir bar. The solvent is then degassed with a nitrogen stream (from a disposable pipette-fitted nitrogen line) with stirring for ten minutes. While this operation is taking place, sodium dispersion (once again in paraffin) is added. Hydrocarbon solvents are ideally dried with this material, as the paraffin slowly dissolves to give a very large surface area - essentially thousands of tiny "sodium mirrors". The flask is then placed on a nitrogen blanketed distillation apparatus, where it is allowed to reflux for several hours to dissolve the paraffin and then distilled into another flask containing the sodium dispersion and stir bar. This flask is then placed on the high vacuum line, degassed several times (cool and pump) and distilled into another 1ℓ flask with stir bar. This flask has a thick walled glass tube fitted to the side. The tube allows for the addition of purification reagents prior to distillation while argon gas purges the system. For hexane purification, an excess of 1.5M n-BuLi (10 mls) is added to a small amount (0.1-0.2 mls) of diphenyl ethylene at low temperature. After addition, a serum stopper is placed over the opening and the system is evacuated. The tube is then heat sealed and the flask is further evacuated. After a suitable vacuum is reached ($\sim 10^{-5}$ torr) the hexane is distilled trap to trap simply by cooling the receiver with an ice bath.

The diphenyl ethylene/n-BuLi combination is utilized for the following reasons:

1) The adduct, diphenyl hexyl lithium is a bright red carbanionic species which will form only in anhydrous conditions, thus indicating dryness.

2) n-BuLi reacts much more slowly than s-BuLi, which may react explosively with DPE due to the very high reactant concentration.

3) DPE will react much more slowly than styrene, which will again help to control this very concentrated exothermic reaction.

4) The adduct is soluble in hexane.

After letting the solution of DPHL/n-BuLi in hexane stir for several hours at room temperature, the bright red color associated with anionically pure conditions should be begin to appear. The hexane may then be distilled into a clean, dry flask for further use and storage.

The anionically pure solvents are typically stored in round bottom flasks fitted with serum stoppers under nitrogen or argon blankets. When a portion of the solvent is to be used, it is pressured out via a cannula (double-ended needle) or syringe.

c) Toluene (Fisher HPLC grade) is purified as n-hexane, except it is not stirred over concentrated H_2SO_4 due to toluene's propensity toward electrophilic aromatic substitution.

2) Initiators

a) 1,1-Diphenyl Ethylene (DPE) (Eastman) is a viscous, oily liquid. B.P. = 270°, M.P. = 6°, density = 1.03. It is best purified by high vacuum distillation from n-BuLi, i.e. from diphenyl hexyl lithium. It has also been successfully purified by distillation from dibutyl magnesium (DBM). The apparatus employed for this short path vacuum distillation is shown in Figure 7.

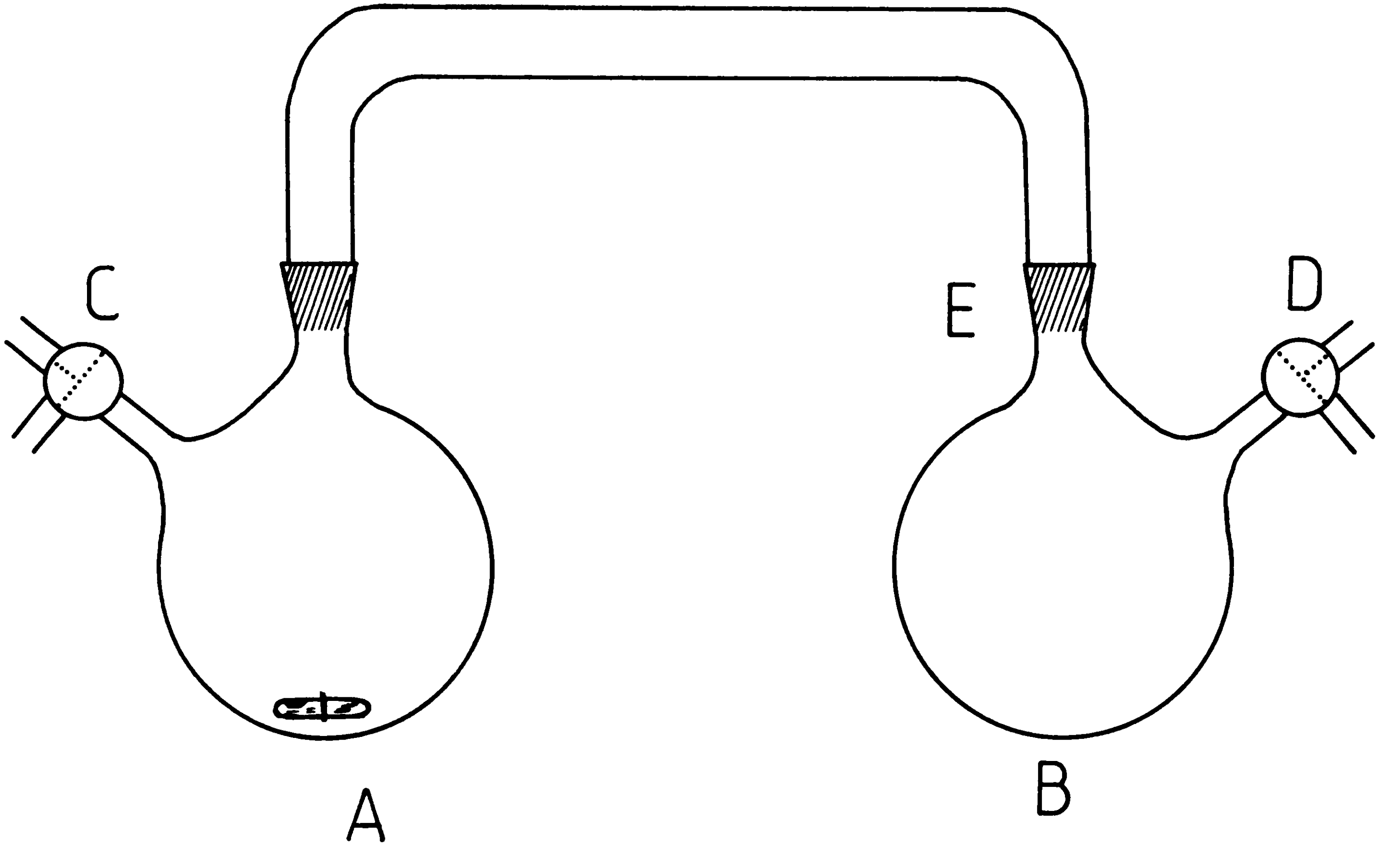


Figure 7. Vacuum Distillation Apparatus for DPE.

Stopcock C is attached to the N_2 manifold while stopcock D is attached to the receiver (B) and vacuum manifold. Typically DPE (~20g) is added thru C into A with a syringe. The apparatus has of course already been flamed, evacuated, and purged. The purifying agent (n-BuLi in hexanes) is then added dropwise via syringe. Initially, green colors are seen but as more drops of n-BuLi are added, the red color associated with DPHL begins to form. It should be noted that this is a very slow reaction, thus the addition of n-BuLi should be stopped soon after the first signs of red are seen, as this color will grow much deeper in the next several hours. After two hours, the hexanes are removed by pumping while going through several freeze-thaw cycles. Distillation is then performed with a continually applied vacuum (D is always open) (10^{-2} torr) while heating A with oil bath to 70-80°C and cooling B with liquid nitrogen temperatures. Distillation is usually complete within several hours or less. The apparatus is then filled with nitrogen, disassembled at point E and sealed with a serum stopper. This purified diphenyl ethylene is stored under nitrogen for relatively long time periods without noticable degradation in performance.

Note: Aldrich DPE has also been used, but with poor results, even after purification by the above methods. Chromatographic (GLC) capabilities in our lab did not permit analysis, but it appears that Aldrich DPE is not suitable for anionic polymerization work, while Eastman DPE appears to be of much higher purity. The problem associated with obtaining high (anionic) purity DPE have long been appreciated [119]. Traces of benzophenone, an easily formed oxidation product, are extremely difficult to remove, and of course will exert a profound influence on most anionic syntheses. The presence of benzophenone probably explains the green colors associated with the initial stages of n-BuLi purification, as the adduct $R\text{-}C(Ph)_2\text{-}O^- Li^+$ is a green colored species. The reactivity of n-BuLi toward benzophenone and DPE, coupled with its low volatility and highly colored reaction products, affords a DPE which is probably the highest purity obtainable. The propensity of DPE toward oxidation should always be kept in mind after purification, i.e. during storage and use. Much care should be taken to prevent oxygen contamination of the DPE storage flask. This fact encourages the frequent purification of small quantities of DPE.

b) sec-butyl lithium (s-BuLi) (Lithium Corp. of America) is packed as a 1.4 m solution in cyclohexane. It is used as received with no further purification. The molarity is checked using the Gilman "double titration" method [120] with 1,4-dibromobutane.

3) PURIFICATION AGENTS

a) n-butyl lithium (n-BuLi) (Aldrich) is packed as a 1.6M solution in hexanes. It is used as received with no further purification.

b) Dibutylmagnesium (DBM) (Lith. Corp.) is packed as a 15 wt% solution in ISOPAR E (hydrocarbon mixture). It is used as received.

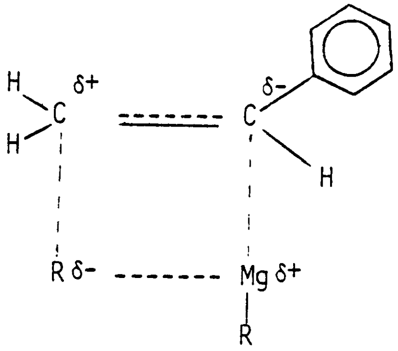
c) Triethyl (TEA) and Trioctyl (TOA) aluminum - were generously supplied by Ethyl Corp; they are packaged as 25 wt.% solutions in hexanes and are used as received.

HANDLING OF AIR SENSITIVE REAGENTS

All the initiators and purification agents listed are moderately air sensitive (DBM and TOA) to highly air sensitive (TEA). They are always handled under dry, purified nitrogen with clean, dry glass syringes. All transfers are performed via syringe, stainless steel cannula or polyethylene tubing with stainless steel needles and adaptors. All glassware is cleaned, evacuated, flamed and purged prior to use. For more detailed information regarding the handling of air sensitive reagents see Aldrich's "The Safe Handling of Air-Sensitive Reagents" [121].

4) MONOMERS

a) Styrene (Aldrich) 145°C B.P. is first stirred over finely ground calcium hydride for several days, then vacuum distilled. This is a preliminary drying step which also removes inhibitor and polymer from the monomer. As this step is tedious and the distillation is difficult (bumping of the CaH_2 slurry often occurs), alternatively the monomer may be stored in a nitrogen purged brown glass bottle containing activated alumina, which seems to do a fine job of removing most of the moisture and inhibitor. Long term storage of this pre-purified monomer takes place in a clean, dry, nitrogen purged brown glass bottle in the freezer. Next, the dry styrene is introduced into the nitrogen purged monomer distillation rig (see Figure 7). After degassing (freeze-thaw), DBM is added dropwise until a stable, yellow color is maintained. The presence of this complex denotes the systems "anionic" purity. This method has been used by Fetters to prepared high purity styrene monomer for ultra high molecular weight ($>10^7$) polystyrene synthesis [8]. This bright yellow complex, although partially ionic in nature, is not basic enough to initiate styrene polymerization. It may be considered to have a structure similar to that shown below:



The monomer/complex is allowed to stir for >1 hour (in the dark) and then is slowly cooled down to freezing while pumping. This is a combination degassing and Isopar E removal step. After two or three freeze-thaw cycles, all the Isopar E will be removed and the vacuum distillation is allowed to proceed at 40°C at ~10^{-2} torr.

b) t-Butyl Styrene (TBS) (Dow Chemical). B.P. 219°C is purified similarly to styrene, although the first (CaH_2) step is optional, as TBS is more hydrophobic than styrene and has also less polymer contamination.

c) 1,3-Isoprene (Goodyear) is purified by employing packed columns. The isoprene is first pressured through an activated alumina column to remove the inhibitor and then through a 4Å molecular sieve column to remove water. It may also be quite easily distilled from DBM, if extremely pure monomer is desirable, e.g. in block polymer synthesis.

d) 1,3-Butadiene (Phillips, Polymerization Grade) is also purified using the packed column technique.

e) Methyl Methacrylate (MMA) (Rohm and Haas) B.P. = 100°C, (and all other alkyl methacrylates) is purified as follows.

Methacrylate Purification

A large batch of MMA (300-400g) is typically stirred over finely ground calcium hydride (CaH_2) under nitrogen for several days, then distilled from CaH_2 under vacuum after degassing to remove traces of water, inhibitor, polymer, and oxygen. This large amount of "conventionally pure" monomer is then transferred into a dry, nitrogen purged, septum capped brown glass bottle for long term storage in a freezer. Experience indicates that monomer of this purity can also be stored for long times in a refrigerator without noticable polymer buildup. When needed, desired quantities of this CaH_2-pure MMA can be transferred into the nitrogen filled monomer purification apparatus via syringe or cannula. This apparatus is shown in Figure 7.

The glassware involved in this apparatus is generally baked out in a glass shop annealing oven at a maximum temperature of 575°C overnight prior to use. The glassware is carefully cleaned and treated with a base washing solution. After rinsing with distilled water, it is placed in a drying oven overnight (112°C). The glassware is assembled hot, followed by vigorous flaming under vacuum with a mechanical pump ($\sim 10^{-2}$ torr). A vacuum-flame-nitrogen purge cycle is performed three times. Finally, the apparatus is filled with nitrogen gas (prepurified) which has been passed through two columns containing 4Å sieves, 13x sieves, and CaH_2. The CaH_2-pure MMA is added to flask A through a rubber septum and three-way valve C using a syringe or cannula. The monomer is then degassed several times using freeze-thaw techniques. It should be noted that this monomer had already been degassed prior to storage. We feel, however, that utmost care should be taken to remove all the oxygen before the addition of trialkyl aluminum, as it has been reported that trialkyl aluminums will, in the presence of oxygen, lead to free radical polymerization of MMA [122]. [We have experienced that when MMA is not carefully degassed, less than 50 percent of the monomer is recovered by distillation before polymerization takes place. When careful precautions are taken, however, greater than 90 percent of MMA is recovered after distillation.]

To the "conventionally pure" and scrupulously de-oxygenated MMA is then slowly added the 25 wt. percent solution of trialkyl aluminum (in hexanes). The aluminum alkyl is added slowly to the stirring MMA so as to avoid both exotherms and more importantly, local concentration buildup of TEA in MMA, as these conditions may lead to reactions of the ester group [123-124]. The use of diluted alkyl aluminum will help in these regards and also alleviate problems in handling the highly pyrophoric bulk TEA. Diluted TEA is only mildly pyrophoric, and diluted TOA is almost inert. After the alcohol and other protic impurities have reacted with the alkyl aluminum, complex formation will rapidly take place with addition of more alkyl aluminum, thus resulting in a bright yellow endpoint. This straightforward behavior is witnessed with the simple primary ester containing methacrylates, e.g. methyl, ethyl, n-butyl. More unusual behavior is apparent when higher (secondary and tertiary) methacrylates are employed, e.g. iso-propyl, cyclohexyl, and t-butyl methacrylates. This behavior will be elaborated upon in a later chapter. After the endpoint is reached, 10-30 percent more TEA (or TOA) is then added, to give a more intense yellow color. It should be mentioned that we are still working with a very low molar concentration of trialkyl aluminum, typically 1-5 mole percent, depending on the inherent impurity, i.e. alcohol content, of the CaH_2-pure methacrylate monomer.

Following the addition of the alkyl aluminum, the monomer is slowly cooled while vacuum is applied from 3-way "B" in Figure III. This pumping is necessary to rid the system of both the hexane diluent and the alkane byproduct from the alcoholysis reaction, especially when TOA is used, i.e. octane is the byproduct. Low levels of hydrocarbon diluent in the alkyl methacrylate will not have an adverse effect on the polymerization, but will result in a loss of vacuum upon vaporization which will not allow for the desirable low temperature distillation. Virtually all volatile hydrocarbon may be removed by pumping on the monomer/complex while going through several slow freeze-thaw cycles. The vacuum generated using this technique allows for rapid distillation of ~95% MMA at temperatures below 10°C. After the distillation, the apparatus is pressurized with nitrogen. The ultra-high purity of this methacrylate monomer is such that it is very sensitive to storage. These monomers are best used immediately after distillation, as polymerization will occur quite rapidly on standing unless precautions are taken to keep the monomer frozen and in the dark.

f) Ethyl Methacrylate (EMA) (Rohm and Haas) B.P. = 117°C. Purified same as MMA.

g) n-Butyl Methacrylate (NBMA) (Aldrich) B.P. = 163°C. Purified same as MMA.

h) iso-Butyl Methacrylate (IBMA) (Rohm and Haas) B.P. = 155°C. Purified from CaH_2 only. Highly pure monomer.

i) tertiary-Butyl Methacrylate (TBMA) was obtained from Rohm Tech), (courtesy of Dr. W. Wunderlich) is purified as is MMA, but allowing longer times for TEA to react with impurities. Thus, TEA is added, yellow complex forms, and the system is kept in the dark for one hour and then checked for color before distillation.

j) 2-Ethyl Hexyl Methacrylate (EHMA) (Polysciences) B.P. = $110°_{14}$ was purified as MMA but its pathway was covered with tin foil and vacuum is open through-out distillation.

k) Cyclohexyl Methacrylate (CHMA) (SARTOMER) B.P. 44°(0.3). This, as in the TBMA case, requires longer time periods to let the alcohol contaminant react. Several additions of alkyl aluminum to the monomer may be required over a long time period.

B) POLYMER SYNTHESIS

All polymerizations herein were conducted under the inert atmosphere conditions necessary for non-terminating anionic polymerizations. Nitrogen was most often used as the inert gas, although argon was used in preliminary work. The low temperature polymerization work was conducted with a specially constructed vacuum-nitrogen duel manifold system seen in Figure 8. The use of

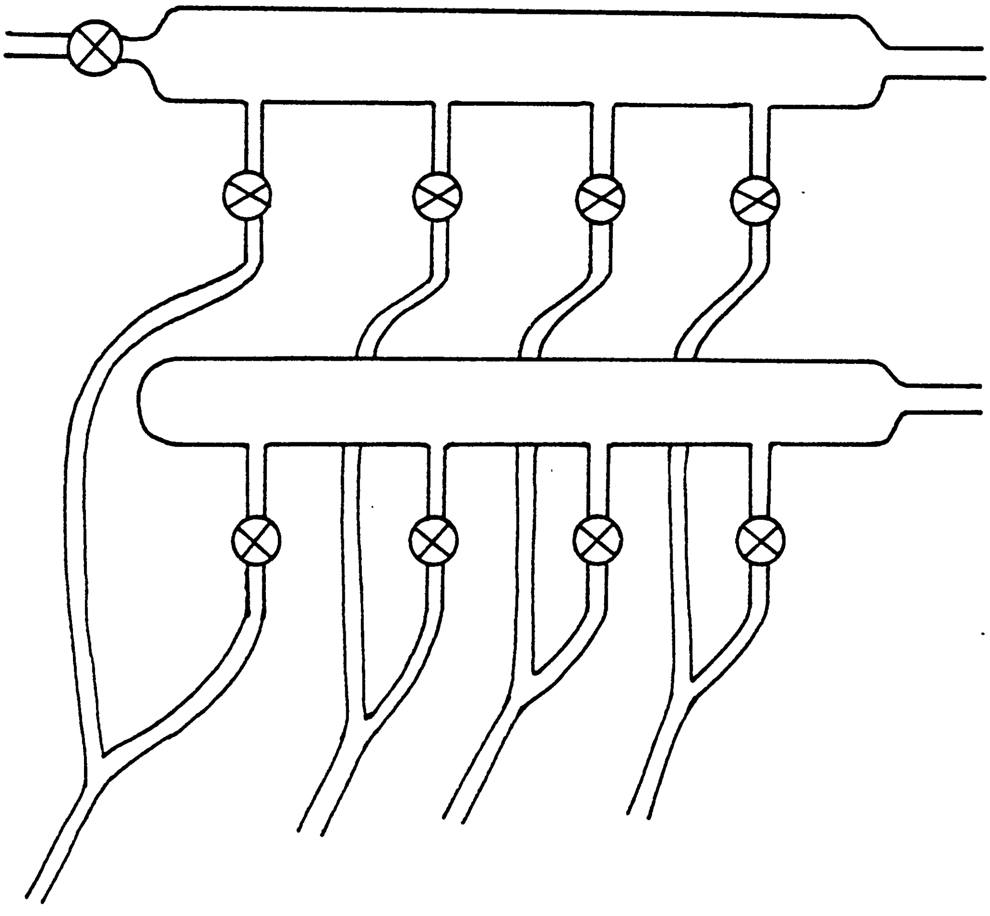


Figure 8. Vacuum-Nitrogen Dual Manifold System.

Teflon Rotaflow Stopcocks is encouraged to minimize contamination the system with silicon grease. The vacuum manifold is connected to a mechanical pump via a cold trap, which is cooled with liquid nitrogen during use to avoid pump contamination. The vacuum is generally monitored using a McCleoud gauge. Vacuum approaching the limits of the gauge (10-2 torr) are commonly obtained with this system. Pre-purified nitrogen gas was most commonly used in this work. It was further purified and dried by passing through two 3 ft. columns of 4A molecular sieves, 13x sieves and finally calcium hydride. The use of a gas wash bottle has also been considered. A typical washing medium may be sodium-naphthalene in a high boiling ethereal solvent such as 2-ethoxy ethyl ether (B.P. = 202°C).

The glassware involved in this work is normally baked out in a glass shop annealing oven at a maximum temperature of 575°C overnight prior to use. The glassware is carefully cleaned and treated with a base washing solution (dilute sodium hydroxide). After rinsing with distilled water, it is placed in a drying oven overnight at 112°C. The glassware is then assembled hot, often under a nitrogen stream, followed by vigorous flaming under vacuum. A vacuum-flame-purge cycle is performed three times. Finally, the apparatus is filled with nitrogen gas.

A typical polymerization reactor used in the low temperature work simply involves a septum capped round bottom flask fitted with a teflon coated stirring bar (glass coated stir bars may be prefferable) and a nitrogen-vacuum line fitted with an adapted needle. A small amount of silicone grease is generally applied to the outside collar of the flask to maintain an air tight seal. The septum is tightly wired with 16 to

18 gauge copper wire. A purge needle is used for pressure release.

Ambient or high temperature anionic polymerizations, for example polydiene syntheses, are carried out in a high pressure, temperature controlled, 0.8ℓ glass bowl reactor [125]. This reactor is shown in Figure 9. Low levels of impurities are "terminated" using alkyl lithium titration, just prior to polymerization.

1) Methacrylate Homopolymers

a) sec-Butyl Lithium Initiated Polymerizations

To a 100 ml septum-capped round bottom flask is added 30 ml purified THF. The flask is cooled to -78°C with a dry ice-isopropanol bath, while nitrogen pressure is continually maintained. The sec-butyl lithium initiator is then charged at -78°C. The addition of sec-butyl lithium at -78°C to THF results in a yellow color being formed. It has yet to be determined if this color is due to an interaction or solvation of alkyl lithium by THF, or if a small amount of alkyl lithium reacts with THF, even at -78°. Recent evidence, to be discussed in the Results and Discussion chapter, indicate that the color is due to ring cleavage of THF by s-BuLi at -78°C which produces the enolate anion of acetaldehyde. The color disappears upon addition of purified monomer (again at -78°). The amount of monomer and initiator added is determined by both the desired molecular weight and the final polymer concentration (percent solids). For example, if a polymer with molecular weight of 10,000 is desired, in an amount which gives a 10(w/w)% solution, then the following calculation is in order for a reaction of 50 grams total weight (Scheme VIII).

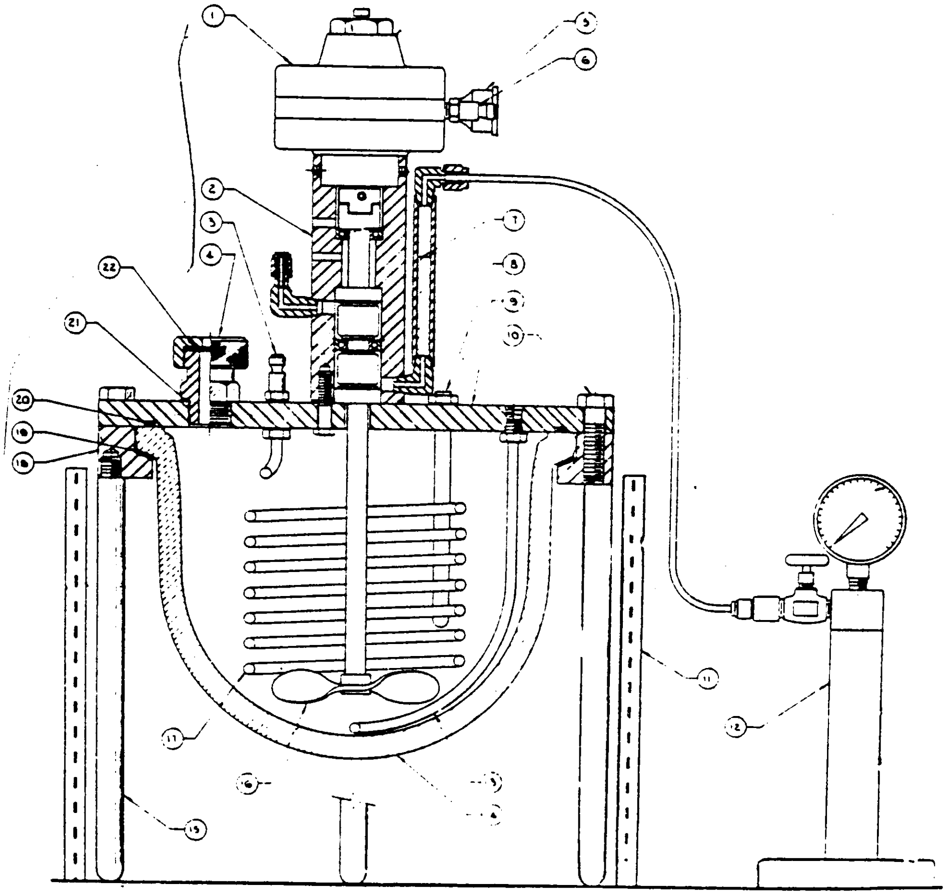


Figure 9. Glass Bowl Pressure Reactor for Anionic Polymerizations.

Scheme VIII

Molecular Weight Calculation for Living, Monofunctional Anionic Polymerization

wt. Solvent & wt. Monomer = 50g

at 10% solids:

45g solvent + 5g monomer = 50g

and

$$M_{Stoichiometric} = \frac{\text{g monomer}}{\text{moles initiator}}$$

$$M_{Stoich} = 10^4 \text{ g/mole}$$

$$g_{monomer} = 5\text{g}$$

thus

$$\text{moles initiator} = \frac{5\text{g}}{10^4\text{g/mole}} = 5\text{x}10^{-4} \text{ mole}$$

if [initiator] = 1.0 molar

then

$$\text{initiator charge} = 5\text{x}10^{-4}\ell = 0.5 \text{ ml.}$$

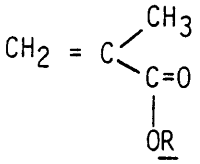
After allowing the polymerization to proceed for 10 minutes, the reaction was terminated with methanol, although methanol/acetic acid mixtures were used in later experiments for more rapid termination. Poly(alkyl methacrylates) were then precipitated in methanol, methanol/water or hydrocarbons (hexanes or petroleum ether), depending on the solubility characteristics of the polymer formed (see Table 18).

b) Diphenyl Hexyl Lithium Initiated Polymerization in Polar Solvents:

The bulky, less basic initiator diphenyl hexyl lithium (DPHL) is synthesized by reacting butyl lithium (secondary or normal) with

Table 18

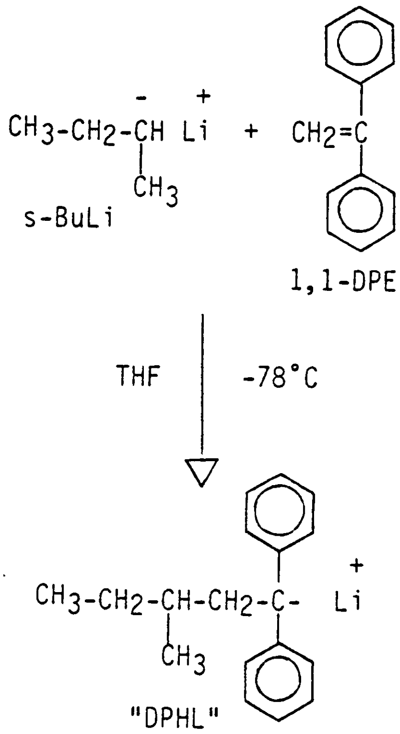
Precipitation Solvents for Various Poly(Alkyl Methacrylates)



R	Abbreviation	Precipitation Medium
$-CH_3$	MMA	Hexanes or Pet Ether
$-CH_2-CH_3$	EMA	Pet Ether
$-(CH_2)_3-CH_3$	NBMA	Methanol or $MeOH/H_2O$
$-CH_2-CH-(-CH_3)_2$	IBMA	Methanol or $MeOH/H_2O$
$-C(-CH_3)_3$	TBMA	Methanol or $MeOH/H_2O$
$>C_5$	All Higher Esters	Methanol

1,1-diphenyl ethylene (DPE) in THF at -78°C as in Equation 1. Thus,

Equation 1



diphenyl ethylene (2-4 mmoles) is added to 25 - 50 mls of purified THF in a round bottom polymerization flask. After cooling the flask to -78°C, with a constant nitrogen make-up pressure, sec-butyl lithium is slowly dripped in with stirring. After several drops have been added, a persistant red endpoint appears, due to the blood red color of the highly resonance stabilized DPHL anion (λ_{max} = 430 nm). The desired amount of initiator (1 mmole) is then charged. After waiting five minutes for any exotherm to subside, the purified monomer is slowly added to the initiator solution. Fast initiator is evident even at -78°C, as the red color disappears after the first few drops of monomer have been added. Experience indicates that if the monomer and THF are of extreme purity, the polymerization, i.e. the methacrylate anion, is colorless. The remaining monomer is added in a very slow, dropwise fashion to avoid exotherms which would cause side reactions. Calculations of monomer and initiator charged are again based on both the desired molecular weight and the preferred percent solid level. Thus, calculations would follow the same form as in Scheme VIII. A typical polymerization "recipe" for a 50,000 g/mole PMMA is given in Table 19. After the monomer addition is complete, the polymerization is terminated after several minutes by adding a small amount of an acetic acid/methanol mixture. The polymers are then precipitated, as before, according to Table 18. Typically, poly(alkyl methacrylates) are then filtered as white fluffy powders and placed in a vacuum oven overnight at 80°C.

c) Diphenyl Hexyl Lithium Initiated Polymerization in Hydrocarbon Solvents

The reaction between 1,1-diphenyl ethylene (DPE) and s-BuLi in THF (Equation 1) occurs almost instantaneously, even at -78°C. The kinetics of this process are changed dramatically when hydrocarbon solvents, in this case hexane or toluene, replace the interacting solvent THF. The reaction is so slow that high temperatures (60°C) are required to get the addition to go to completion in reasonable times, i.e. several hours [126]. If one is planning on performing more than one of these hydrocarbon based polymerizations, many problems are alleviated by making one large batch of initiator in a large reactor at higher than ambient temperatures. The use of the high pressure glass bowl polymerization

Table 19

Typical Anionic Polymerization Recipe for 50K PMMA

THF	>50 mls.
DPE	~0.3 mmole (.05 ml)
s-BuLi	0.1 mmole (.07 ml)
MMA	5g

reactor in Lab 120A, Davidson Hall [125], has been found to be most suitable for diphenyl hexyl lithium (DPHL) synthesis in hydrocarbon solvents. This route solves many of the problems listed above.

1) The reactor is temperature controlled, i.e., running a reaction at 60° is no problem.
2) Large batches (up to 600 mls) of DPHL/Hexane or DPHL/Toluene may be prepared at one time, ensuring uniformity for a multi-reaction study.
3) The prepared initiator may easily be stored in the reactor for periods of 1 week or more.
4) The reactor contents are easily transferred into a round bottomed polymerization reactor by attaching a syringe needle to the reactor sampling port.

Thus, a known weight or volume of purified hexane or toluene is transferred via nitrogen pressure into the empty high pressure glass bowl reactor through the syringe port by means of a cannula. The volume should be accurately known as it will effect molarity of the initiating solution and thus stoichiometric molecular weight. Weighing the solvent reservoir before and after filling up the high pressure reactor is normally the method of choice for volume determination (via density). After the solvent has been charged, diphenyl ethylene, in excess of alkyl lithium (3-4 mole) is charged. Then, at 60°C, the reactor is titrated clean of impurities with s-BuLi, followed by the desired s-BuLi charge (1 mole vs. DPE). After waiting several (2-4) hours for the reaction to reach completion, the temperature is lowered to room temperature, and the resulting solvent/initiator blood-red solution is charged into prepurged, anionically pure septum-capped polymerization flasks via a 6" syringe needle adapted to the sampling port. The weight of these polymerization flasks before and after filling determine the moles of initiator, and thus the monomer change. The deep red solution is then cooled to the desired polymerization temperature (making sure nitrogen make-up pressure is available) and the purified methacrylate monomer is then added. After typically one hour, the deep yellow polymerization is terminated with acetic acid/methanol (1/2 parts), causing the solution to go colorless. The polymer is precipitated in pure methanol or pet ether (see Table 1), making sure no water is present in the precipitation medium, as the polymerization solvent is required to be miscible with the precipitant in order for clean precipitation to take place.

d) Free Radical Bulk Polymerization

A typical procedure is to first weigh AIBN (DuPont VAZO 64) into a clean, dried 100 ml round bottom flask. Then, place a greased serum cap (septum) over the mouth of the flask and wire down well. Evacuate the flask and back-fill with nitrogen repeatedly (3-4 times) on a dual manifold system via the needle-adapted line. Finally, the reactor is filled with nitrogen followed by addition of degassed, purified monomer via syringe. The mixture is shaken to fully dissolve the AIBN. The polymerization flask is then placed in a constant temperature bath at 60-70°C and allowed to polymerize for several hours (absolute time depends on desired yield). A typical bulk polymerization recipe for PMMA is listed in Table 20. After suitable time has been allowed for the polymerization to reach high yield (2 hrs), the polymerization is allowed to cool down to room temperature, at which time the pressure is carefully released with a purge needle. The polymer formed is dissolved in chloroform or THF and precipitated in pet ether.

Table 20

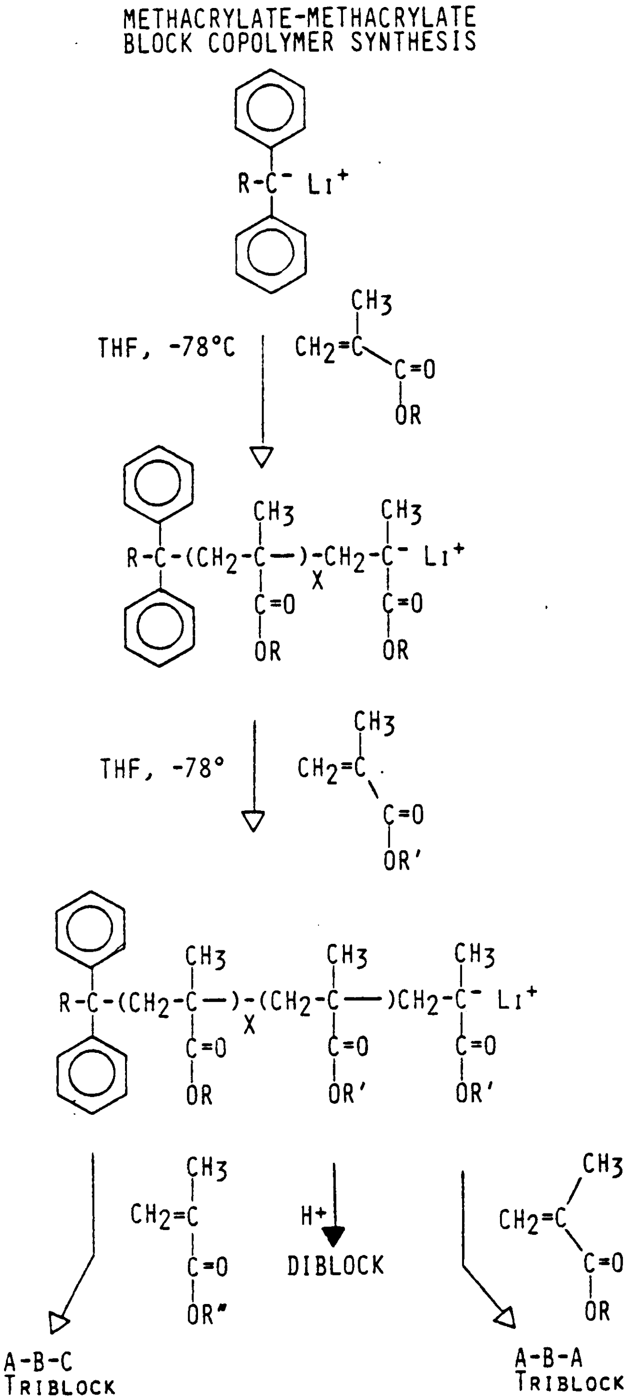
Free Radical Bulk Polymerization of MMA

AIBN (VAZO 64)	0.011g (0.1 wt%)
MMA	10g
temp.	70°C
time	2 hrs.
yield	90%

2) All Acrylic Block Copolymers

The synthesis of methacrylate-methacrylate block copolymers is performed exactly as DPHL initiated methacrylate homo-polymerization (in THF) with the exception of the use of at least two monomers for copolymerization instead of one for homopolymerization. Thus two monomer purification rigs (see Figure 7) must be assembled at the same time, as these purified methacrylates are best used as soon as possible. The preparation for and synthesis of these all-acrylic block copolymers are best suited for a team of two researchers, especially if the synthesis of more than 1 block copolymer is desired. As mentioned above, as with the homopolymerization procedure, the initiator (DPHL) is first prepared in THF at -78°. This step is followed by the slow addition of the first monomer (M_1) for synthesis of the "front" or "first" block. After waiting several (3-5) minutes to ensure full reaction of M_1, the second monomer (M_2) is slowly added. Experience indicates that a 5% solids level is useful for controlling viscosity buildup near the ends of these block polymerizations. This reaction sequence is clarified in Scheme IX.

Sampling of the first block $(M_1)_x$ before the addition of M_2 simplifies the characterization of final diblock material. One major drawback with the polymerization reactors used in these low temperature studies is the difficulty in finding a non-terminating sampling technique. Two possibilities for sampling without termination are via a syringe or a cannula. The syringe technique is more effective, in that it allows far more controlled sampling of the reaction mixture. This is demonstrated as follows:



Scheme IX. Synthesis of All Acrylic Block Copolymers.

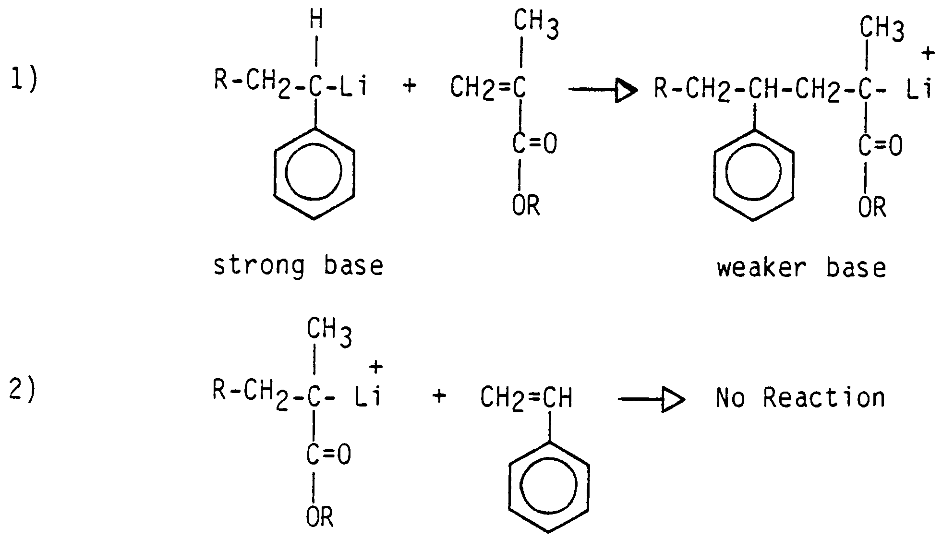
The syringe (5-10 ml) needle is inserted into the reaction mixture before titration. An assistant needs to hold down the plunger due to the pressure in the reactor (3-5 psi). The DPE/THF solution is then titrated with s-BuLi, followed by addition of the initiator charge. This procedure ensures the chemist that no termination will take place via entry of a non-purged object (syringe needle) into a living system. When the first block is complete, (i.e. the M_1 charge has been completed for several minutes) the plunger is released, allowing the living first block to be sampled. After several mls. have been withdrawn, the material is rapidly injected into a nitrogen purged container with a small amount of methanol/acetic acid for termination. The second block $(M_2)_x$ is then synthesized with no further changes of the normal procedure.

3) Styrene-Methacrylate Block Copolymers

Due to the reactivity difference of the styryl anion and the methacrylate anion (Scheme X), the polystyrene block (or any non-polar block) must be synthesized first, before the methacrylate block. After the synthesis of the polystyrene "front" block, the polystyryl anion may then initiate methacrylate polymerization. The nucleophilicity of this styryl anion is such, however, that a percentage of attack will occur at the ester carbonyl (1,2 attack) and not the desired carbon-carbon double bond (1,4 attack). To avoid this deleterious termination reaction, the nucleophilicity of the polystyryl anion is lowered by "capping" with 1,1-DPE to form the more sterically hindered, less basic diphenyl alkyl-type anion used in the methacrylate homopolymerization work. The addition of the purified methacrylate follows to form the polystyrene-

Scheme X

Differential Anion Reactivity



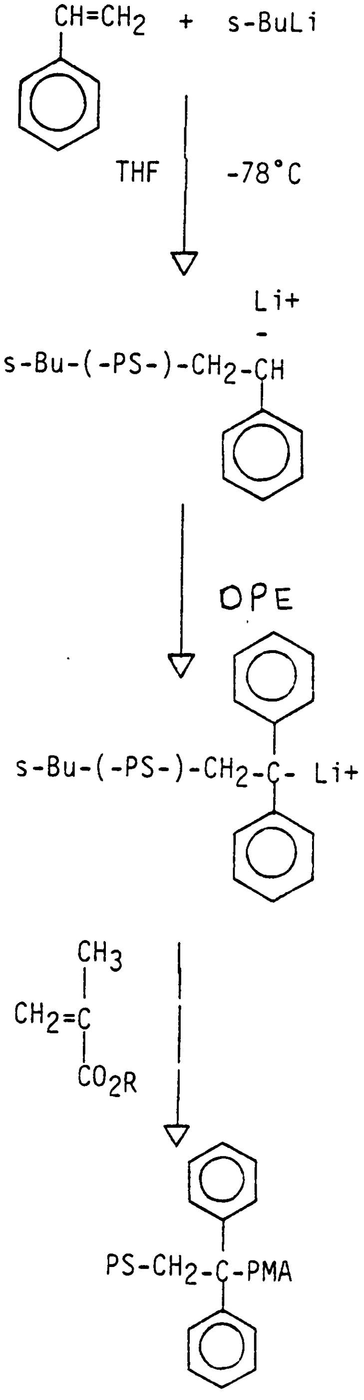
poly(alkyl methacrylate) diblock. Thus, DBM-purified styrene monomer is added to THF in a polymerization flask. When the rapidly stirring mixture is cooled to -78°C, the initiator (usually s-BuLi) is charged quickly. After several minutes (the styrene reacts immediately), DPE is added (2-4 mmoles vs 1 mmole Li) to turn the orange-red polystyryllithium into the cherry red colored "capped" polystyrene macromolecular initiator. This "capped" polystyrene block is then sampled for GPC analysis. This sampling (1-2 percent of the reaction mixture) is followed by slow addition of a purified methacrylate monomer. The initiation of the methacrylate block is fast as witnessed by the rapid color change from cherry red to colorless after several drops of the monomer are added. After this slow monomer addition has been completed, the polymerization is terminated (after several minutes) with methanol/acetic acid. The block polymer is precipitated in methanol, filtered and dried in a vacuum oven overnight at ~80°C. This synthetic methodology is elaborated upon in Scheme XI. It should be noted that these block copolymers may become quite viscous in THF at -78°, and the overall solids level should be adjusted accordingly (<5%).

4) Diene-Methacrylate Block Copolymers

At first glance, the anionic synthesis of diene-methacrylate block copolymers may seem to be very similar to the previously discussed styrene-methacrylate case. There are many complications in this synthesis, however, which must be dealt with in order to "cleanly" synthesize diene-MMA block copolymers. It is well documented [8] that butadiene polymerization in THF gives a product with high (80-90%) 1,2

Scheme XI

Synthesis of Styrene-Methacrylate Diblock Polymers



content with an unacceptably high Tg (0°C). Thus, the first step (diene polymerization) in the diene-methacrylate diblock synthesis is performed in hexane to give a high (90%) 1,4 polybutadiene or polyisoprene with a low glass transition temperature. Several problem arise in the next several steps of the synthesis, seen in Scheme XII, however:

1) The "capping" step, with 1,1-DPE is very slow (k_2) with dienyl lithium anions in hydrocarbon solvents.
2) It is difficult to ensure complete "capping", as $k_1 >> k_2$.
3) Polybutadiene precipitates in hexane at -30 to -40°C, and remains insoluble at -78°C.
4) MMA does not undergo proper living anionic polymerization with lithium counterions in hydrocarbon solvents.

Both problems 3 and 4 may be addressed by adding THF to the system. The addition of THF both solubilizes the polybutadiene and allows for a cleaner PMMA synthesis. The amount of THF added exerts a dramatic effect on the structural integrity of the final product.

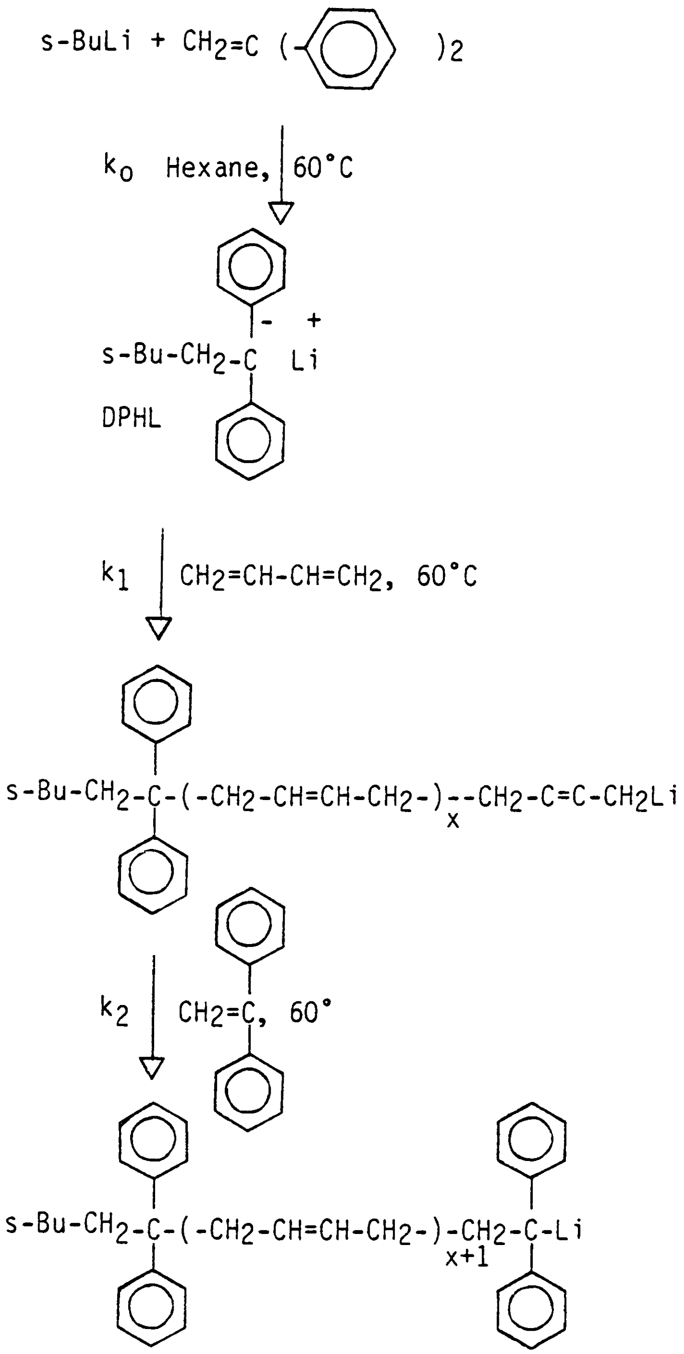
Taking the complications stated above into consideration, the synthetic methodology employed for polybutadiene-PMMA diblock polymers is given below:

Step I: Formation of the Initiator: to 525 mls of highly purified hexane is added 5-10 mmoles of DPE. At 65°C, the reactor is titrated with 1 drop of 1.3M s-BuLi. After the titration endpoint, 1 mmole of s-BuLi is added.

Step II: Butadiene Polymerization. Two hours later, at 60°C, 40g Butadiene is added to the reactor. This time is represented as being "t_0". Initiation is achieved upon mixing, as seen by the reaction color instantly turn from blood red to colorless. The reaction shows a

Scheme XII

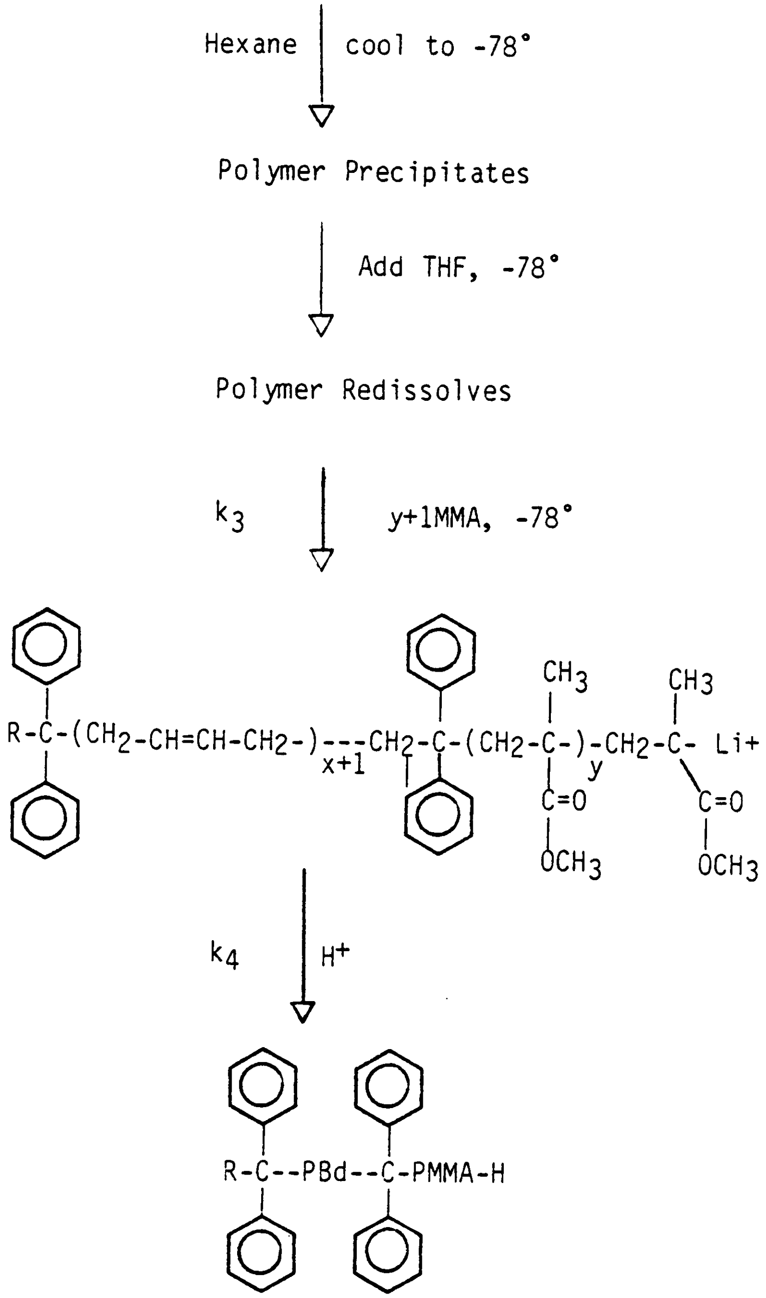
Synthesis of Butadiene-MMA Diblock Polymer



Macromolecular Initiator

Scheme XII(continued)

Synthesis of Butadiene-MMA Diblock Polymer (cont.)



Kinetic Scheme

$k_4 > k_3, k_1 > k_0 >> k_2$

gradual viscosity increase for 1-2 hours. After this point, ~99% of the monomer has polymerized.

Step III: Capping. The capping step is an in-situ reaction, as there is no need to add more DPE to the system. The kinetics discussed earlier dictate that only one DPE unit is incorporated into the chain (as the initiator) until very high butadiene conversion. Even so, k_2 is so slow that color formation, due to the strongly absorbing diphenyl carbanion, does not begin to occur for four hours (after polymerization was started at 60°C), i.e., t = 4 hrs. At t = 5 hours, the reaction color is only pale yellow. Not until t = 8 hours is the reaction deep red, characteristic of diphenyl carbanions of moderate concentration.

At t ≈ 12 hours, the reactor head space is flushed several times to remove traces of unreacted butadiene. While still at 60°C to avoid redissolving unreacted monomer, the capped polybutadiene, or "macromolecular initiator" is charged (in a known amount - usually 100 mls) into anionic purity serum-stoppered 250 ml flasks for subsequent low temperature work. This solution is then cooled to -78°, with nitrogen make-up pressure, which initiates polybutadiene precipitation. At this point, THF (highly pure!) is added in a known amount, e.g. 10% (V/V) to the reaction, which causes the capped polybutadiene to rapidly redissolve and also causes the reaction color to turn deeper red, due to either further conversion of the diene chain ends to diphenyl carbanions, or a shift of the λ_{max} of these carbanion to higher wavelengths.

Step III: Methacrylate Block Synthesis. After waiting ten minutes to ensure reaction mixture is at -78°, MMA is added very slowly. After three drops MMA has been added, the reaction mixture is colorless, indicating very fast initiation.

Step IV: Termination. After thirty minutes, 0.2 ml of methanol/acetic acid are injected into the polymerization mixture at -78°C. The reaction is then allowed to gradually warm, lowering the viscosity of the solution. Precipitation is performed in a blender using methanol as the coagulant.

5) Isoprene-Methacrylate Diblock Synthesis

As expected, the synthesis of isoprene-methacrylate diblock polymers is quite similar to butadiene-methacrylate block copolymer synthesis. The most notable difference, however, involves the capping step, represented in Scheme XII for the butadiene case with the rate constant k_2. Poly(isoprenyl lithium) reacts much faster with DPE than butadienyl lithium, i.e. $k_{2\,\text{Isoprene}} > k_{2\,\text{Butadiene}}$. This ensures a much faster synthesis. Another notable difference is the solubility of polyisoprene in hexane at -78°C. Thus, a pure hexane (no THF) control may be performed with isoprene, but not with butadiene. The overall polymerization procedure is very similar to the butadiene case, except as mentioned above, the reaction times involved change.

C) POLYMER MODIFICATION

1) Ester Hydrolysis

a) Acid Hydrolysis of TBMA

Polymers containing the methacrylate ester functional group may be hydrolyzed to carboxylic acids or metal carboxylates with acids or bases with varying degrees of success. Polymers containing tert-butyl methacrylate (TBMA) units are readily hydrolyzed with dilute acid. The reaction set-up involves a 250 ml. round bottom flask with stir bar, a thermometer adapter with side arm, a thermometer, condenser, and collection flask. This is illustrated in Figure 10.

Typically 5g of the polymer to be hydrolyzed is added to the 250 ml round bottom flask using a powder funnel, followed by 100-125 ml of 1,4-dioxane Note: The carcinogenic properties of dioxane are established, thus extreme caution should be practiced in its handling. The handling of this solvent in a good hood with rubber gloves is therefore encouraged. After the polymer has dissolved, N/10 HCl is added to the hot solution (Dioxane and water form a low boiling azeotrope at 85-88°C) until the cloud point, or until a slight haziness develops. This is followed by the addition of more dioxane (10-25 ml) which will again fully solubalize the system, turning the solution from hazy to perfectly clear. The exact amount of N/10 HCl added will depend on the composition of the polymer to be hydrolyzed and its concentration. For example, more dilute HCL may be added to a dioxane solution of 20% TMBA containing polystyrene than a 20% TBMA containing poly-t-butyl styrene before precipitation begins to take place.

The hydrolysis reaction takes place at 85-88°C, above the boiling point of the reaction byproduct, t-butanol (or possibly the dehydrated product isobutylene). The reaction byproducts, as well as the H_2O-dioxane azeotrope, are collected in the receiver. The reaction time

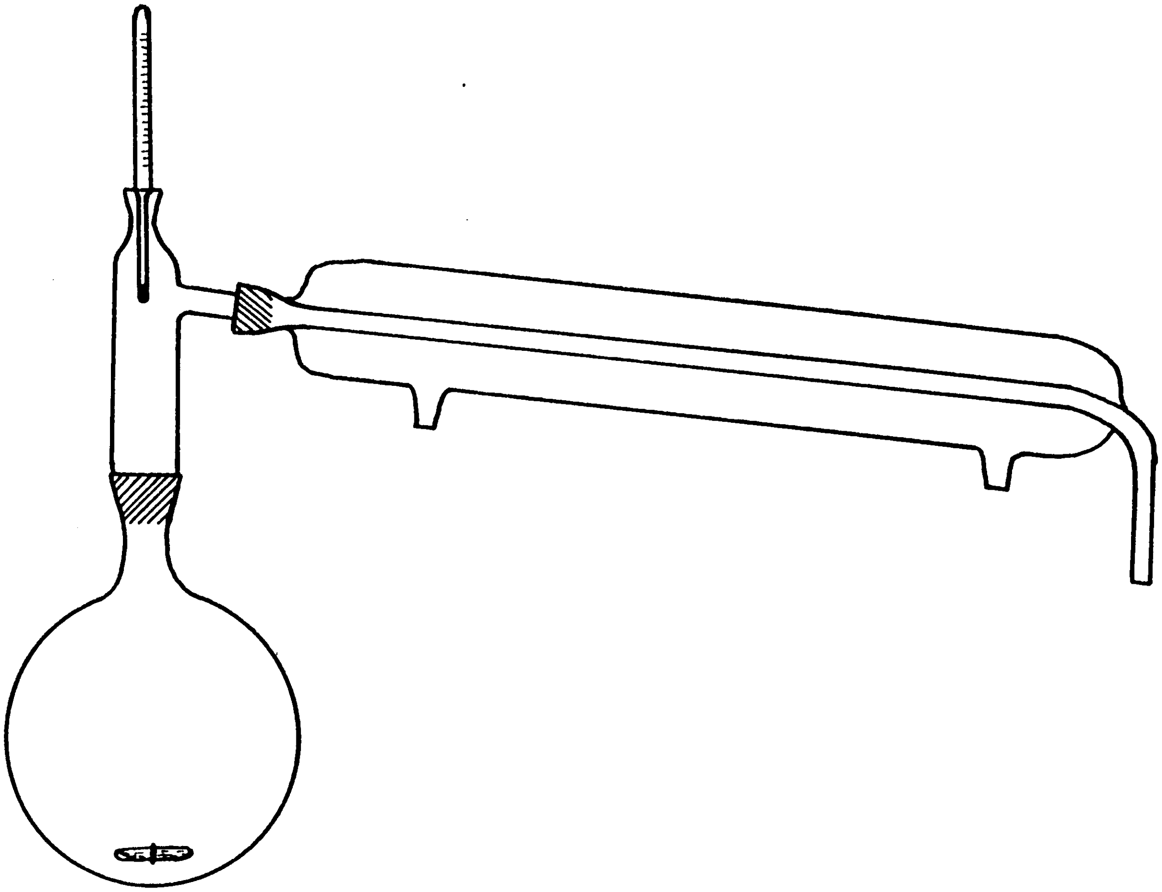


Figure 10. Apparatus for the Acid Hydrolysis of Methacrylate Polymers.

depends on the degree of hydrolysis desired, although a high extent of reaction (>90%) often takes place in less than two hours. It should be noted that reaction rate will depend on several variables, including N/10 HCl concentration, TBMA concentration, and TBMA stereochemistry.

After the reaction, the polymer is precipitated in a non-solvent (usually methanol), redissolved and reprecipitated, and placed in a soxhlet extractor and extracted overnight with boiling water. It is then dried in a hot (80°C) vacuum oven for at least 24 hours. The polymer may be converted to the carboxylate ionomer by titration with an appropriate metal hydroxide.

b) Superoxide Hydrolysis of Poly(alkyl methacrylates)

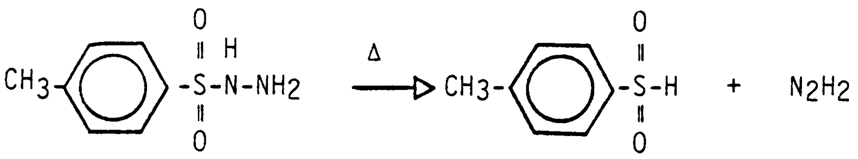
A more general route to ester hydrolysis involves potassium superoxide cleavage of a variety of esters. The simple reaction apparatus used involves a 250 ml 2 neck round bottom flask with magnetic stir bar, a thermometer, reflux condenser, dying tube and oil bath. Typically 3-5g of the polymer to be hydrolyzed is dissolved in THF or toluene. To this homogeneous solution is added a maximum amount of dry DMSO (distilled recently under vac. from finely ground CaH_2, stored under N_2 in a serum stoppered 500 ml resevoir) until the cloud point is reached. The polymer solvent (THF or Toluene) is then again added until the clear point is reached. This homogeneous solution is then heated and stirred until the desired reaction temperature is reached, (this temperature is highly dependent on DMSO concentration and ester alkyl group) followed by addition of finely ground KO_2 (Alfa). This solid is highly water sensitive, and is best ground in a dry box. A 3-4 molar excess of KO_2 to ester groups is utilized. When the reaction reaches completion, the heat is removed and distilled water is slowly added as a quenching agent. The precipitated polymer suspension is then poured into more water, filtered and washed, then dried for several hours (or overnight) in a heated vacuum oven. It is then redissolved if possible. Note: It is often easier to purify these materials in the pre-ionomer or carboxylic acid state. These ionomers can be readily converted into carboxylic acids by swelling the material in THF and adding an excess of conc. HCl dropwise. When the -COOK groups are converted, the polymer will readily dissolve and KCl may drop out. The polymer is then reprecipitated in hot water, followed by soxhlet extraction (again hot water) overnight. These materials are then dried for several days at 80°C in a vacuum oven.

2) Sulfinalation

The functional termination of "living" polymers with sulfur dioxide is most easily performed with the high pressure glass bowl reactor. A regulated lecture bottle of SO_2 (LINDE) is attached to the reactor through the sampling port after previous reactions and samplings have been completed. An exess of SO_2 is then bubbled through the reactor with high stirring rates, followed by full pressurization of the reactor to maximize the solubility of the SO_2 in cyclohexane at the reaction temperature employed. Visual evidence of the rate of reaction is provided by first capping the living polymer with 1,1-DPE to form the highly colored diphenyl alkyl chain end. Reaction of this hindered carbanion appears to take place quite quickly (several minutes) in cyclohexane at temperatures of 50°C.

3) Hydrogenation of Polydienes

A chemical (stoichiometric) hydrogenaton method was utilized for the conversion of polybutadiene- or polyisoprene- based materials to their saturated analogues. The chemical agent employed was para-toluene sulfonyl hydrazide (PTSH) (Aldrich, 97%) which forms hydrogen via an in-situ decomposition reaction (Scheme XIII) to form the hydrogenating agent diimide.



Scheme XIII. Decomposition of PTSH.

The reaction, polymer isolation and purification are as follows: Three grams of the diene-containing polymer are charged with 300 ml xylenes (Aldrich) to a 500 ml, 3-neck round bottom flask in an oil bath. A nitrogen inlet, outlet, thermometer, and condenser are fitted to the flask. Irganox 1010 (0.03g) was added to the dissolving polymer to help prevent side reactions during the hydrogenation [127-128]. An excess of PTSH (3 moles of diimide per mole double bonds, i.e. 200% excess) is added while the solution is heated. The reaction temperature is carefully maintained at 130-135°C for five to ten hours. After the reaction is run, the hot, heterogeneous reaction mixture is filtered through a Buechner funnel. (Note: This procedure applies to polymers with little or no crystallinity, i.e. relatively low 1,4-polybutadiene contents in the starting material.) After the homogeneous hydrogenated polymer is isolated by filtration, the solution is added to hot methanol and precipitation ensues. The white, fluffy polymer is then stirred in hot water (80°C) overnight, although soxhlet extraction with hot water or methanol would presumably be more effective. It should also be noted that all reaction by products (impurities) are acetone soluble, thus it should be an ideal soxhlet solvent and its use is to be encouraged. After the polymer is reisolated, it is dried in a vacuum oven overnight at 30°C.

D) STRUCTURAL ANALYSIS

Structural characterization of anionically synthesized materials generally involves GPC analysis to give polydispersity information as well as relative M_n and M_w (to polystyrene or PMMA standards). The use of absolute methods (osmometry, light scattering) is highly recommended if available. Chemical composition is most often determined using FTIR (qualitative or semi-quantitative) and NMR (quantitative). Both ^1H NMR and ^{13}C NMR analyses are often highly useful. These spectroscopic methods are necessary for determining changes in composition from polymer modification reactions, as well as polymer stereochemistry.

Thermal analysis is then employed to help provide insight on structure property relationships. Although DSC is most commonly employed, TMA is of great value, especially for multiphase systems. More sophitsticated information is gleaned from dynamic mechanical analysis (DMTA). Stress-strain on tensile testing offers useful information regarding the ultimate properties of a polymeric system.

1) FTIR Analysis

a) Instrumentation

All infrared spectra were obtained with a Nicolet MX-1 FTIR Spectrometer. Samples were generally run as thin cast films on KBr or NaCl windows, or as compression molded or solution cast films with no salt plates. This second technique, although more difficult and time consuming, leads to spectra with no background noise, while the use of salt plates leads to transmission cut-off at 500 cm^{-1} and often noise in the 2000-1500 cm^{-1} region due to bound water, a nuisance when carbonyl studies are being performed.

b) Hydrolysis Reaction Studies

These studies are normally carried out in the abosrbance mode, which allows for greater computational ease. The absorbance ratio, i.e. the ratio of the acid to ester carbonyl absorbances is indicative of the level of hydrolysis. The transmittance mode is used as a qualitative indication of the extent of hydrolysis. The ester peak (~1735 cm^{-1}) and carboxylic acid peak (~1702 cm^{-1}) are the absorbances of interest. The carboxylic acid O-H stretch is too diffuse and broad for practical quantitation, and also overlaps with the C-H stretching region.

c) Diene Hydrogenation and Microstructure

The FTIR spectrophotometer is a useful tool for quantitatively determining the microstructure of diene-containing polymers, especially for the polybutadiene case [127]. Extinction coefficients are known for the three absorbances due to the =C-H out of the plane wagging frequencies. The absorbance wavelengths and extinction coefficients for the three geometrical isomers of polybutadiene are given in Table 21.

These microstructural peaks may be used for determining roughly the extent of hydrogenation, although the C=C stretching peak at 1640 cm^{-1} is not complicated by peak overlap and may give a more accurate answer, provided a constant absorbance is present (from another constituent) in which this peak may be ratiod.

2) Proton NMR

^1H NMR analysis is performed with either a Bruker WP-270 superconducting multi nuclear NMR or a Varian EM-390 90 MHz instrument.

a) Tacticity Determination

It has long been appreciated [129] that the tacticity of PMMA can be determined by ^1H NMR by analysis of the methacrylate α-methyl resonances. These protons split into three resonances due to the three stereochemical triads possible. These resonances and their assignments are shown in Table 22. An example of the α-methyl spectrum of PMMA, synthesized anionically in THF at -78° using the bulky initiator DPHL is shown in Figure 11.

This technique is unfortunately complicated by signal overlap when higher esters are evaluated. Figure 12 shows, for example, the spectrum of poly(ethyl methacrylate). The determination of stereochemistry for these higher esters must involve total hydrolysis, followed by methylation with diazomethane, as advocated by Yuki, et. al. [3] or ^{13}C analysis of the carbonyl region [130].

Table 21

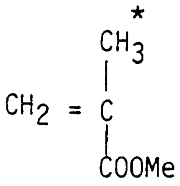
Polybutadiene Microstructural Data [127]

Structure	Band Position (cm-1)	Extinction Coefficient, ε
trans-1,4	965	86
cis-1,4	735	25
vinyl-1,2	910,	120
	990	-

Table 22

^1H NMR Resonances for α-Methyl Protons[a] of PMMA

δ^b(ppm)	Triad Assignment
0.8	rr (syndio)
1.0	mr (hetero)
1.25	mm (iso)

a) 

$CH_2 = \underset{COOMe}{\overset{\overset{*}{CH_3}}{C}}$

b) ppm from TMS

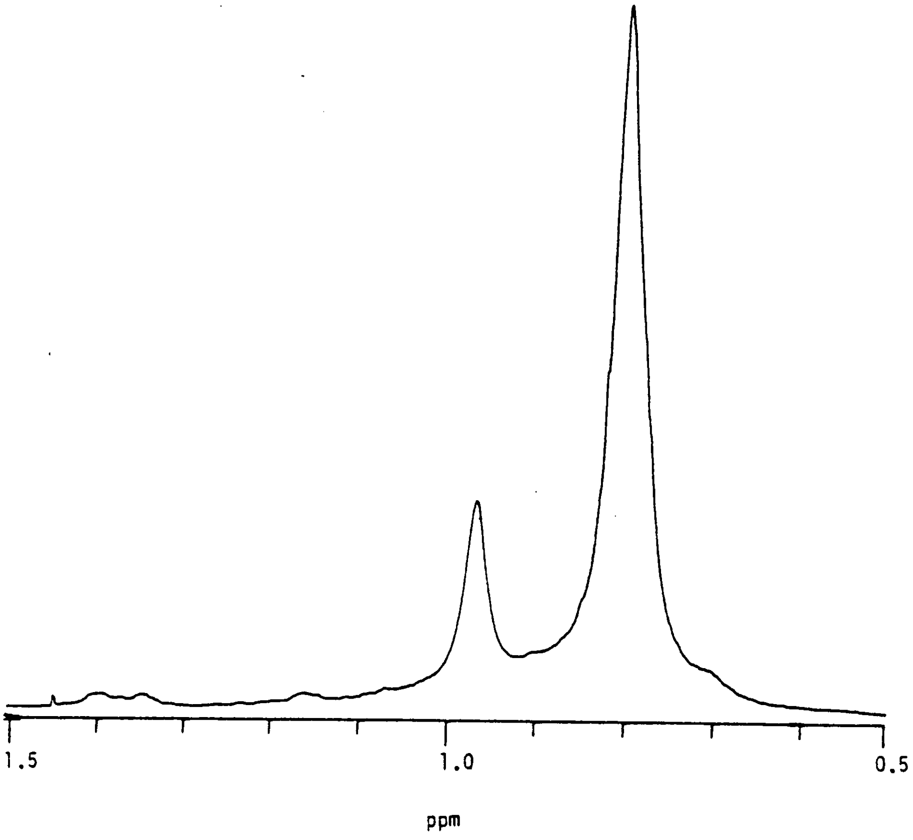


Figure 11. ¹H NMR Spectrum of PMMA (α-methyl Region).

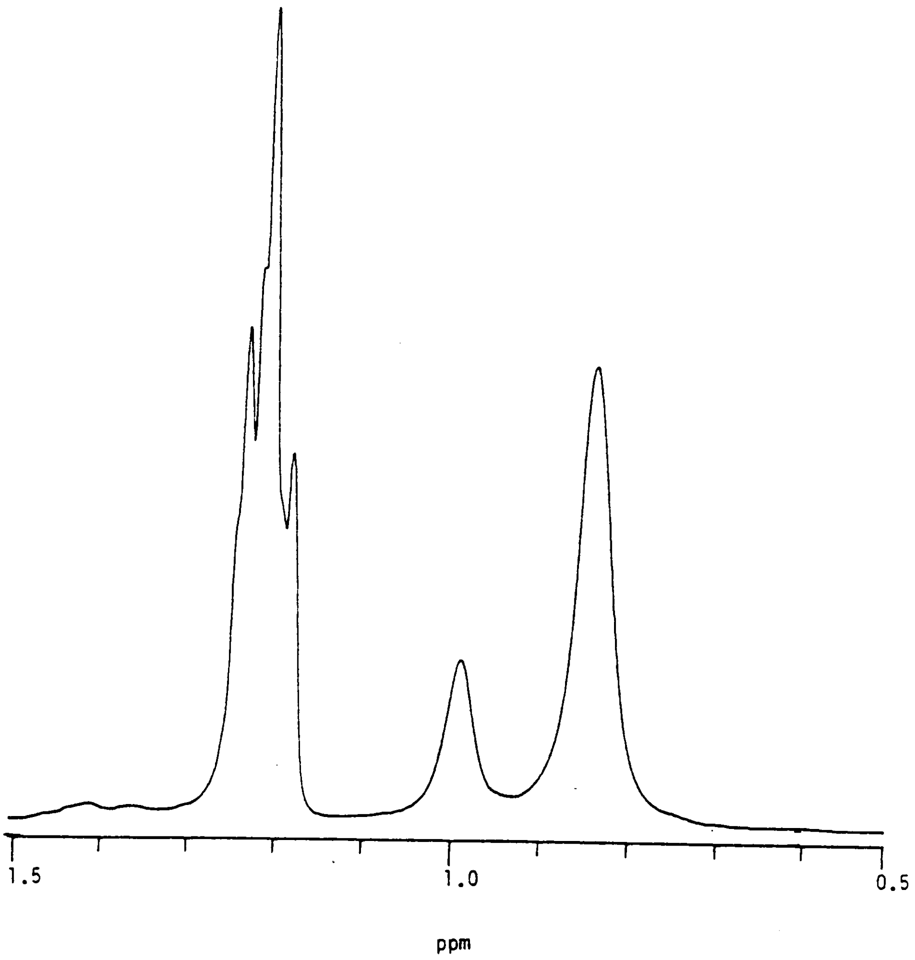
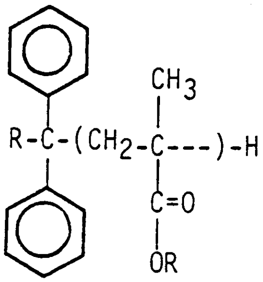


Figure 12. ^1H NMR Spectrum of PEMA (α-methyl Region).

b) Molecular Weight Determination

Number average molecular weights for low molecular weight (<10,000g/mole) poly(alkyl methacrylates) synthesized anionically via the DPHL initiator may be determined using high resolution ^1H NMR spectroscopy. Due to the diphenyl end group in these polymers which contains 10 protons, the end group may be ratioed against a resonance in repeat unit, e.g. $-OCH_3$ in PMMA, or $-O-C(-CH_3)_2-\underline{H}$ in isopropyl methacrylate (IPMA) to give an M_n which can be compared to the GPC M_n.



c) Composition

^1H NMR has been used for chemical composition determination of methacrylate containing copolymers. For example, for a polystyrene-poly(isobutyl methacrylate) block copolymer, the composition may be determined by averaging the phenyl resonances (7.0 ppm) of polystyrene with the $-O-C\underline{H_2}-R$ resonance of the isobutyl group (3.6 pm).

3) Molecular Weight Analysis

Molecular weights and their distributions were determined by size exclusion chromatography (GPC) with a Waters 150C variable temperature instrument with typically a four column set of (500Å, 10^3Å, 10^4Å and 10^5Å) microstyragel columns. Typical GPC solvents used were THF as cyclohexanone.

4) Thermal Analysis

Thermal analysis (TMA, DSC, and TGA) were performed on a Perkin-Elmer System 2 instrument. Typical heating rate was 10°/min.

5) Dynamic Mechanical Analysis

Dynamic mechanical data was determined with a Polymer Labs DMTA instrument at 1 Hz.

V. RESULTS AND DISCUSSION

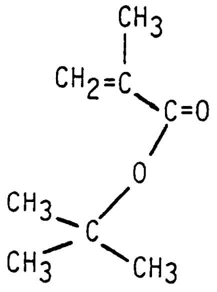
A. Synthesis of Alkyl Methacrylate Homopolymers

The original goal of this research was to establish polymerization conditions which would result in poly(alkyl methacrylate)-containing homo- and copolymers with the controllable molecular weights, narrow distributions and high degrees of structural integrity associated with anionically prepared materials. In our original range-finding investigations, we studied the effects of monomer and initiator structure and reactivity on the anionic polymerization characteristics of alkyl methacrylates. This work stemmed from several landmark investigations which were reviewed in the historical chapter of this thesis.

The investigations of Wiles and Bywater [50] and Rempp and coworkers [49] revealed that the organolithium initiator of choice is 1,1-diphenyl hexyl lithium, the adduct of butyl lithium and 1,1-diphenyl ethylene. Alkyl lithium initiators are preferred for their versatility, solubility and applicability to the synthesis of methacrylate polymers of widely ranging tacticities [3]. The synthesis of "hydrocarbon"-methacrylate block polymers further favors the use of organolithium reagents over organometallic compounds based on the heavier alkali metals, as the lithium-based initiators are required for full synthetic control in many polymerizations of non-polar monomers [131-134].

The solvent employed for anionic methacrylate polymerization has been shown to profoundly effect both the microstructure (tacticity) [1,3] and the "living" nature of the enolate anions [135]. For example, while hydrocarbon solvents such as toluene provide highly isotactic polymers, initiation and propagation of MMA in this medium is accompanied by continual carbonyl attack, as indicated by the formation of lithium methoxide throughout the polymerization, even at low temperatures. This terminating side-reaction leads to polymers with very broad molecular weight distributions. Polymerizations in THF or other polar solvents [49-136] may lead to "living" polymerizations which produce quite highly syndiotactic methacrylate polymers in the presence of suitable initiators at low temperatures. Polymers with narrow molecular weight distributions often result from these conditions.

Muller has studied the effect of ester group on both the polymerization kinetics and temperature stability for methyl- and t-butyl methacrylate [137]. For Na^+ and Cs^+ counterions, the propagation of TBMA proceeds without side reactions even at room temperature, contrary to the temperature dependence of MMA propagation. Muller postulated that this dramatic effect was due to electronic factors and not steric effects. The positive inductive effect of the t-butyl ester (1) lowers appreciably the reactivity of the ester group toward nucleophilic attack.



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An assembly of these wideranging facts lead us to investigate the following variables early in the study:

1. Monomer Effects. A range of alkyl methacrylates from MMA to TBMA were investigated.
2. Initiator Effects. Two organolithium initiators of very differant reactivity were chosen, s-butyl lithium (s-BuLi) and 1,1-diphenyl hexyl lithium (DPHL).
3. Solvent Effects. The polar solvent (THF) and non-polar solvent (toluene or hexane) were chosen to demonstrate polymerization solvent polarity effects.
4. Temperature Effects. The effect of temperature on polymerization characteristics was demonstrated.

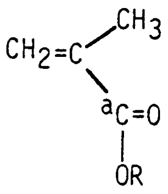
Monomer and Initiator Effects

To negate complications in the study of monomer and initiator structure and reactivity, polymerization solvent and temperature were chosen which would not to have negative effects. This "best case" was the use of THF at -78°C. Monomers chosen for polymerization with the two organolithium initiators were the alkyl methacrylates of the ester group methyl (MMA), ethyl (EMA), n-butyl (NBMA), iso-butyl (IBMA), and t-butyl (TBMA). The sec-butyl ester monomer (SBMA) was too impure to use in these studies. Monomers were purified by double distillation from calcium hydride. Polymerization times were 10 minutes.

In light of Muller's statements regarding ester inductive effects, it was first attempted to demonstrate the extent of this inductive effect of the ester-alkyl group on the electron density of the carbonyl. The dramatic effect associated with the ester group in methacrylate monomers arises from Mullers electronic argument, steric effects, or both. The use of ^{13}C-NMR to determine the chemical shift (and thus electron density) of the carbonyl carbon was performed to determine the extent of electronic effects of the methacrylate ester group, and thus the nature of carbonyl protection. The chemical shift data is listed in Table 23. Several interesting factors are apparent. The electronic environment of the carbonyl carbon is effected to a small degree by different substituents. For example, the methyl ester group (MMA) which is the least "electron pushing" has a corresponding chemical shift (relative to TMS) 1.2 ppm downfield from the most shielded carbonyl, that belonging to TBMA. It is unlikely that the dramatic differences Muller found for these esters could have been due solely to electronic effects. A more dramatic finding is that the chemical shifts (electronic environment) for the three methacrylate esters based on primary alcohols (ethyl-, n-butyl-, and iso-butyl methacrylate) are identical. The equal electronic "protection" of the carbonyl of these three monomers, coupled with the very different steric protecting capabilities offer an excellent tool for studying the nature of the protection of the methacrylate carbonyl to terminating side reactions. The relative steric behavior [138] of a series of alkyl groups is given in Table 24. Note the thousand-fold rate difference between methyl- and iso-butyl, the more than thirty fold increase in hinderance from ethyl to isobutyl, and the more than doubling of hinderance from ethyl to n-butyl. In summary, the electronic (^{13}C chemical shift) evidence indicates identical reactivity toward EMA, NBMA, and IBMA, while MMA and TBMA show a small electronic difference. Sterically speaking, however, the reactivities of these methacrylate esters should be very different.

Table 23

Use of ^{13}C NMR to Determine Nature of Protection



	a*
MMA	167.95
EMA	167.49
NBMA	167.49
IBMA	167.49
TBMA	166.78

*PPM from TMS.

Table 24

Average Relative S_N2 Rates for Alkyl Substrates [138]

R	Relative Rate
Methyl	30
Ethyl	1
n-Butyl	0.4
iso-Butyl	0.03
Neopentyl	10^{-5}
Allyl	40
Benzyl	120

To determine the nature of carbonyl protection, the monomers listed in Table 1 were polymerized in THF at -78° for ten minutes using the reactive initiator s-BuLi which is capable of high ratios of 1,2 to 1,4 addition. The definition of 1,2 addition is nucelophilic attack across the carbonyl, while 1,4 addition is nucleophilic attack at the carbon-carbon double. These polymerizations are generally very complex and are characterized by fairly high conversions at long times (24 hrs) [3] but gave only low yields (<15 percent) in the short times of this experiment. The analysis of the molecular weight distribution of these polymers showed that bimodal distributions occurred regardless of the monomer used, i.e., two separate peaks were observed, a lower molecular weight peak (A) and a higher molecular weight peak (B) which are separable by GPC in most cases. The ratios of these two molecular weight peaks changes with methacrylate monomer, the high molecular weights being favored for the lower alkyl groups (MMA and EMA), and the lower molecular weights being favored for the higher alkyl groups, with almost imperceptible high molecular weight peaks for isobutyl-and t-butyl methacrylates. The GPC chromatograms for PMMA and PEMA are shown in Figure 13, while the chromatograms for the bulkier NBMA and TBMA polymers are shown in Figure 14. The ratio of the relative area of the peaks in these bimodal distributions (A/B) is given in Table 25.

It is immediately obvious that while the electronic (or inductive) effect does not correlate with this data, the steric parameters (Table 24) for the various alkyl groups correlate quite well. The electronic arguments would predict very similar GPC data for EMA, NBMA, and IBMA. In fact, EMA shows the greatest extent of high molecular weight material

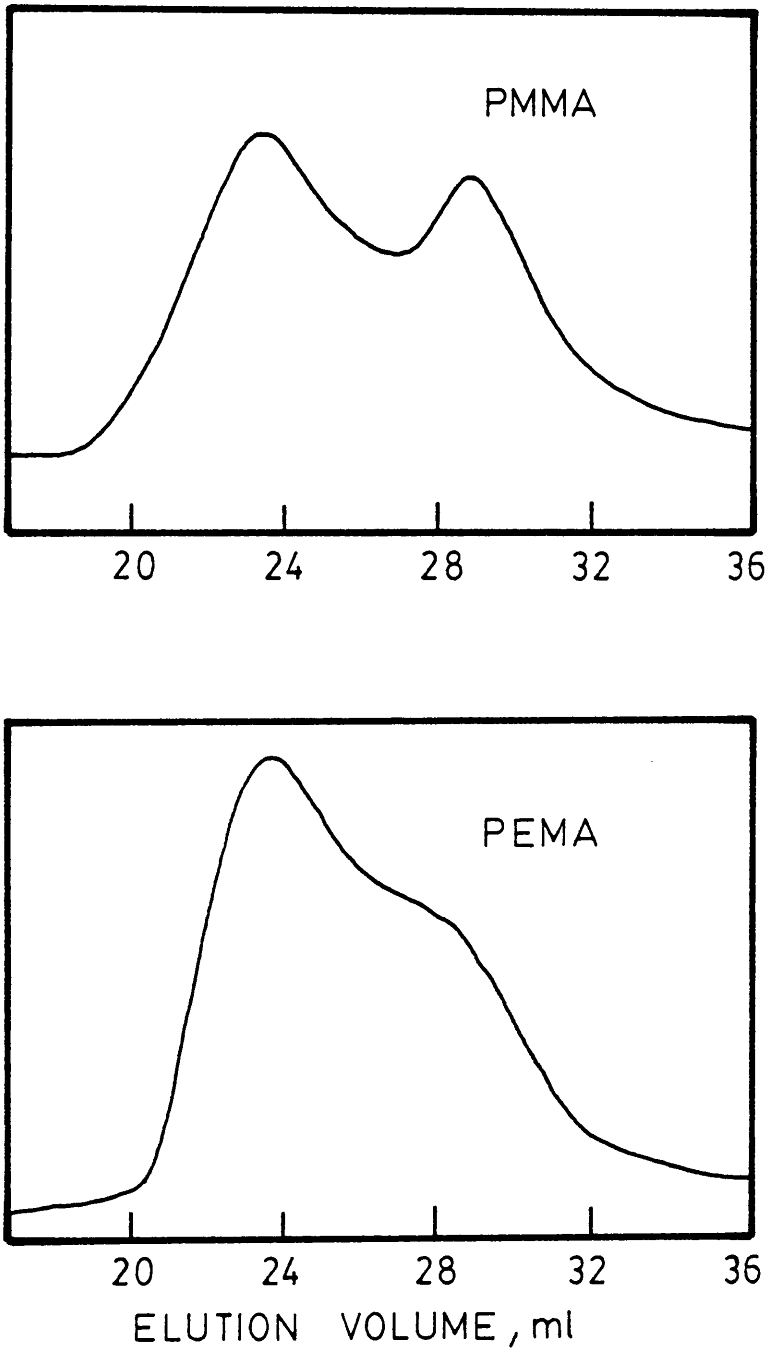


Figure 13. GPC Chromatograms of PMMA and PEMA Synthesized by s-BuLi Initiation in THF at -78°C.

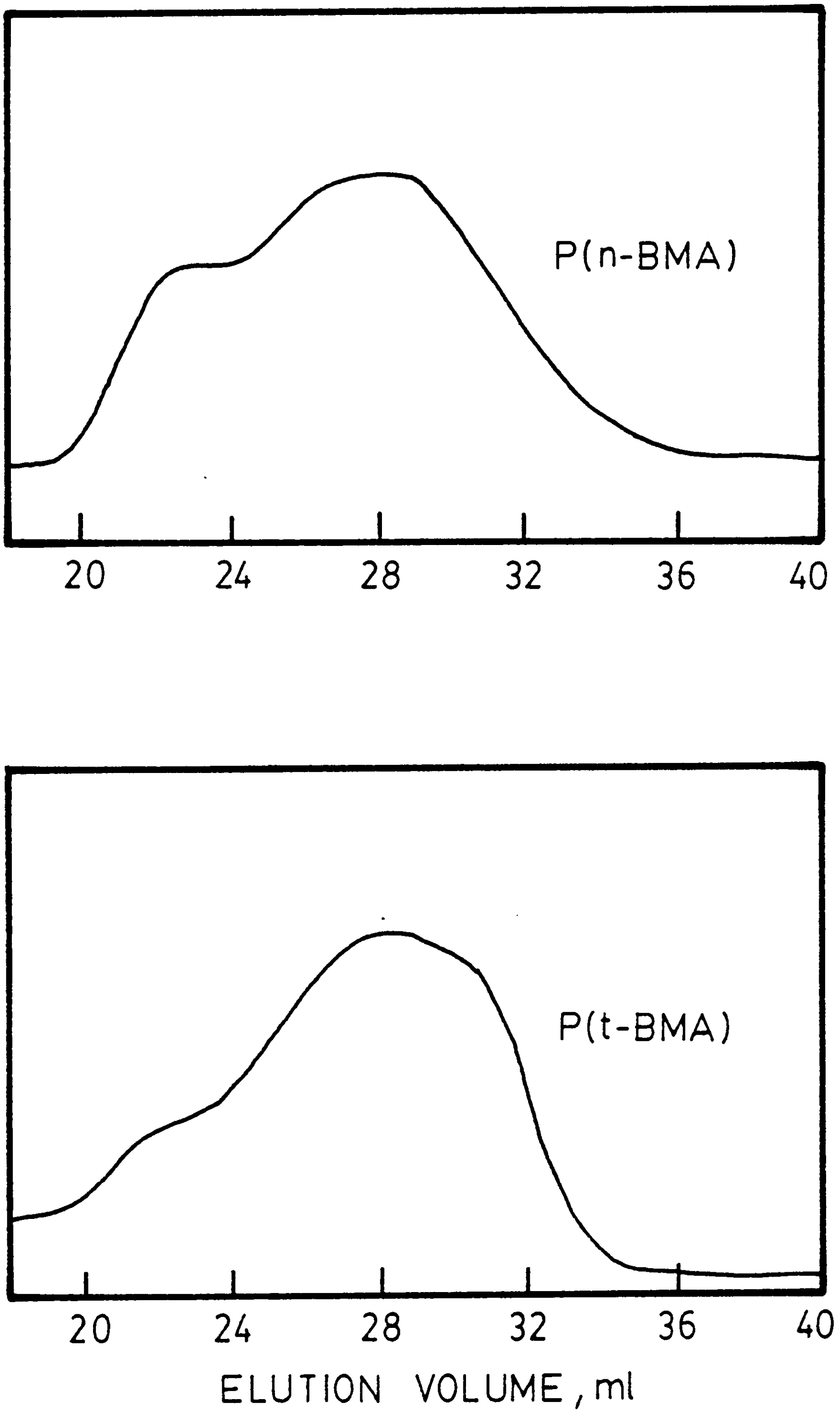


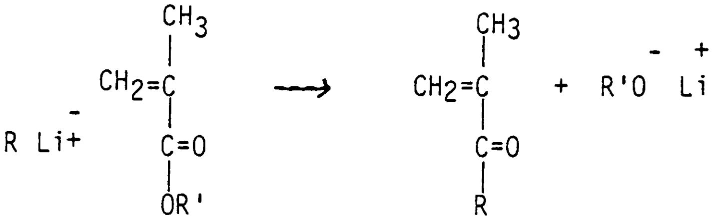
Figure 14. GPC Chromatograms of PNBMA and PTBMA Synthesized by s-BuLi Initiation in THF at -78°C.

Table 25

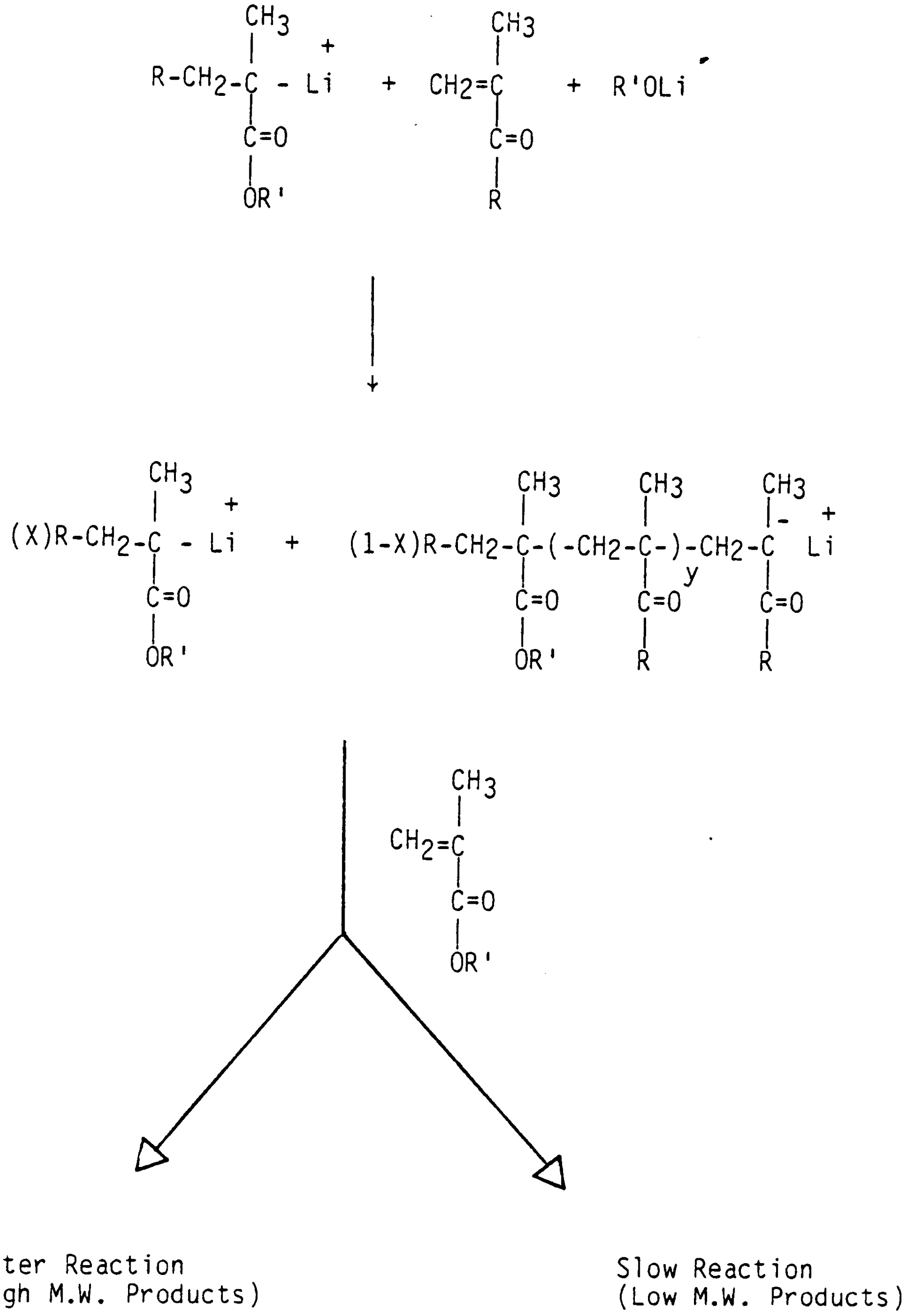
Relative Ratio of Low and High Molecular Weight Peaks (A/B) vs. Alkyl Methacrylate

Monomer	A/B
MMA	0.9
EMA	0.67
NBMA	1.5
TBMA	3.2

(lowest A/B ratio), NBMA is intermediate in behavior, and IBMA, although not listed, has an almost undetectable level of high molecular weight material. In other words, an increase in steric constraints (which presumably lowers the extent of carbonyl attack) favors formation of lower molecular weight products and limits the formation of very high molecular weight products. This bimodality, coupled with the curious molecular weight effects, is difficult to explain if one takes into account only alcoxide formation due to reaction of the initiator at the carbonyl group. As seen in Scheme XIV, the accompanying side product from carbonyl attack is butyl isopropenyl ketone which forms a highly stabilized (non-reactive) species when initiated and reacts only very slowly with methacrylate monomers (Scheme XV). If one assumes that relatively long segments of ketone monomer form on some fraction of chains, these species will be psuedo-terminated, resulting in a drastically lowered methacrylate anion concentration which will clearly initiate more monomer to form a high molecular weight product. The lower molecular weight product arises from the much slower initiating rate of the ketone capped oligomers. This scheme, however, does not readily account for the reverse situation, where bulkyl ester groups presumably prevent excessive carbonyl attack. The formation of low levels of <u>high</u> molecular weight product is difficult to explain. Perhaps the influence of alcoxides (formed during carbonyl attack) which are known to influence the rate of polymerization [139] is the key to these unanswered questions. It would seem that this is unlikely, however, since if clean initiation is performed (using bulky initiators to be described later), monomomodal and narrow distributions will result



Scheme XIV. Alkyl Lithium Attack at the Methacrylate Carbonyl (1,2-addition).



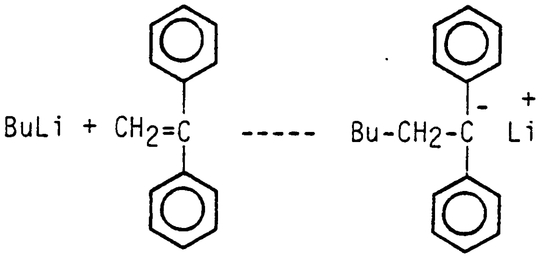
Scheme XV. Possible Sequence Leading to Bimodal Molecular Weight Distribution.

regardless of alcoxide concentration. For more discussion regarding the complex sequence of events initiated by (1,2-) or carbonyl attack, the interested reader is referred to two short reviews [140,144].

In conclusion, it has been shown that alkyl group effects in anionic methacrylate polymerization are predominately steric in nature, in contrast with the conclusions of Muller [137]. As has been widely reported [2,139], butyl lithium polymerization of alkyl methacrylates results in bimodal molecular weight distributions. This bimodality has been found, however, to depend on the specific methacrylate ester involved, showing that the ratio of 1,2-to 1,4-addition changes with the steric nature of the ester-alkyl group. Much mechanistic work is needed to elucidate the exact sequence of events leading to the bimodality. Alcoxide-free initiators (distilled s-BuLi) with highly purified monomers will be required to measure exactly the role of alcoxides and ketone on this bimodal polymerization. This route is further complicated by the well known alcoxide-enolate forming reaction of s-BuLi with THF, even at -78°C [120]. Thus the less reactive initiator n-BuLi may be a wiser choice in this case. Structural characterization, by HPLC, GPC, ^{13}C NMR and FTIR, of the products produced from various initiator/monomer ratios with the various alkyl methacrylates should help in the mechanistic elucidation. Analysis of the alcoholic byproducts (termination of alcoxides) using gas chromatography (G.C.) would provide complimentary data. Several interesting monomers in addition to those already studied include neopentyl methacrylate, a super-hindered monomer (see Table 2) which should have the same carbonyl electron density as EMA, NBMA, and IBMA. This monomer would shed further light on the steric vs. electronic argument which has been discussed in detail above.

Effect of Initiator

The effects of s-Butyl lithium initiation on a variety of alkyl methacrylates has been discussed above in some detail. Although the results are highly interesting from a physical organic or mechanistic view, simple alkyl lithium initiators are of very little value synthetically due to the side reactions which result in low yield and very broad polydispersities. As mentioned previously, the discovery of Rempp and coworkers [49] and the Canadian group of Wiles and Bywater [50] that diphenyl ethylene capped anions (Scheme XVI) are clean initiators for methacrylates sparked interest in the use of this route.



Scheme XVI. Formation of Hindered, Resonance Stabilized Initiators for Methacrylate Polymerization.

The bulky, resonance stabalized initiators derived from DPE are considered to be ideal methacrylate initiators due to the following:

1. The hindered, less basic nature of the carbanion prevents carbonyl attack at sub-ambient temperatures.
2. This methodology is amenable to use in block polymer synthesis, as hydrocarbon based "living polymers" will readily add across the DPE double bond to form the "macro-molecular initiator".

3. The formation and reactions of this initiator do not involve electron transfer processes, which allows one to work in non-ethereal solvents and aids in the synthesis of certain hydrocarbon-methacrylate block polymers.

The same monomer series studied in the butyl lithium investigation was initiated with DPHL in THF at -78°. Monomers were conventionally purified by double distillation from finely crushed calcium hydride. In most cases, yields were quantitative with quite narrow polydispersities when stoichiometric molecular weights of ca. 10,000g/mole were sought. The synthesis of methacrylate polymers of significantly higher stoichiometric molecular weights, arrived at by increasing the monomer/initiator ratio, lead to irreproducible results, often with little or no isolated polymer yield. The Rohm and Haas monomers EMA and IBMA gave the best results, while MMA (Rohm and Haas) typically gave much broader polydispersities and TBMA (Polysciences) often gave no polymer yield at all. The effect of initiator on the final polymer is dramatic when very pure monomers are slowly added to the THF/initiator solution at -78°. This difference is evident in Figure 15, which shows EMA polymerization by both s-BuLi initiation (a) and initiation by DPHL (b). Isolated polymer yields were 12 percent for route (a), and 95 percent for route (b). Once again, it should be noted that chromatograms like (b) are only obtained when highly pure monomers can be obtained. An elaboration of the reaction sequence is shown in Scheme XVII. As can be seen in Scheme XVII, slow, continuous addition of methacrylate monomer to the living system is performed to avoid exotherms which could result in thermal termination at temperatures above -65°C [141]. When very low molecular weights are desired, the monomer impurities become

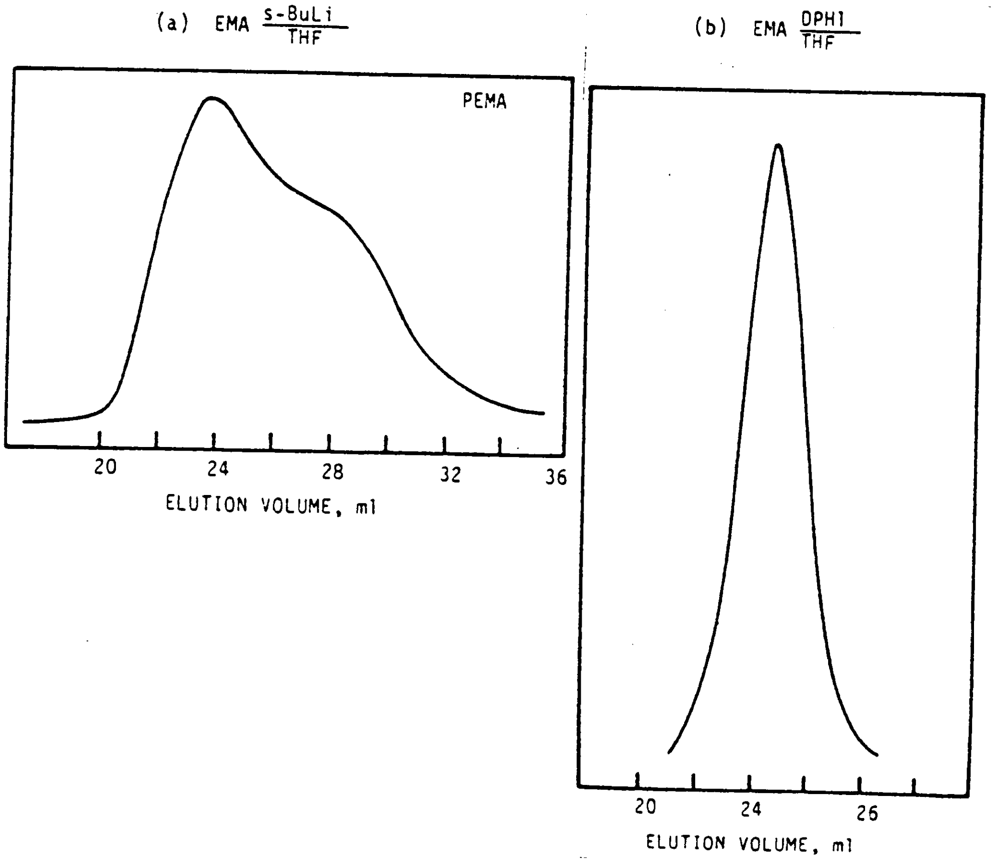
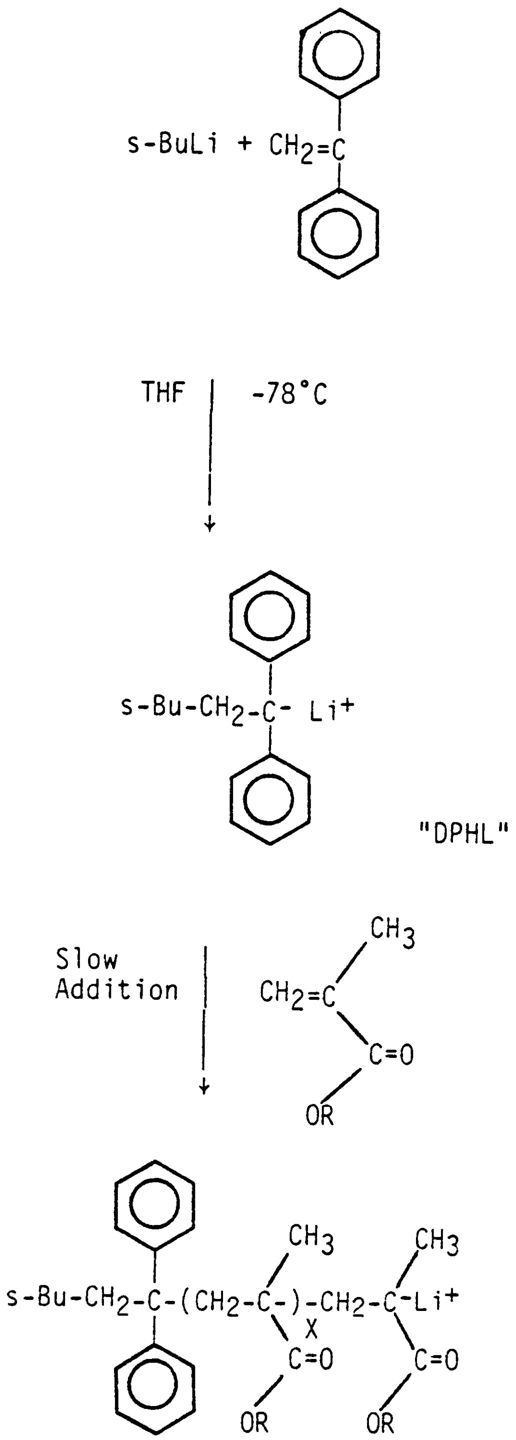


Figure 15. Effect of Initiator an EMA Polymerization in THF at -78°C.



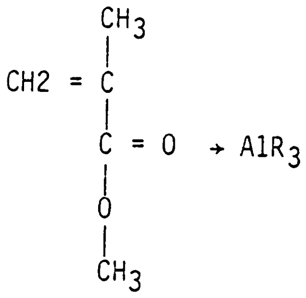
Scheme XVII. Anionic Synthesis of Poly(alkylmethacrylates).

insignificant. However, as most polymer properties are adversly effect by molecular weights below ca. 30,000 - 50,000g/mole, higher molecular weights need often to be synthesized. Molecular weights approaching 100,000 g/mole are often desirable, especially in block copolymer synthesis. A living polymerization would require 100 gm MMA and 1 mmole DPHL to obtain a 100,000 molecular weight PMMA. Methacrylate monomers usually contain impurity levels above 1% and below 5%. The major impurity in MMA is methanol (see Literature Review) which rapidly terminates anionic polymerizations. Assuming 1% methanol content, every gram MMA added would contain 0.01 gm methanol, or on a molar basis, 0.3 mmoles. Thus, after only 3g MMA added (out of 100g total) 90% of the chains would be terminated. After one more gram MMA is added, the system is totally terminated. Even with "high purity" monomers (e.g., 99.9%) total termination would take place before half the MMA had been added. This question of methacrylate monomer purity cannot be overly stressed. Suitable methods are available for the scrupulous purification of hydrocarbon monomers. For example, the organometallic reagent dibutyl magnesium (DBM) has been well documented as a highly sensitive reagent which reacts with water, oxygen, and other protic impurities present in styrene and diene monomers which may terminate anionic polymerizations [8]. The presence of a bright yellow complex is a useful indicator, assuring the chemist that the monomer is highly pure. Unfortunately, DBM and most other similar compounds rapidly polymerize methacrylates.

Monomer Purification

Calcium hydride is currently the established purification agent for methacrylate monomers. This "drying agent" falls short in two respects concerning methacrylate purification. First, due to the heterogeneous nature of calcium hydride dispersed in a polar monomer such as methyl methacrylate, the hydrophilic MMA may be difficult to fully dry. More importantly, as the higher methacrylate monomers are generally synthesized via transesterification of MMA with the appropriate alcohol (which in most cases has a boiling point close to the resulting methacrylate -- not to mention azeotropes), alcoholic, terminating impurities are present in most commercially available methacrylates. Calcium hydride unfortunately does not react appreciably with these higher alcohols. Thus, most higher methacrylates cannot be used for anionic polymerization with any degree of success. This places severe limitations on the potential properties one may obtain via anionic methacrylate polymerization. We arrived at these conclusions after many months of inconsistent results, due to what was later found to be non-removable "impurities" in most of these monomers.

After experiencing difficulty in gaining consistent polymerization results, especially with the higher alkyl methacrylates, it was decided that the search for a new purification technique should be initiated. As residual alcohols are the major impurity in most alkyl methacrylates, purification agents which react with alcohols (and water) but do not react with methacrylates were sought. Initial experiments were with conventional organic alcohol scavengers such as calcium chloride ($CaCl_2$) and 5Å molecular sieves. More intriguing, however, was the possibility of using trialkyl aluminums as methacrylate purification agents. This stemmed from a series of papers by P.E.M. Allen, et al. [122-124] in which triethyl aluminum (TEA) was investigated as a possible initiator for methacrylate polymerization. Although radical polymerization of MMA may occur by photoinitiation, anionic polymerization does not occur. It was also found that if an excess of MMA is present, a stable yellow complex of the structure 1 was formed. Allen also tried triethyl aluminum as a final purification of MMA before a dilatometry experiment, [124A] but then turned to the hetereogenous sodium benzil purification which he thought to be more amenable to high vacuum work [142].



$$CH2 = C(CH_3)-C(=O \rightarrow AlR_3)-O-CH_3$$

1

These factors lead to the belief that trialkyl aluminums may be ideal purification agents for methacrylate monomers, as the requirements for the ideal methacrylate purification agent are:

1. No reaction with or polymerization of methacrylates.
2. Rapid reaction with alcohols and water.
3. Rapidly forms color upon total purification of <u>most</u> methacrylate monomers, i.e. the methacrylate's impurities are titrateable.

The reactive properties of trialkyl aluminums with alcohols (Scheme XVIII) and water are well known. A combination of the above facts lead to the utilization of trialkyl aluminums for methacrylate purification.

As a model system which represents an impure methacrylate, MMA "doped" with n-propyl alcohol (NPA) was chosen. This combination was arrived at due to the relative hydrophilicity and availability of MMA, and more importantly, the very close boiling points of NPA and MMA (97° and 100°C, respectively). Thus, no possibility existed for separation by simple distillation. A stock solution was prepared which contained 96% MMA and 4% NPA. The heterogeneous purification agents were allowed to interact with an aliquot of this stock solution for one week. After filtration (when necessary) the solution was distilled under vacuum and the resulting product was slowly added to a solution of DPHL in THF at -78°C. The distillate was also checked for residual NPA using a GOW-MAC gas liquid chromatograph (GLC). The results are listed in Table 26.

GLC results confirmed the presence of very slightly depressed levels of NPA after distillation in experiments 1-3. Analysis of experiment 4 by GLC was complicated, however, due to the hexanes introduced with TEA, which is used as a 25% solution in hexanes. The column used in the GLC analysis was the non-polar DC-200 (15%) on a Chromosorb P solid support. The more polar n-propyl alcohol elutes just prior to the elution of the non-polar (but lower boiling) hexane peak. The "hexane peak" is actually two peaks, probably corresponding to two structural isomers. The only problem with peak overlap occurs with the hexane peaks and an impurity intrinsic to Rohm and Haas MMA, possibly a reaction byproduct from the acetone-cyanohydrin process (ACH).

$$\begin{tikzcd} R_3Al + R'OH \arrow[d, "k_1"'] \\ R_2AlOR' + R\text{-}H \arrow[d, "k_2"', "R'OH"] \\ RAl(OR')_2 + R\text{-}H \arrow[d, "k_3"', "R'OH"] \\ (R'O)_3Al + R\text{-}H \end{tikzcd}$$

$$k_1 > k_2 > k_3$$

Scheme XVIII. Reactions of Trialkyl Aluminum Reagents with Alcohols [143].

TABLE 26

Purification Study on NPA-Doped MMA

EXPT	AGENT	AGENT/STOCK SOLU.	Polymerization
1	CaH_2	4g/50 ml	No Polymer
2	$CaCl_2$	4g/50 ml	No Polymer
3	5Å Sieves	4g/50 ml	No Polymer
4	Triethyl Aluminum	Titrate	Polymer (formed in quantitative yield)

Chromatogram (A) of Figure 16 shows the 1% NPA doped MMA prior to reaction with tri n-octyl aluminum (TOA). The peaks of interest are the air spike at 0.35 minutes, NPA at 0.65-0.70 minutes, the intrinsic impurity at 0.9 minutes, and MMA at 1.2-1.5 minutes.

Chromatogram (B) shows the system after titration with tri-n-octyl aluminum (TOA) followed by distillation. Note the absence of the alcohol peak at 0.65 minutes, the two hexane isomers at 0.8-1.0 minutes, the MMA at 1.2-1.5 minutes, and a new peak and 2.2 minutes. This new species was at first confusing. Addition of small amounts of methanol into the MMA/TOA side of the distillation apparatus, followed by distillation of more MMA into the receiver, and GLC sampling of the distillate revealed that this new peak was now so increased as to be off scale. Referring back to Scheme XVIII shows that the byproduct of the alcoholysis reaction is an alkane derived from the alkyl aluminum. As TOA was the alkyl aluminum used, this new peak must be octane, which is retained in the non-polar GLC column much longer than any other species of interest. Subsequent spiking experiments with 99% n-octane (Aldrich) verified this conclusion. The polymer formed in quantitative yield from experiment 4 showed a fairly narrow polydispersity from GPC analysis. This chromatogram is shown in Figure 17. Also shown is a PMMA resulting from TEA purification of "undoped" MMA. These polymers are in the molecular weight range of 50-70,000 g/mole and were both synthesized quantitatively. Also included is a PMMA standard (Polymer Labs) of slightly lower molecular weight.

Having the capability to scrupulously purify alkyl methacrylate monomers, the major objectives are to synthesize poly(alkyl

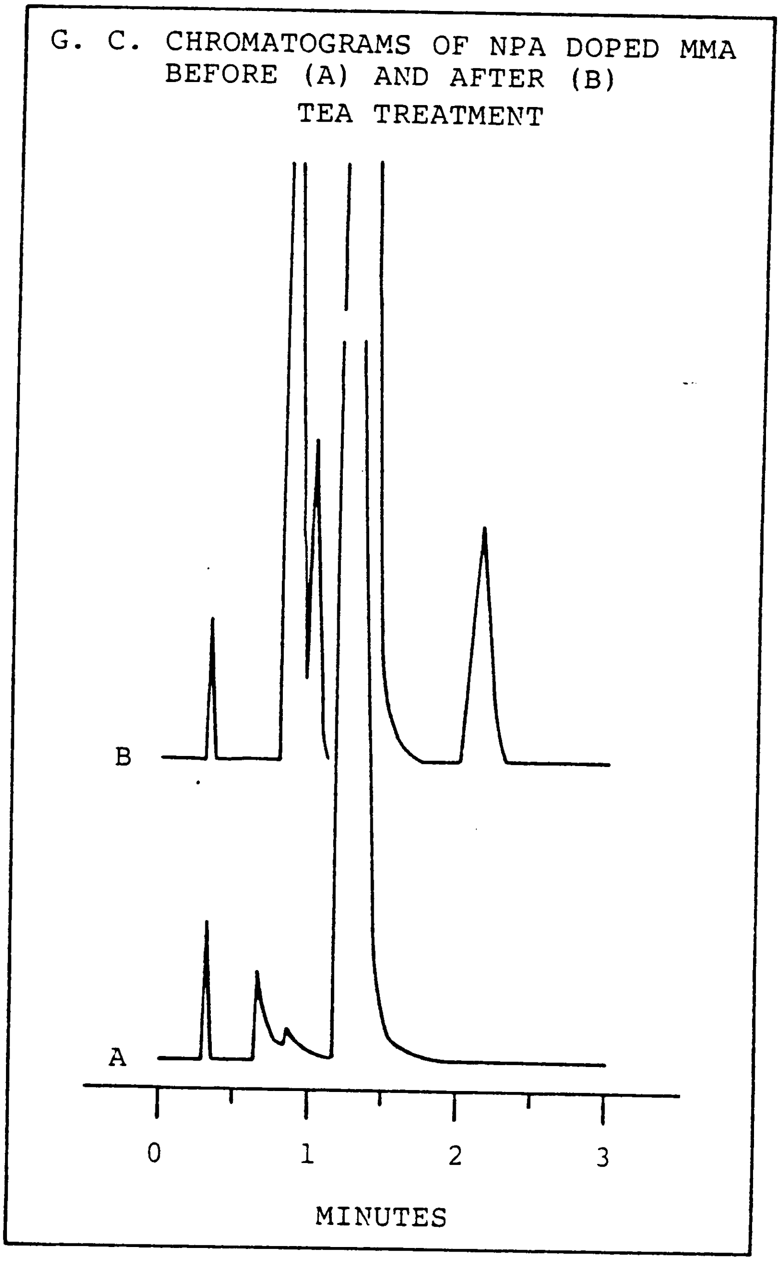


Figure 16. G. C. Chromatograms of NPA Doped MMA Before (A) and After (B) Tea Treatment.

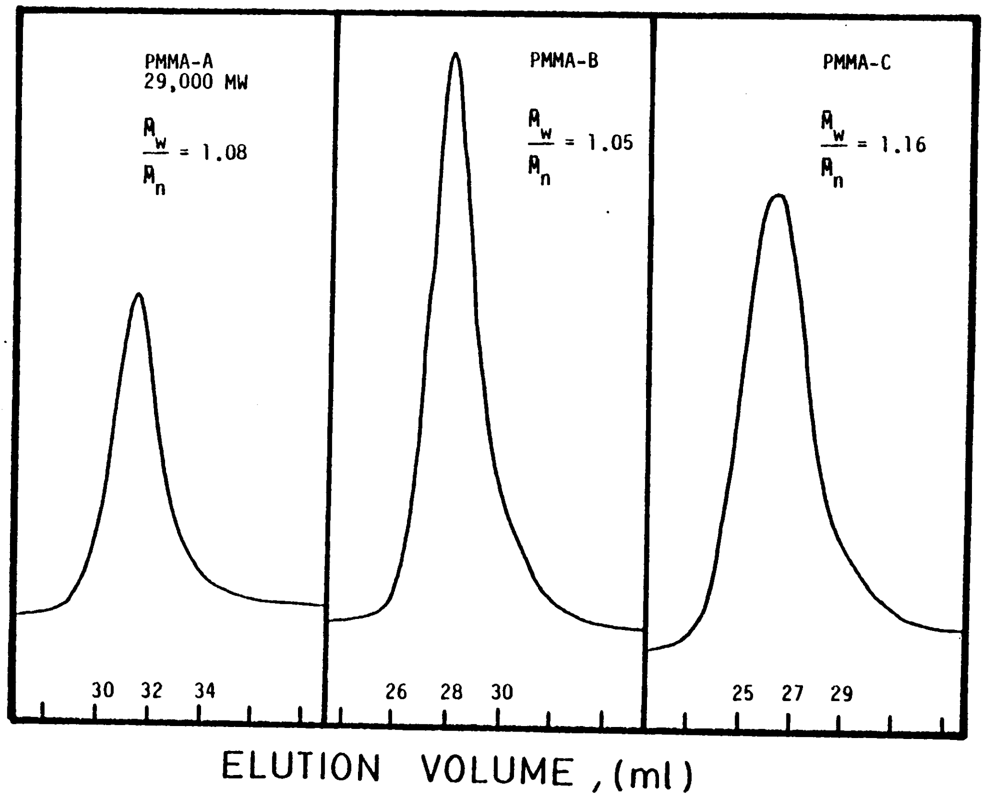


Figure 17. GPC Chromatograms of:
A) PMMA Calibration Standard
B) PMMA from "Undoped" MMA, TEA Treated
C) PMMA from NPA-"Doped" MMA, TEA Treated

methacrylates) with predictable and controllable molecular weights with fairly narrow molecular weight distributions, obtain high molecular weights if desired, and synthesize methacrylate-methacrylate block copolymers with high structural integrity. A series of poly(ethyl methacrylates) were thus synthesized employing these new purification techniques in a DPHL/THF/-78°C polymerization. The monomer/initiator ratio was varied and the resulting molecular weights have been determined by GPC using PMMA standards. The results are listed in Table 27. A plot of the monomer/initiator ratio ($M_{theoretical}$) versus GPC molecular weight is shown in Figure 18. The data all fall within experimental error of the GPC and the difference in hydrodynamic character of the PMMA standards and the PEMA samples. The high correlation coefficient of the plot ($r=0.97$) demonstrates the ability to precisely control the desired molecular weight in these methacrylate homopolymers. This data demonstrates the high purity of these trialkyl aluminum-purified monomers, having the capability of synthesizing high molecular weight polymers (100K) in quantitative yields with narrow polydispersities.

Further evidence for molecular weight control as well as a demonstration of the living nature of anionic methacrylate polymerization under the appropriate conditions (DPHL initiation, low temperatures, polar solvents and highly purified monomers) was furnished by a "sampling" study, where a 10 gm charge of TOA-pure MMA was slowly added to DPHL in 150 ml THF cooled to -78°C. At various times throughout the MMA addition, small amounts of living PMMA were withdrawn from the reactor with a cannula and terminated. Samples were withdrawn

TABLE 27

Anionic Polymerization of Ethyl Methacrylate: Molecular Weight Control

SAMPLE	M_T*	M_{GPC}**	M_w/M_n
PEMA-1	10,000	6,200	1.20
PEMA-2	50,000	63,000	1.09
PEMA-3	100,000	94,000	1.15

$$M_T = \frac{\text{g. EMA}}{\text{moles RLi}}$$

**M_{GPC} = M_n, PMMA Standards

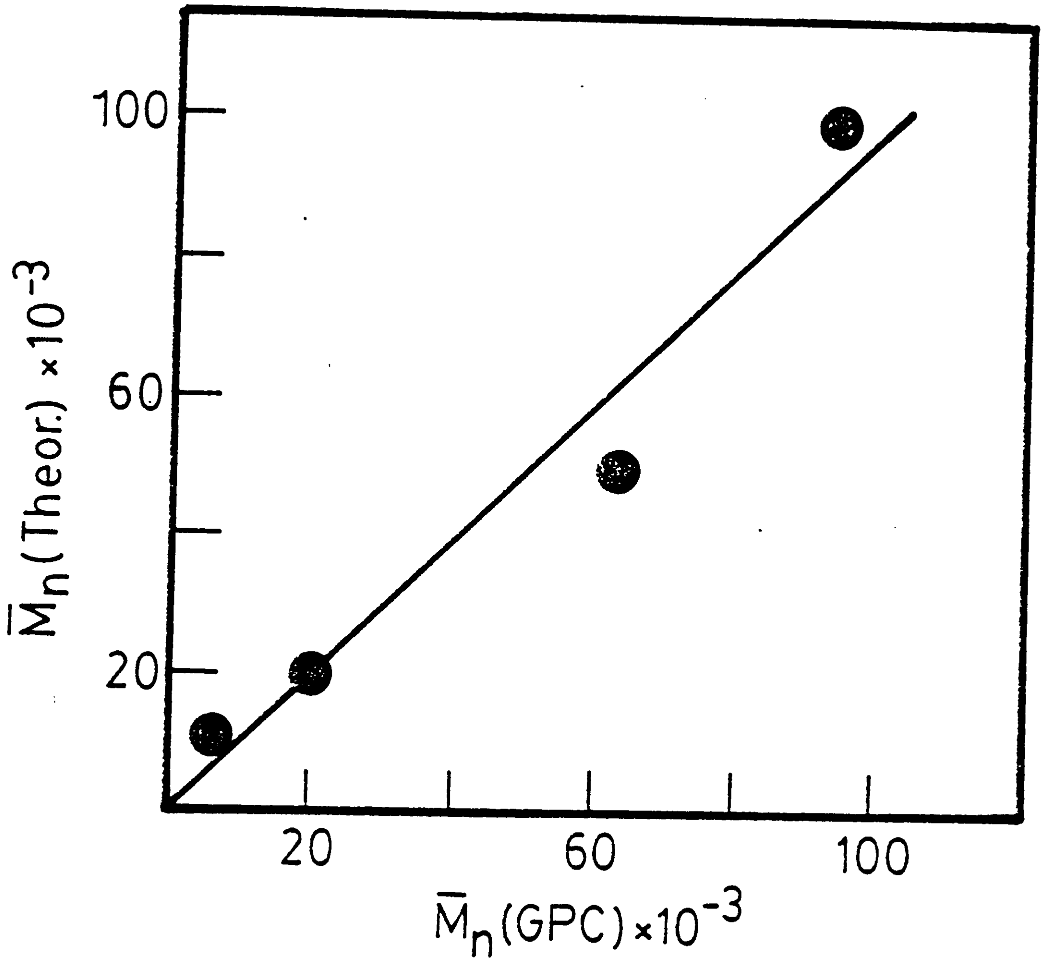


Figure 18. Plot of Stoichiometric vs. Experimental Molecular Weights in Ethyl Methacrylate Polymerization.

after 4,6,8 and finally 10 gm of MMA were added. Molecular weight analysis (GPC-PMMA standards) revealed a linear increase of molecular weight with time, a relationship held only with living systems. Figure 19 shows a theoretical plot of molecular weight vs. percent conversion for normal chain reaction polymerization, step growth polymerization, and living (usually anionic) polymerization. Figure 20 shows the molecular weight-conversion data found in the sampling experiment (in this case conversion equals the gm MMA added, due to its almost instantaneous polymerization) for living methacrylate polymerization. The key features of this data are as follows:

1. Conversion is linear with molecular weight, i.e., this is without a doubt a living polymerization.
2. The polydispersities of these polymers were narrow (<1.3) throughout the polymerization. The sampling operation does not introduce terminating impurities.
3. The end molecular weight is 130,000, with a narrow polydispersity, showing the ultra-pure nature of these monomers.
4. The data correlation is extremely high (r=0.9995), once again an indication of a living, termination-free system.
5. The y-intercept is non-zero; presumably due to the lowered chain end concentration which sampling produced.

The trialkyl aluminum purification route has been shown to work extremely effectively for a variety of "primary" methacrylic esters, dramatically increasing the variety of polymer structures which may be synthesized. Methacrylic esters including methyl, ethyl, n-butyl, 2-ethyl hexyl, and allyl methacrylate have been purified by the above approach without complication. This straightforward purification behavior was not in effect when cyclohexyl methacrylate (1) was treated

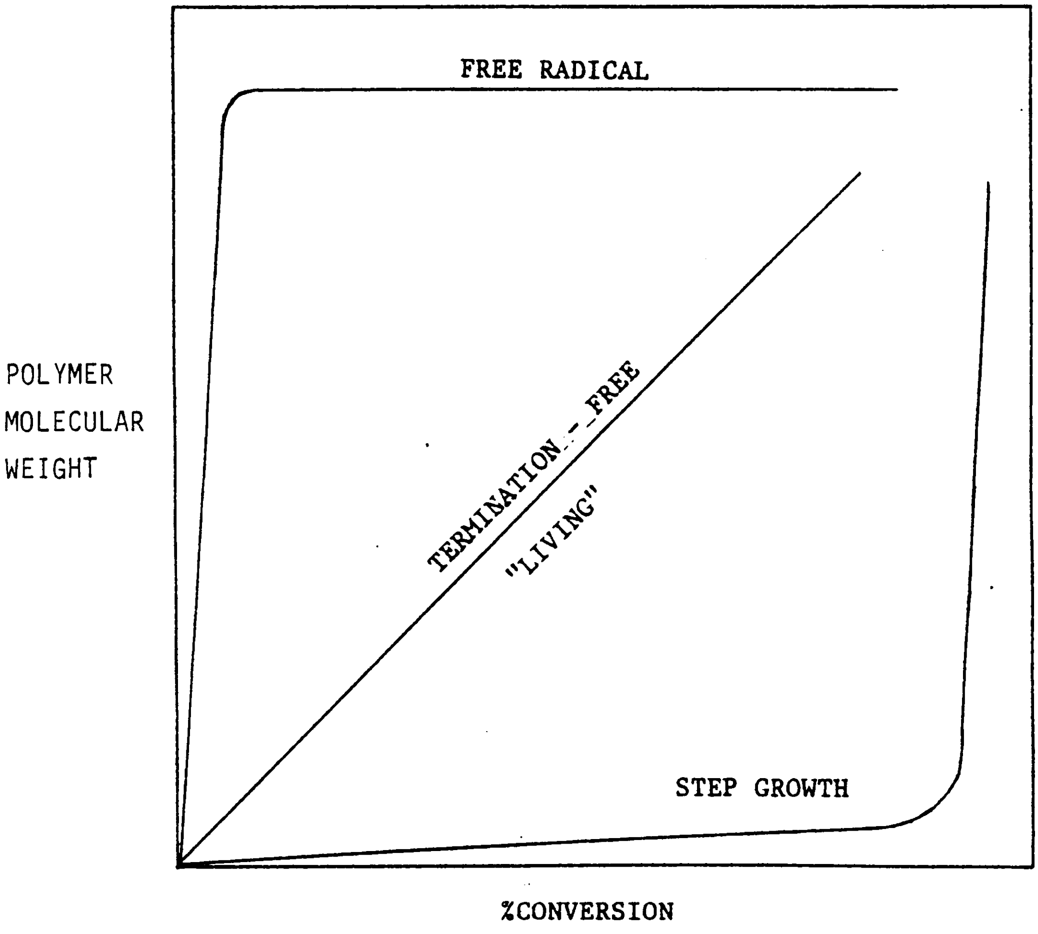


Figure 19. Polymerization Type vs. Polymer Molecular Weight.

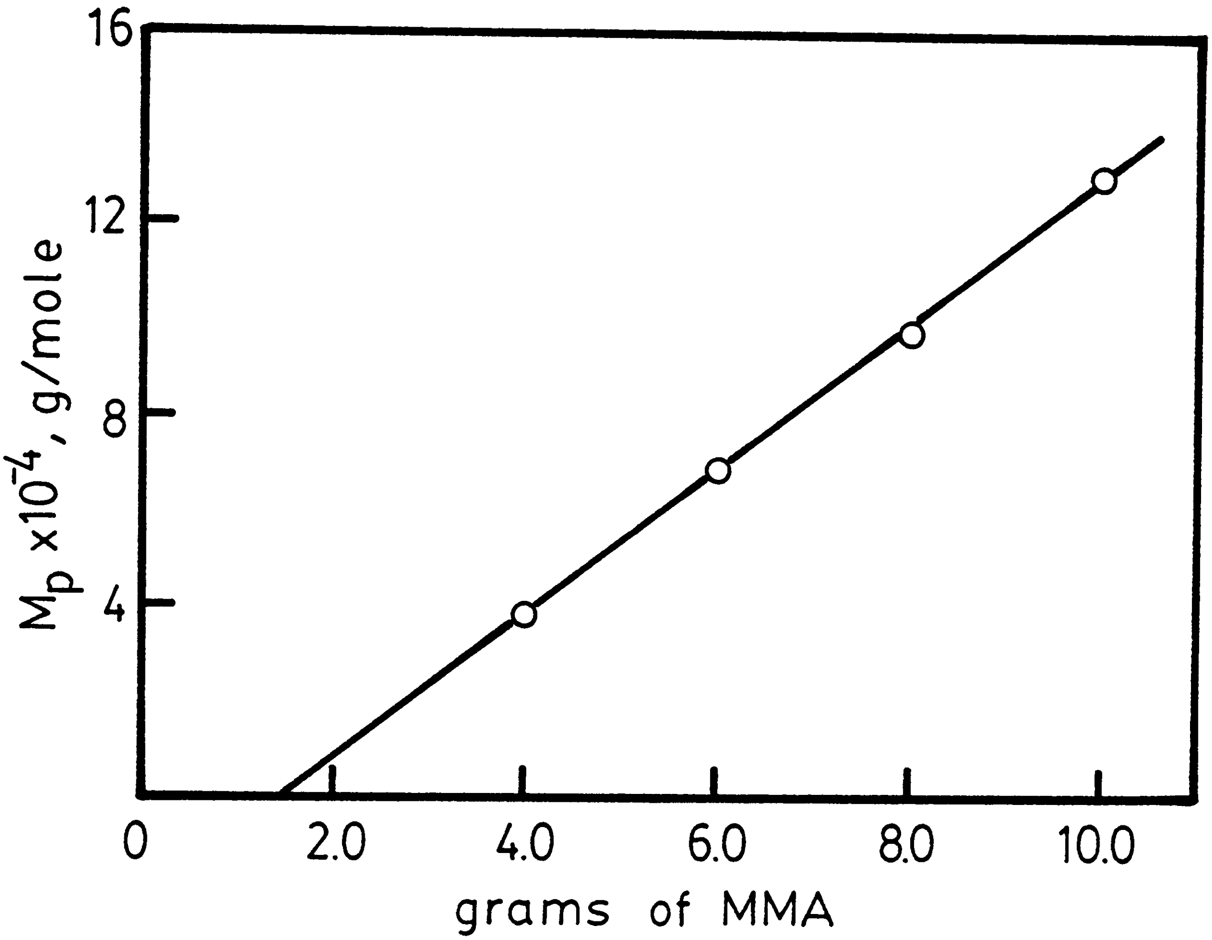
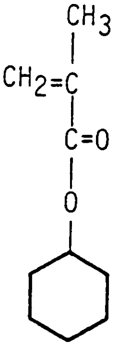


Figure 20. Plot of GPC Peak Molecular Weight vs. Monomer Charge for MMA Polymerization.

with triethyl aluminum, however.



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No polymer had been produced when the CaH_2-pure monomer (doubly distilled) was subjected to the standard polymerization conditions (DPHL, THF, -78°). When treated with TEA, the characteristic yellow endpoint appeared. During the subsequent distillation, however, the yellow color characteristic of anionic purity disappeared, alluding to destruction of the TEA•CMA complex. Although polymer was produced when this distilled monomer was polymerized, yields were generally below 50% with broadened molecular weight distributions. Figure 21 shows a typical GPC chromatogram of poly(cyclohexyl methacrylate) produced in the above mentioned manner.

This curious end point destruction was not again witnessed until the attempted purification of isopropyl methacrylate in conjunction with T. E. Long. The same color change was observed during distillation (yellow → colorless) as occurred during the distillation of CHMA. The major commonality in these two cases is the nature of the alcoholic impurity. Both esters are based on <u>secondary</u> alcohols, isopropyl alcohol for IPMA and cyclohexanol for CHMA.

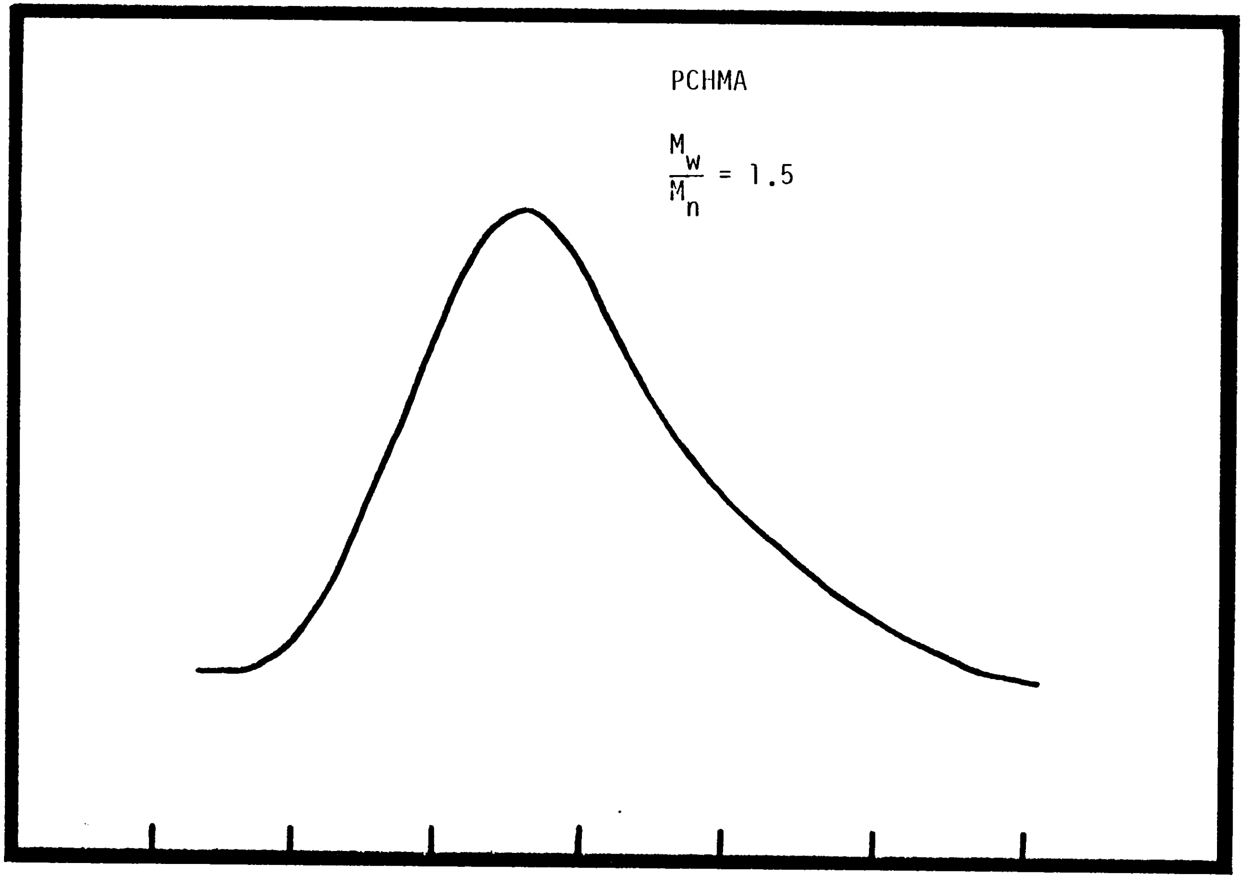
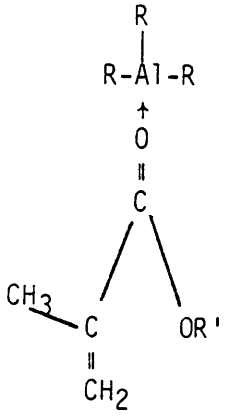


Figure 21. GPC Chromatogram of PCHMA after TEA Purification and "Endpoint" Destruction".

with triethyl aluminum, however.

A theory was thus developed to account for the strange and difficult purification characteristics of these monomers, and is known as the Long-Allen theory. Two competing events, steric and electronic, occur during titration (purification) of methacrylate monomers: complexation of the ester carbonyl which arises in the yellow "endpoint" and alcoholysis of the aluminum alkyl to form aluminum alcoxides and alkanes. Complexation, an electronic effect, (Scheme XIX) occurs relatively slowly with methacrylates based on primary alcohöls, (e.g. MMA) and somewhat faster with higher (2° and 3°) methacrylates, based on electronic induction into the carbonyl from the ester group. At the same time, alcoholysis occurs very rapidly with 1° alcohols, slower with 2° alcohols and <u>very</u> slowly with 3° alcohols, due to the steric nature of the higher alcohols (Scheme XX). In fact, t-BuOAlR$_2$ is typically prepared by the reaction of potassium-t-butoxide with trialkyl aluminum [143]. Impure "primary" methacrylates (e.g., MMA + methanol) undergo alcoholysis very quickly and complexation (relatively) slowly, so the color change corresponds to a true endpoint, i.e., the point at which all the alochol has reacted. Conversely, an impure t-butyl methacrylate (TBMA + t-butanol) undergoes complexation very quickly followed by <u>very</u> slow alcoholysis. This yellow "endpoint" is quite deceptive, as it occurs while much 3° alcohol remains unreacted. The color loss during distillation found with both CHMA and IPMA was presumably due to rapid complexation followed by decomplexation and alcoholysis (Scheme XXI).

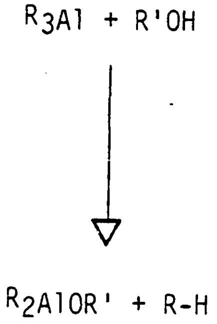
To test this theory, MMA was "doped" with 1°, 2°, and 3° alcohols (n-propanol, i-propanol and t-butanol, respectively). After addition of



Rate of complexation (R')

3° > 2° > 1°

Scheme XIX. Complexation of Methacrylate Esters by Trialkyl Aluminums.

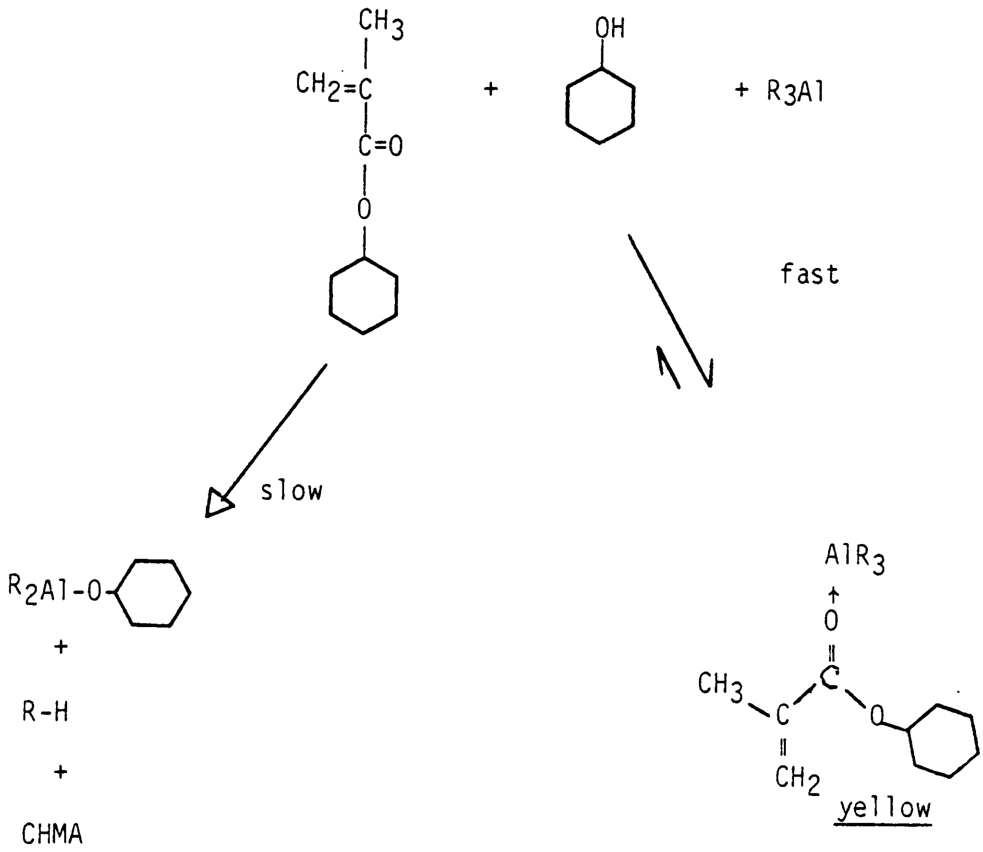


$$R_3Al + R'OH \longrightarrow R_2AlOR' + R\text{-}H$$

Rate of Alcoholysis (R')

1° > 2° > 3°

Scheme XX. Alcoholysis of Trialkyl Aluminums [143].



Scheme XXI. Proposed Sequence of Events During CHMA Purification: The Long-Allen Theory.

trioctyl aluminum, samples were extracted at various times and analyzed (G.L.C.) for octane content and alcohol content. The MMA/NPA (1°) experiment showed no NPA peak in the G.C. chromatogram immediately after the endpoint was reached. The MMA/IPA (2°) experiment showed total disappearance of the alcohol peak ten minutes after "endpoint" or complex formation. The MMA/TBMA experiment showed very different results. Ten minutes after complex formation, a small octane peak had begun to grow accompanied by a slight decrease in the t-butanol peak. After twenty minutes, the octane peak had grown larger, and the t-butanol peak was barely perceptable. After 1 hour, the t-butanol had been totally reacted.

It has thus been demonstrated that purification of higher (2° and 3°) alkyl methacrylates will occur only if modified techniques are employed. The transitory nature of the "endpoint" during titration of these materials may be deceptive. An appreciation of the competitive mechanisms involved in the alkyl aluminum purification of the monomers is essential for obtaining anionic polymerization grade materials. Several periodic charges of alkyl aluminum over a relatively long time period to the impure higher methacrylates are necessary. The complexed monomer should be allowed to stir in the dark between alkyl aluminum charges so as to avoid premature polymerization.

Polymerization Solvent Effects

Large alterations in the properties of poly(alkyl methacrylates) occur when the polymerization solvent composition (polarity) is altered due to changes in polymer stereochemistry. The typical anionic methacrylate polymerization solvents (THF) favor a predominately syndiotactic stereochemistry which arises in a higher than "normal" glass transition temperature, i.e., higher than that of a methacrylate polymer arising from a free radical polymerization. Conversly, hydrocarbon polymerization solvents (e.g. hexane or toluene) favor isotactic growth with a resulting low Tg (see literature review).

The first example of pronounced solvent sensitivity encountered in this work involved the polymerization of isobutyl methacrylate (IBMA) in four different solvent compositions which would presumably lead to four distinct polymers. THF and hexane were used to provide a range of dielectric constant media, from pure THF (relatively high D.C.) to pure hexane (very low D.C.). Hexane was the non-polar solvent of choice as it both dissolves PIBM and will not freeze at polymerization temperatures (as will cyclohexane and benzene). Toluene is another non-polar solvent with the above-mentioned attributes. Polymerizations were initiated as before with DPHL at -78°C, with stoichiometric molecular weights (g IBMA/mole DPHL) of 10,000. This relatively low molecular weight was chosen due to the low levels of alcoholic impurities in IBMA monomer, i.e., this work was performed <u>before</u> the advent of alkyl aluminum purification. If higher molecular weights had been chosen, polydispersities would have broadened and yields would have dropped. The Rohm and Haas IBMA (distilled twice from CaH_2) used provided polymers in near quantitative yields in these experiments.

The molecular weight characteristics (number average molecular weight vs. PMMA standards and polydispersity via GPC) for the four different PIBM's synthesized are shown in Table 28A. The thermal

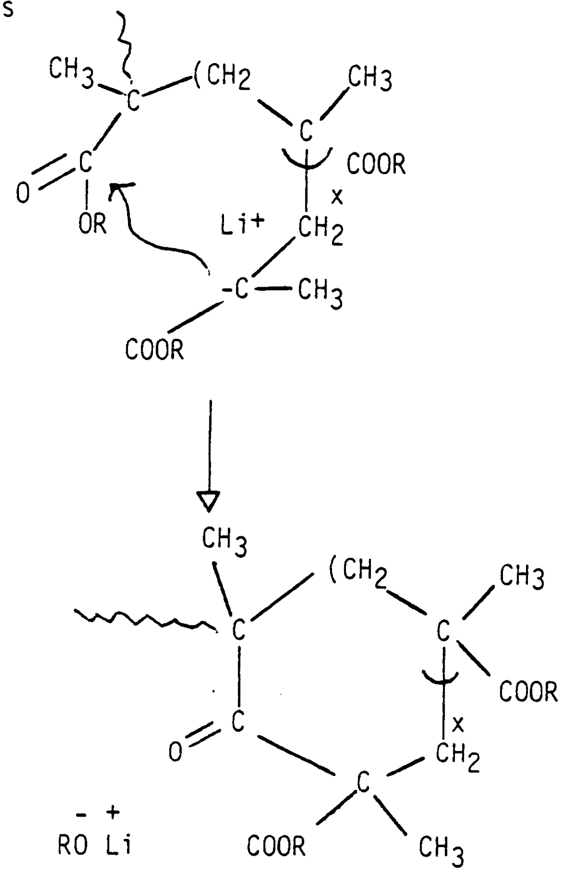
TABLE 28A

Molecular Weight* Characteristics of Various Poly(Isobutyl Methacrylates)

Polymer	Polymerization Solvent	$\overline{M}n$	$\overline{M}w/\overline{M}n$
PIBM-I	THF	16,500	1.24
PIBM-II	THF/Hexane (75:25)	12,400	1.21
PIBM-III	THF/Hexane (25:75)	20,500	2.00
PIBM-IV	Hexane	31,000	1.73

*GPC, PMMA Standards, THF solvent, 30°C.

properties (DSC) of these materials are shown in Table 28B. The first detail of note is that there is a general trend twoard broadening of the molecular weight distribution with a lowering of the dielectric constant of the polymerization media. While the polymerizations in THF and media high in THF are "living" in the classical sense, i.e., no termination or transfer reactions (at -78°C with the appropriate initiators), methacrylate polymerization in hydrocarbon (low D.C.) media are subject to continual termination, probably intramolecular backbiting reactions, as seen in Scheme XXII. Table 29 shows the ring produced as a consequence of this



Scheme XXII

Proposed Intramolecular Termination During Methacrylate Polymerization in Hydrocarbon Media.

TABLE 28B

Thermal Properties* of Various Poly(Isobutyl Methacrylates)

Polymer	Polymerization Solvent	Tg(°C)	Tm(°C)
PIBM-I	THF	68°	-
PIBM-II	THF/Hexane(75:25)	67°	-
PIBM-III	THF/Hexane(25:75)	42°	357
PIBM-IV	Hexane	12°	350
"Conventional"	PIBM	53	-

*DSC, Heating Rate = 10 deg./min., results from second run.

TABLE 29

Ring Sizes Produced Via Termination by Backbiting

X(#Repeat Units)	Ring Size
0	4
1	6
2	8
3	10

backbiting reaction in hydrocarbon media. It is clear that this intramolecular termination probably forms either six or eight membered rings, as these ring closures are energetically favored over smaller rings and macrocycles. Thus, the chain ends in the terminated fraction should bear rings of six or eight members.

It is immediately clear from inspection of PIBM-II in Table 28A and 28B that low levels of hydrocarbon solvent do not change either the polymerization charcteristics of IBMA or the microstructure. This is evidenced by the virtually identical polydispersities and glass transitions of PIBM-I and PIBM-II. Only when the medium becomes hexane-rich does the polymerization characteristics begin to change. The polymer made in predominately hexane with relatively low levels of THF (PIBM-III) shows a braodened polydispersity, higher average molecular weight, and significantly lower Tg. When no THF is present (PIBM-IV), the average molecular weight is higher yet and the Tg is significantly lowered. It should be noted that the calculation of polydispersities is prone to high degrees of error for the samples synthesized in low dielectric constant media, as these polymers exhibit GPC traces with severe low molecular weight tailing. Thus the choice of a appropriate baseline dramatically influences the calculated result. Suffice it to say that the polydispersities of PIBM III and PIBM IV are much greater than typical polymers produced by "living" methods, and are quite possibly greater than 2.0. The distribution of PIBM-IV is in fact bi-modal, with a small high molecular weight peak which was not taken into account in the calculations. The TMA spectra of these various PIBM's are overlayed in Figure 22. As the penetration curves for PIBM-I and II

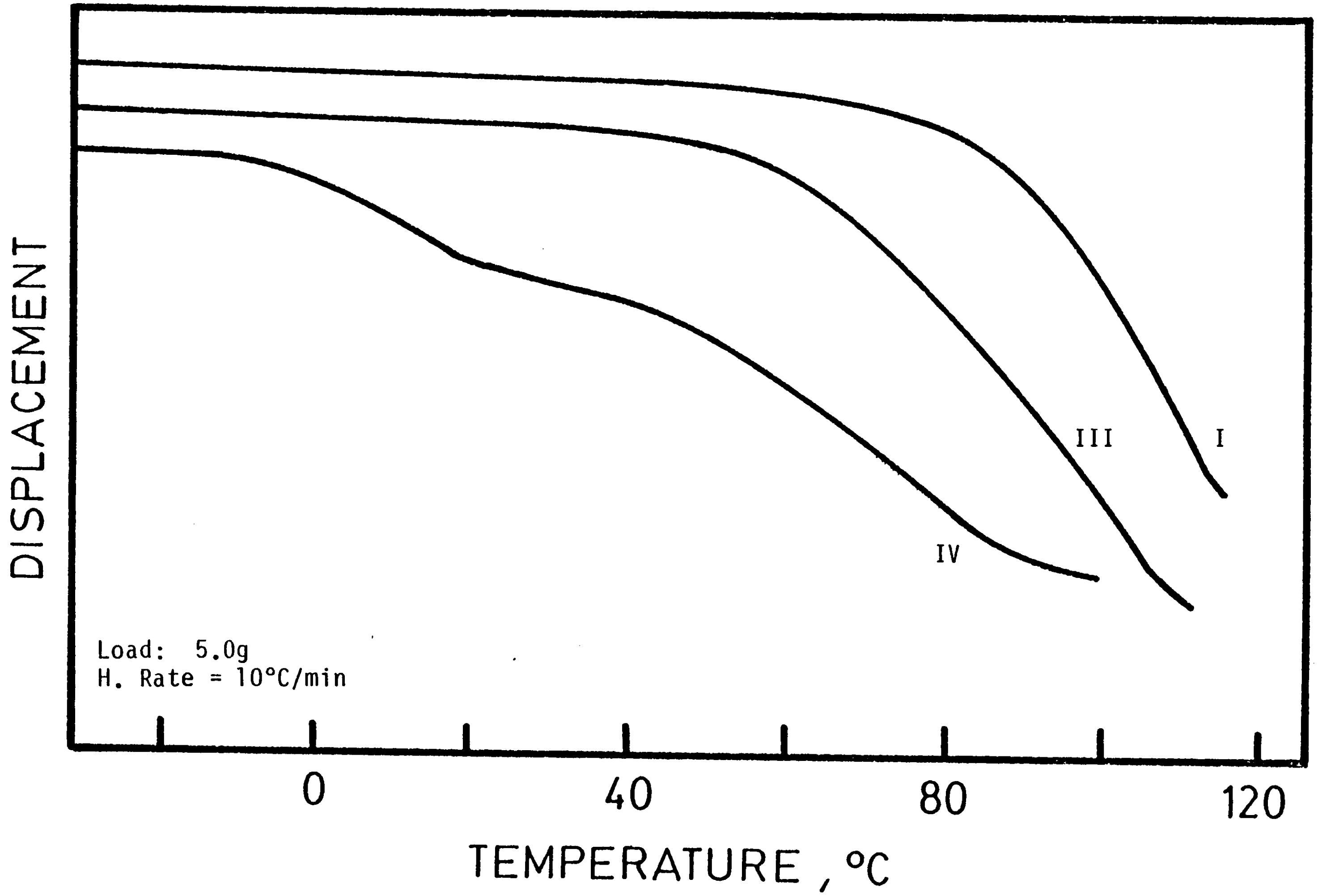


Figure 22. TMA Penetration Curves for PIBM's of Various Stereochemical Compositions.

are identical, only PIBM-I has been shown. The widely different glass temperature behavior of these materials is readily apparent in the TMA experiment. Also apparent is the existance of what appears to be a small rubbery plateau present after Tg in PIBM-IV. This may be due to low levels of crystallinity in highly isotactic materials. It should be noted that in conjunction with this data, DSC results from PIBM III and IV show small melting endotherms at very high temperatures (ca. 350°C) close to or exceeding the initial polymer decomposition temperature. The DSC and TMA results indicate low levels of crystallinity, but with melting at very different temperatures. Thermogravimetric analysis cast further doubt on the issue, as high levels of degradation at 300°C are indicated.

Several important generalities may be gleaned from the above discussion:

1. While low levels of hydrocarbon have no effect on the polymerization of methacrylates in THF, low levels of THF dramatically effect the polymer properties of methacrylate polymers synthesized in hydrocarbon solvents.

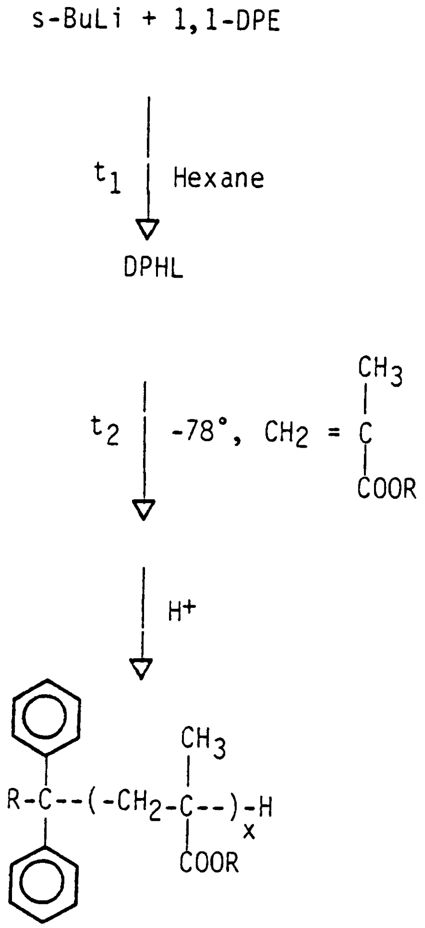
2. The breadth of the glass transition (isotactic-syndiotactic) window has been shown in the PIBM case to be at least 60 degrees. It should be noted that this difference would be more pronounced at higher molecular weights. High molecular weight PIBM-I would have a Tg approaching 80°C. It should also be noted that these materials are not purely isotactic or syndiotactic, but mixtures of stereoisomers with high isotactic and syndiotactic contents, respectively.

3. Polydispersities of methacrylates polymerized in hydrocarbon solvents may show monomodal distributions but have severe low molecular weight "tails", due presumably to slow but continuous termination, or perhaps "psuedoterminated" species.

4. Methacrylate polymerizations in hydrocarbon solvents show vastly different kinetic behavior than polymerizations in polar media. The polymerizations in hexane procedd with increasing viscosity for over 1 hour at -78°C, while in THF the polymerizations are virtually instantaneous.

It should be noted that very novel high molecular weight elastomeric methacrylates may be readily synthesized in high yields by polymerizing long chain methacrylates (e.g., 2-ethylhexyl methacrylate) in hydrocarbon solvents. Preliminary results show that while isotactic poly(n-butyl methacrylate) is a rigid (semicrystalline) solid, branched higher alkyl group analogues do not permit sufficient packing regularity to form semicrystalline materials. Isotactic poly(2-ethylhexyl-methacrylate), for example, has been found to be a soft, extremely tacky, colorless, elastomer with a glass transition below -30°C. Not yet investigated but of supreme fundamental and technological interest is the properties of a variety of long chain isotactic methacrylate materials. A comparison of the characteristics of isotactic n-butyl-, n-hexyl- and n-octyl-methacrylates could potentially provide materials with very low Tg's (below -40°C) which possibly possess low levels of crystallinity and superior oxidative and light stability.

The initial experiments with 2-ethylhexyl methacrylate provided quantitatively yielding elastomer in relatively short times (~20 min.) at -78°C in hexane solvent with the bulky DPHL initiator. The resulting GPC chromatogram revealed a bimodal molecular weight distribution. Inspection of the reaction scheme reveals the more complex series of events necessary for the synthesis of methacrylate polymers in hydrocarbon solvents than in polar (THF) solvents. As seen in Scheme XXIII whereas the kinetics of the reaction of BuLi with DPE in THF does not typically enter into the discussion (as it is over virtually upon mixing) the formation of DPHL in hydrocarbon solvents is very slow, taking from hours to days to go to completion, depending on the temperature, specific hydrocarbon solvent employed, and reactant concentrations. Polymerization initiated when "initiator formation" has not yet gone to completion would involve a complex initiation reaction



Scheme XXIII

Synthesis of Isotactic Poly(alkyl methacrylates) by BuLi, DPHL, or more likely some difficult to define mixed aggregate of DPHL-BuLi. A "reaction-time" study was thus undertaken to determine the effect of both time of initiator formation (t_1) and polymerization (t_2) on the yield, polymerization rate, and molecular weight distribution.

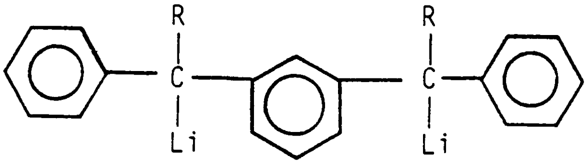
The effect of t_1, (i.e., the time allowed for DPHL formation in hexane at room temperature, using a known excess of DPE (5/1 vs. s-BuLi)) confirmed the earlier hypothesis that bimodal molecular weight distributions occur due to insufficient times needed for full conversion of s-BuLi to DPHL. When the time allowed for DPHL formation t_1 was less than three hours, bimodal molecular weight distributions resulted. With t_1's greater than three hours, distributions were monomodal with low molecular weight tailing, as expected when DPHL is the sole initiating species in these polymerizations. Another notable feature of the effect of t_1 is its dramatic influence or the apparent polymerization kinetics (as indicated by the viscosity of the reaction mixture with time). At short t_1's rapid viscosity increases occur (usually within 15 minutes after monomer addition), whereas with t_1's over three hours, when DPHL is the sole initiating species, much longer times are required to obtain ultimate viscosities (>1 hr.). The complex behavior of the proposed DPHL•BuLi aggregate profoundly influences the polymerization kinetics and mechanism, as seen in the resulting bimodal molecular weight distributions. More systematic work is required to carefully elucidate the complex chemistry occuring with the "mixed-initiators". A series of mixed aggregates may be readily prepared in hexane by varying the reaction times (t_1). Model polymerization with methyl methacrylate initiated by these various complexes (with varying DPHL/BuLi ratios) would provide kinetic, molecular weight, and stereochemical (tacticity) data that would greatly help in the characterization of these complex systems.

A "first-pass" study of the effect of t_2 (the time allowed for polymerization) showed kinetic behavior far different than the data presented for the polymerizations in THF (Figure 20). After allowing suitable time for DPHL formation ($t_1 > 3$ hours), 2-EHMA was added to two flasks of DPHL at -75° in hexane. Flask A was terminated after ten minutes and flask B was terminated after 1 hour. The isolated polymer yield after ten minutes was 50 percent. The quantitative nature of the polymer obtained in flask B (1 hour) and the fact that the viscosity had increased up to ~fifty minutes, showed preliminary evidence that the kinetics are in fact non-linear. This is proof that the polymerization is non-linving, as one criteria for living polymerization is linear conversion - time behavior. The kinetics of these isotactic polymerization processes deserves further attention.

A study was initiated to determine the effect of small amounts of a polar cosolvent on the polymerization kinetics, stereochemistry, glass transition temperature and molecular weight characteristics of these rubbery methacrylate materials. The hypothesis behind this study was the hope that small amounts of a polar "agent" would protect the chain end from termination without appreciably altering the thermal character (Tg) of the elastomer. The polar agent employed was THF to slightly modify these hexane-based polymerizations. The procedure involved the formation of DPHL in hexane over long time periods as before (>3 hrs.), employing a large excess of DPE to accelerate the reaction. The DHPL/hexane solution was then cooled to -78°C, followed by the addition of the appropriate charge of purified THF. It immediately became apparent that the original intent of narrowing the distribution by the addition of low levels of THF was not feasible, as immediate precipitation of the initiator was produced by the addition of the first drop of THF. A bright orange-red dispersion (which had the appearance of V-8 juice) was formed which could be redissolved by the addition of monomer. This heterogeneous initiator lead to polymers of high polydispersity, however.

This heterogeneous initiator is a fascinating example of the complexities of organolithium chemistry. The initiator DPHL is readily soluble in hexane at -78°C, readily soluble in THF at -78°C, but insoluble in hexane with trace levels of THF. The precipitate formed will redissolve upon the addition of more than 30% (V/V) THF. Conversly, when the initiator is synthesized (DPE + s-BuLi) in 30% THF + 70% hexane (as in the n-BMA study), the system is homogeneous throughout.

While persuing this notion of polar modifiers with a more easily characterized system (MMA polymerization), DPHL was modified with both THF and pyridine. Due to the insolubility of PMMA in hexane, toluene was the hydrocarbon solvent employed. When THF was added to the toluene solution of DPHL at -78°C, no precipitation occurred. Organolithium reagents are widely known for their solubility in hydrocarbon solvents [120]. The anomolous behaviour discovered to take place in hexane but not in toluene can be explained in terms of ion-pair concepts coupled with dielectric constant arguments. Table 30 shows the significant changes in dielectric constant encountered in the various hydrocarbon solvents employed in typical anionic polymerization work. Note that hexane and toluene are at the extremes of the hydrocarbon systems. It should also be noted that subtle changes in ε dramatically influence organolithium solubility. For example, the dilithium initiator 1 is



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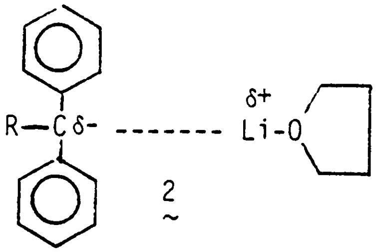
soluble in cyclohexane but insoluble in hexane, [158] which have a very small dielectric constant difference.

A possible explanation for the insoluble initiator in hexane involves organolithium structure and bonding. Organolithiums form higher aggregates in hydrocarbon solvents, with carbon-lithium bonding of largely covelant character [120]. This highly covelant bonding character is largely responsible for the hydrocarbon solubility of organolithium compounds. With the addition of small quantities of the interacting solvent THF, this "covelant" bonding is appreciably alterred, resulting in a solvent separated ion paired species (2) which has sufficient ionic character to promote insolubility in a very low ε media (hexane at -78°C) while remaining soluble in media of higher ε (toluene at -78°C).

Table 30

Dielectric Constants of Anionic Polymerization Solvents [157]

Solvent	$\varepsilon_{25°C}$
hexane	1.89
cyclohexane	2.02
benzene	2.28
toluene	2.38
THF	7.32



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Although this new class of materials may not appear to be immediately useful, organolithium crystals which are insoluble in hydrocarbon (hexane) solvents may fill an important application in the future. Analysis of the crystal structure of these insoluble organolithium compounds by x-ray diffraction may help provide further insight into the anomolous behavior.

The work with MMA in toluene with polar cosolvents (THF and pyridine) produced a variety of PMMA's with a wide range of physical properties. By changing the polymerization media (and thus the PMMA stereochemistry) it is possible to synthesize PMMA with glass transition temperatures from 60°C up to 130°C. The synthetic route, thermal properties, and polymer stereochemistry are given in Table 31. The stereochemistry of these polymers is determined from the α-methyl resonances by ^{1}H NMR. It should be pointed out that these percentages are overall stereochemical contents, and thus say nothing about the polymerization statistics or sequence distributions. Work is presently ongoing using ^{13}C NMR to determine these important variables [159].

As can be seen from the data, a wide variety of PMMA's are readily synthesized by modifying the polymerization media. As seen in the earlier work with NBMA, small levels of polar solvents dramatically influence the polymerization, while quite high levels of hydrocarbon do not appreciably effect THF-based polymerizations. These systems

Table 31

Characterization of PMMA's

Polymerization Conditions	Tg(°C)	% Tacticity iso	hetero	syndio
1. THF	131	1.8	18.6	79.6
2. 80% Toluene 20% THF (by vol.)	122	2.7	22.8	74.5
3. Toluene THF/Li = 100.0	104	26.3	22.3	51.4
4. Toluene THF/Li = 1.0	84.5	81.1	14.5	4.4
5. Toluene Py/Li = 100.0	121	9.1	23.4	67.4
6. Toluene Py/Li = 10.0	97	31.1	26.7	42.2
7. Toluene (Fast monomer addn.)	90	91.0	8.0	1.0
8. Toluene (Slow monomer addn.)	62	91.4	7.6	1.0

(PMMA's) have complexities not yet fully understood, however. For example, several of the samples (bearing the Tg's in the middle of the range) are insoluble to a large extent in THF. These insoluble materials are fully soluble in chloroform, however. The lack of change in the apparent stereochemistry of the two polymers synthesized in pure toluene (no. 7 and 8) is confusing in light of the large Tg difference. These discrepancies point to variations in sequence distribution which may dramatically influence the behavior of these polymers, especially if one envisions blocky sequences of isotactic and syndiotactic structures. It is well known that syndiotactic PMMA and isotactic PMMA form insoluble "stereogels" on mixing. As the early workers in anionic methacrylate polymerization postulated "stereoblock" formation in mixed polymerization solvents [1-2], the polymers synthesized in this study may indeed have non-random mixtures of stereochemical sequences. Further work is being done to elucidate how the polymerization conditions effect the stereochemistry, sequence distributions, and polymer properties [160].

B) BLOCK COPOLYMERS: SYNTHESIS AND CHARACTERISTICS

Methacrylate - Methacrylate Systems

Multiphase systems have achieved widespread importance in the last two decades due to the increasingly rare occurance of the introduction of new polymers. The development and use of block copolymers has catalyzed developments in multiphase systems, especially in light of the discovery of Milkovich of triblock thermoplastic elastomers [145]. Anionic polymerization is well appreciated to be the superior method in the controlled synthesis of well defined block copolymer systems [5,146-174]. Synthetic control over molecular weight, polydispersity, diene microstructure, block architecture and end group functionality is realized using anionic techniques.

The vast majority of investigations regarding the anionic synthesis of block copolymers have dealt with the styrene-diene systems. Several reasons for this bias toward hydrocarbon monomers include their extreme purity, arrived at through the use of organometallic purging agents such as dibutyl magnesium (DBM), the ability of styrene and diene monomers to polymerize in a very clean, living (non-terminating with no side reactions) fashion, and the propensity toward microphase separation that the styrene-diene block copolymers are known for. Conversly, polar monomers such as alkyl methacrylates have been largely ignored as candidates for block copolymer synthesis. This sporadic attention [147-151] is largely due to the difficulty in obtaining non-terminating polymerization conditions. The recent discovery of Group Transfer Polymerization (GTP) has circumvented many of these problems [51-54, 152-154]. Most polar monomers, including methacrylates, inherently terminate due to anionic attack at the polar substituent. Methods have been developed for alkyl methacrylate polymerization which avoid these side reactions [49-50]. These include low polymerization temperatures (-78°C), polar solvents such as THF, and sterically hindered, low basicity initiators such as diphenyl hexyl lithium (DPHL). A much less appreciated aspect of the anionic synthesis of alkyl methacrylate polymers, and also the GTP route, has been the problem of monomer purification. As mentioned previously, suitable methods are available for the scrupulous purification of hydrocarbon monomers. Purification agents used with the styrene-diene systems unfortunately rapidly polymerize alkyl methacrylates. Calcium hydride, which is conventionally used for methacrylate monomer purification, does not react with the alcoholic impurities that contaminate most methacrylate monomers, thus rendering them useless for anionic polymerization work. The development of the trialkyl aluminum purification route has circumvented problems associated with alcoholic monomer impurities, resulting in a variety of anionic polymerization-grade methacrylate monomers.

The use of alkyl methacrylates in anionic block copolymer synthesis increases dramatically the number of available monomer combinations possible, due to the wide variety of alkyl methacrylates available. This methacrylate spectrum provides polymers with a range of solubility parameters, glass transtion temperatures, and tacticities. Also, by utilizing polymer modification reactions such as ester hydrolysis [155], many more structures (and thus properties) are available. The high purity of these methacrylate monomers is essential in the synthesis of advantageous hydrocarbon-methacrylate block copolymers and all-acrylic (methacrylate-methacrylate) block copolymers of high structural integrity.

The synthesis of methacrylate-methacrylate block copolymers places stringent demands on the purity of both methacrylate monomers. As it is difficult to purify these monomers by conventional methods, it is quite difficult to obtain even one methacrylate of high purity. Scheme IX shows the synthesis route utilized to obtain methacrylate-methacrylate block polymers. If conventional (CaH_2) purification methods are applied to most methacrylates, severe broadening of the molecular weight distribution results due to continual termination. This results in very impure diblocks synthesized in less than quantitative yields with high compositional heterogeneities and broadened polydispersities (>1.5). This is demonstrated in Figure 23, which shows GPC chromatograms for three methacrylate polymers. In the center is a typical PMMA homopolymer made in the conventional manner of slow addition to DPHL in THF at -78°C using trialkyl aluminum purification. To the right is shown a PMMA-Poly(ethyl methacrylate)diblock of 50/50 composition and 60,000 total molecular weight, resulting from alkyl aluminum purified monomers. Note the absence of any detectable homopolymer contamination. Films cast from solution with this polymer are optically clear. The chromatogram on the left, however, represents the same objective, a 50/50 composition MMA-EMA diblock of a similar targeted molecular weight. This diblock was arrived at with the same starting materials which had been purified only using CaH_2. The effects are dramatic with considerable broadening of the polydispersity. Films cast from solution of this material are hazy to opaque.

A series of 50/50 MMA-EMA diblock polymers of various molecular weights have been cleanly synthesized. The very slight solubility parameter difference between the constituent blocks leads to phase mixing, very similar to work done on polystyrene-α-methyl styrene diblocks [156]. The DSC data for the MMA-EMA series is given in Table 32. Typical DSC spectra are shown in Figures 9A-9C. These data show that the critical molecular weight for phase separation in this well

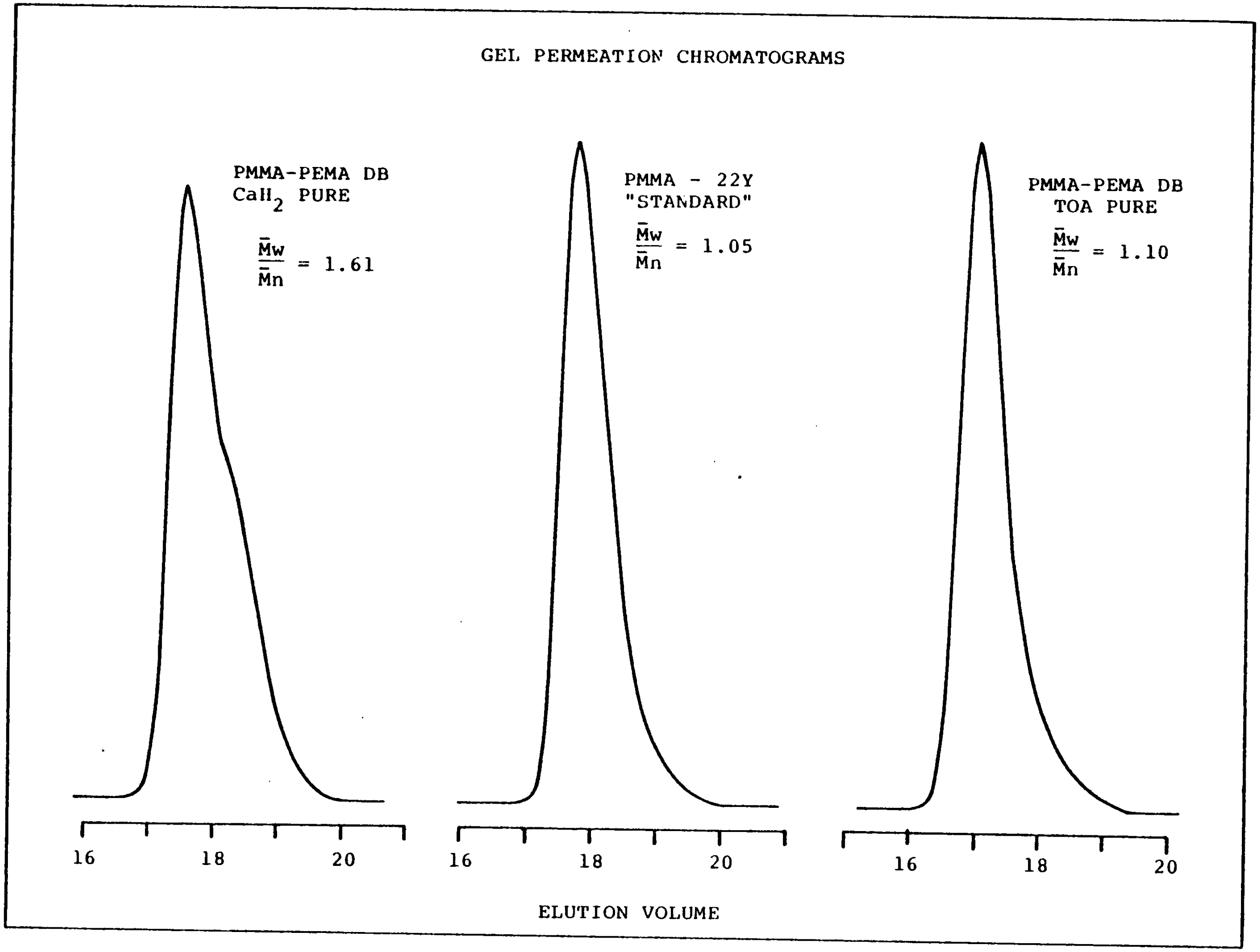


Figure 23. Gel Permeation Chromatograms.

Table 32

Thermal Transitions of MMA-EMA (50/50)

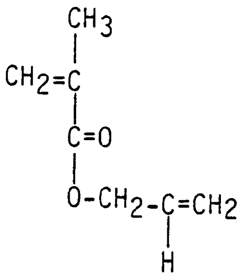
Polymer	MW_{Total}(g/mole)	Tg(°C)	Tg_{Range}
PMMA	100,000	131	26
PEMA	100,000	84	22
PMMA-PEMA	20,000	100	31
PEMA-PMMA	20,000	100	33
PMMA-PEMA	60,000	111	53
PEMA-PMMA	60,000	109 (89,124)*	54 (20,19)*

*Inflection points are slight.

matched system is very close to 60,000 g/mole (30,000 per block). Below this molecular weight, phase mixing takes place as witnessed by one transition. A study of thermal history effects on these novel materials should prove to be quite interesting. The last sample has what looks like two poorly defined transitions, thus the data are presented as both one single broad Tg vs. two overlapping transitions. Dynamic mechanical studies on these systems is thus in order.

Similar studies are also in order for diblock systems bearing different alkyl groups, e.g. MMA-NBMA, MMA-TBMA, NBMA-TBMA, etc. In addition to the possibilities of controlling the block molecular weights, sequence distributions and differential solubilities of these systems, polymers which contain the readily hydrolyzed t-butyl ester group serve as novel precursors to highly controlled ionomer structures. These highly controllable, all-acrylic copolymer systems could be the subject of several doctoral theses in and of themselves.

Preliminary work has been done on a novel acrylic copolymer system which provides the synthetic polymer chemist with an almost unlimited number of defined structures. This system involves the copolymerization of a "conventional" methacrylate (MMA) with allyl methacrylate (AMA) (1). This monomer leads to crosslinking when subjected to free radical



$$CH_2=C(CH_3)-C(=O)-O-CH_2-CH=CH_2$$

(1)

polymerization conditions due to the reactivity of the allylic hydrogens to radical chain transfer [162,163]. This allylic double bond is inert toward anions, especially the enolate anions involved in methacrylate polymer synthesis at low temperatures. Block copolymers have thus been synthesized of MMA-AMA in which quantitative yields were arrived at giving polymers of relatively narrow molecular weight distribution (Figure 24). Cast films of this diblock were perfectly transparent. The synthetic sequence involved slow addition of MMA to DPHL at -78°C, followed by slow addition of alkyl aluminum purified AMA. ^1H NMR analysis (allylic-CH_2 vs. methoxy-CH_3) confirmed the copolymer composition (50/50) equals the charge ratio. It has yet to be determined if reversal of monomer addition (AMA first followed by MMA) effects the polymerization.

It has thus been established that anionic polymerization grade AMA can be cleanly incorporated into methacrylate polymers (or for that matter styrenic polymers) in a living fashion. Polymer structures may be designed that bear allyl groups in pre-determined sequences and/or locations. This novel concept has many important ramifications, from model ionomer synthesis (via sulfonation or hydrolysis) to graft copolymer synthesis (via hydrosilation reactions of Si-H terminal polymers), and like the more conventional all-acrylic systems discussed above, could easily be the subject of an exceptional docotoral study in and of itself.

Styrene-Methacrylate Systems

The synthesis of well defined stryene-methacrylate block copolymers, while of interest in themselves, serve as precursors to ion-

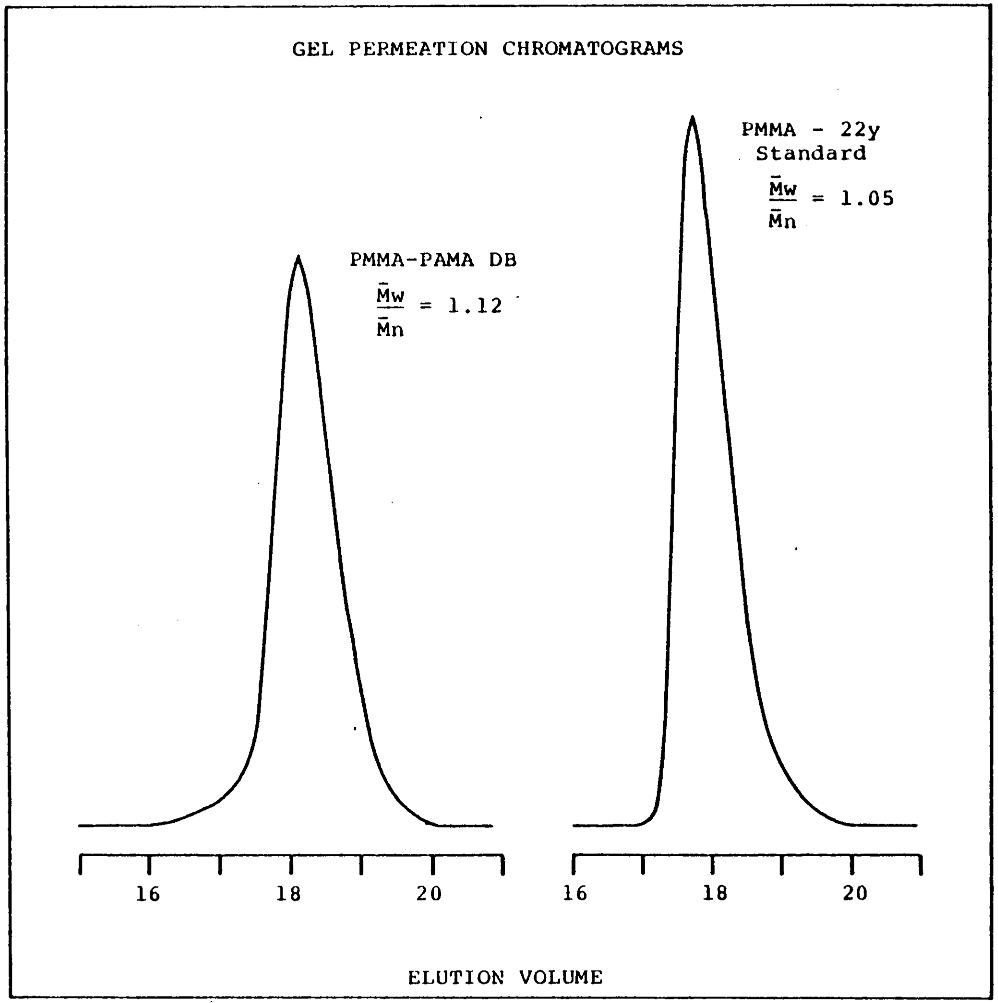


Figure 24. Gel Permeation Chromatograms of Narrow Distribution PMMA Homopolymer and Diblock Polymer with Allyl Methacrylate.

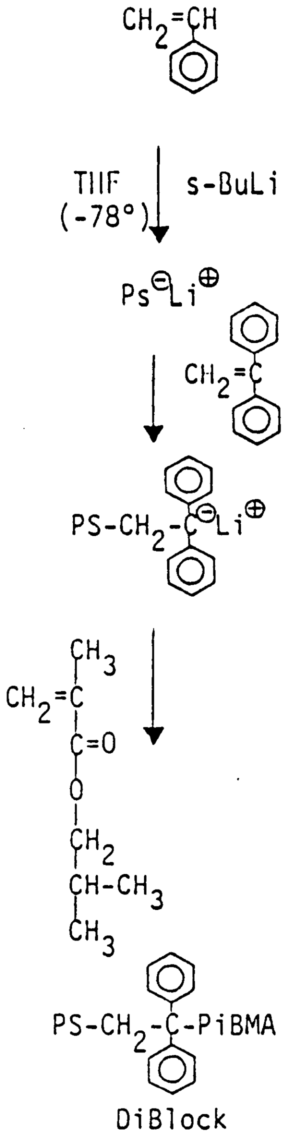
containing block copolymers. This process involves the following synthetic steps.

1. Synthesis of narrow distribution polystyryllithium.
2. Modification of the chain end structure to produce a suitable macromolecular initiator for alkyl methacrylates.
3. Utilization of high purity methacrylate monomers for the synthesis of diblocks with high structural integrity.
4. Partial hydrolysis of the methacrylate block to form the ionomer after neutralization.

Steps 2-3 have been addressed throughout this discussion. The synthesis of styrene-methacrylate diblock ionomer precursors is elaborated on in Scheme XXIV. The capping of the polystyrllithium with 1,1,-DPE a la Rempp is a key feature, along with the polar solvent, highly pure monomers, and low temperatures. The difficulty in this synthesis is the fundamental question of organolithium initiated polymerization of styrene in THF. While s-BuLi is known to react slowly with THF even at -78°C, n-BuLi is inert but consequently is a slow initiator which produces broadened molecular weight distributions. A study of various synthetic methods for the synthesis of this polystyrene "first block" was undertaken. Three organolithium initiators were employed. From the visual observations (these polymerizations are highly colored) as well as the GPC data, the following may be summarized. The rate of styrene initiation in THF at -78° is as follows:

$$\text{s-BuLi} > \text{n-BuLi} \gg \text{DPHL}$$

Polystyrenes with stoichiometric molecular weights of 10,000g/mole were



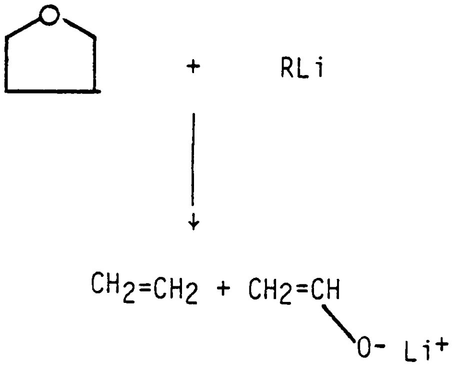
Scheme XXIV. Synthesis of Polystyrene-Poly(isobutyl methacrylate) Block Copolymer.

synthesized by these initiators in THF and cyclohexane. The data are summarized in Tables 33-35.

The addition of s-BuLi to THF at -78° causes immediate yellow color formation due to ring cleavage and alcoxide formation as shown in Scheme XXV. The alcoxide formed is the enolate of acetaldehyde. This reaction is fairly slow at -78°, however. Table 33 shows s-BuLi initiation of styrene, where the THF and s-BuLi were allowed to mix for very short times (<1 min.) and longer times (5 min.). The effect of this holding period is dramatic - a doubling of molecular weight occurs, meaning that 50% of the s-BuLi had reacted with THF at -78° in 5 minutes. No color is associated with the mixing of n-BuLi with THF at -78°C. In fact, it has been reported that no reaction occurs below -35°C for this alkyl lithium-ether pair [120]. Consequently, no change in the molecular weight is detectable with "holding time", although from observations of color changes and polydispersity, it is apparent that n-BuLi initiates styrene quite slowly in THF at -78°.

If the reaction between s-BuLi and THF is to be avoided, the initiator may be added to the monomer solution at -78°. The results from this technique are listed in Table 34. This reaction is fast enough that mixing problems may broaden polydispersities, but the molecular weights are highly predictable and the distributions quite narrow using this technique. The instanteneous exotherm upon addition of s-BuLi is worrisome, nevertheless. The initiation of styrene with n-BuLi is quite slow even by this technique, leading to a doubling of the molecular weight with a very broad distribution.

Control experiments in cyclohexane yielded expected results, with



R = n-Bu

T > -35°C

Scheme XXV. The Reaction of Alkyl Lithium with THF.

Table 33

Effect of contact time of alkyl lithium with THF at -78°C on styrene polymerization[a,b]

Initiator	Contact Time	M_N*	M_W/M_N*
s-BuLi	<1 min.	10^4	1.16
s-BuLi	5 min.	2×10^4	1.12
n-BuLi	<1 min.	3.2×10^4	1.8
n-BuLi	15 min.	3.2×10^4	1.6

[a] $M_{STOICH} = 10^4$ g/mole

*GPC data (Polystyrene Standards)

[b] Purified Styrene added slowly to initiator solution.

Table 34

Polystyrene Synthesis in THF at -78°*b

Initiator	Exotherm	$\overline{M}_N$[a]	$\overline{M}_W/\overline{M}_N$[a]
s-BuLi	-78° → -22°	10^4	1.17
n-BuLi	-78° → -25°	2.1×10^4	1.9

*Styrene + THF $\xrightarrow{-78°}$ add RLi

[a] GPC data (Polystyrene Standards)

[b] $M_{STOICH} = 10^4$ g/mole

Table 35

Effect of Initiator and Solvent on Polystyrene Synthesis[b]

Solvent	Initiator	$\overline{M}_N$ [a]	$\overline{M}_W/\overline{M}_N$ [a]
cyclohexane[c]	s-BuLi	1.2×10^4	1.17
cyclohexane	n-BuLi	5×10^4	1.6
THF[d]	DPHL*	9.7×10^4	1.4
cyclohexane	DPHL*	1.6×10^4	1.25

*DPHL is the adduct of s-BuLi + 1,1-DPE.

a) GPC data (Polystyrene Standards)

b) $M_{STOICH} = 10^4$ g/mole

c) Cyclohexane polymerizations performed at room temperature.

d) THF polymerization at -78°C.

s-BuLi efficiently initiating styrene to give predictable behavior, i.e., narrow distribution with controlled molecular weight. The molecular weight in this experiment was slightly higher than the 10,000 g/mole stoichiometric value, most probably due to the non-rigorous purification of cyclohexane. This hydrocarbon solvent had simply been "column dried" through alumina and molecular sieves, while the THF used in the previous experiments had been rigorously dried by double distillation from sodium/benzophenone. The n-BuLi reacts very slowly and inefficiently with styrene in cyclohexane, producing a high molecular weight polymer with a broad polydispersity (>1.5).

It was felt that s-BuLi is stable in THF when reacted with DPE to form DPHL, and that this might be a promising initiator for styrene. It turns out, however, that DPHL initiates styrene extremely slowly in THF at -78°, leading to macromolecules with molecular weights much higher than predicted from stoichiometric considerations due to the high rate of propagation. In cyclohexane, initiation is still very slow, but it is on the order of propagation, so as to form molecular weights closer to predicted values. The noticable narrowing of the polydispersity is presumably due to the vastly large propagation rate, i.e., $k_p >> k_i$. This interesting re-narrowing of the distribution will be the subject of future work. It is proposed here that it is an oversimplification to assume that if $k_i < k_p$ the distribution must be very broad. It is well appreciated that when $k_i < k_p$, (as with n-BuLi) the distribution becomes considerably broader. But when $k_i << k_p$, very few chains are initiated when the monomer is fully converted to polymer, leading to very high molecular weight polymers with a narrowed polydispersity.

In conclusion, two methods appear to work equally well for synthesizing polystyrene blocks in THF with lithium counterions:

1. Add s-BuLi very quickly to a well mixing solution of styrene in THF at -78°.
2. Immediately after adding s-BuLi to THF at -78°, begin to charge styrene so as to avoid decomposition of the initiator with THF.

Ionomer Synthesis and Structure Property Relations

The knowledge gleaned from the polystyrene/THF synthetic investigation was applied to the synthesis of styrene-methacrylate block polymers. The synthetic route chosen (Method 1, above) consisted of adding s-BuLi rapidly to styrene in THF. The remaining synthetic method is elaborated on in Scheme XXIV.

The purpose of this investigation was to gain insight into the influence of ion-architecture (distribution) on the properties of ionomers. This work was inspired by the findings of I. Yilgor, et. al. [98] who synthesized butyl acrylate-sulfonated styrene ionomers by direct emulsion copolymerization of sodium styrene sulfonate with butyl acrylate. The properties of the resulting ionomers were far different than the "conventional" ionomers studied by Eisenberg and others (see Literature Review). For example, no change in Tg with ion content was found in this system, while at the same time rubber plateau behavior as seen in TMA analysis was highly effected (Figure 25). Stress strain properties also showed dramatic improvements with ion content (Figure 26). Because the ionic groups were dramatically altering the properties of butyl acrylate without effecting its glass transition behavior, Yilgor and coworkers postulated blocky ionomer formation. It was

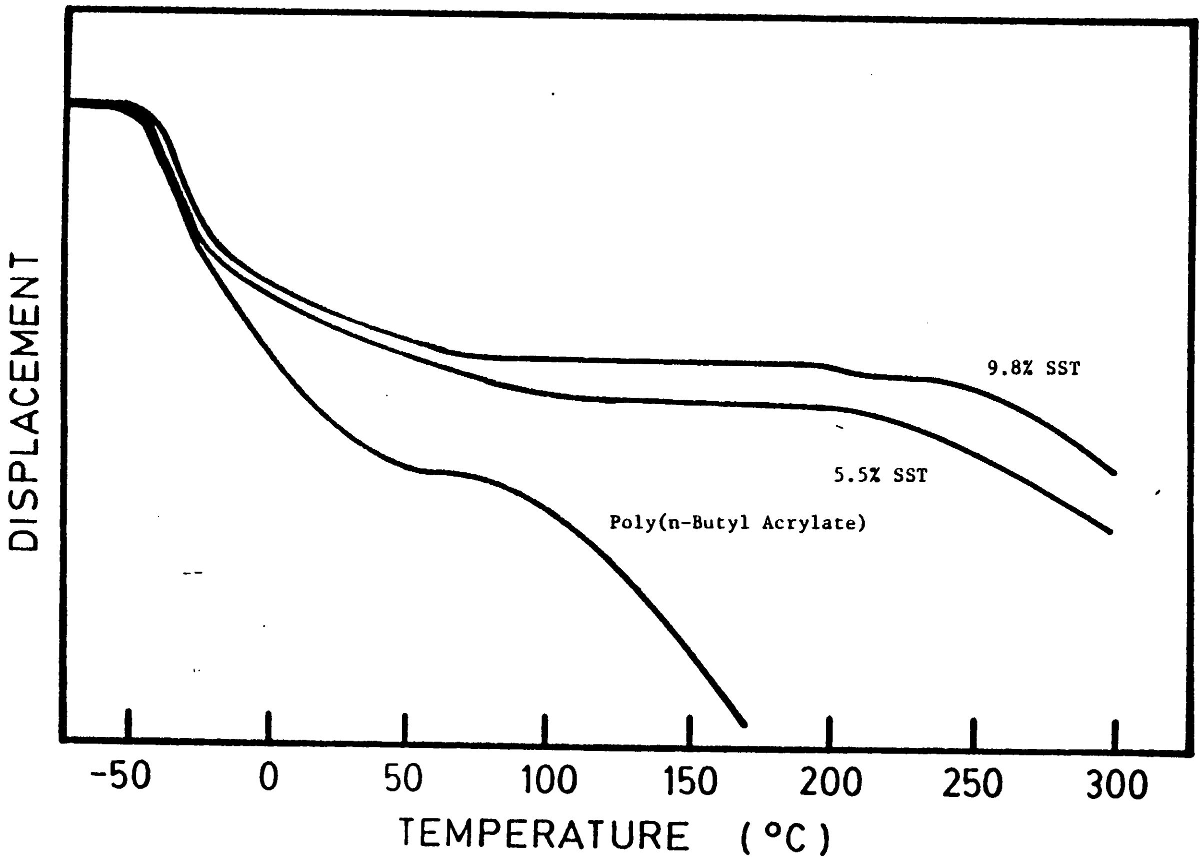


Figure 25. TMA Penetration Curves for n-Butyl Acrylate/Sulfonated Styrene Ion-Containing Copolymers [161].

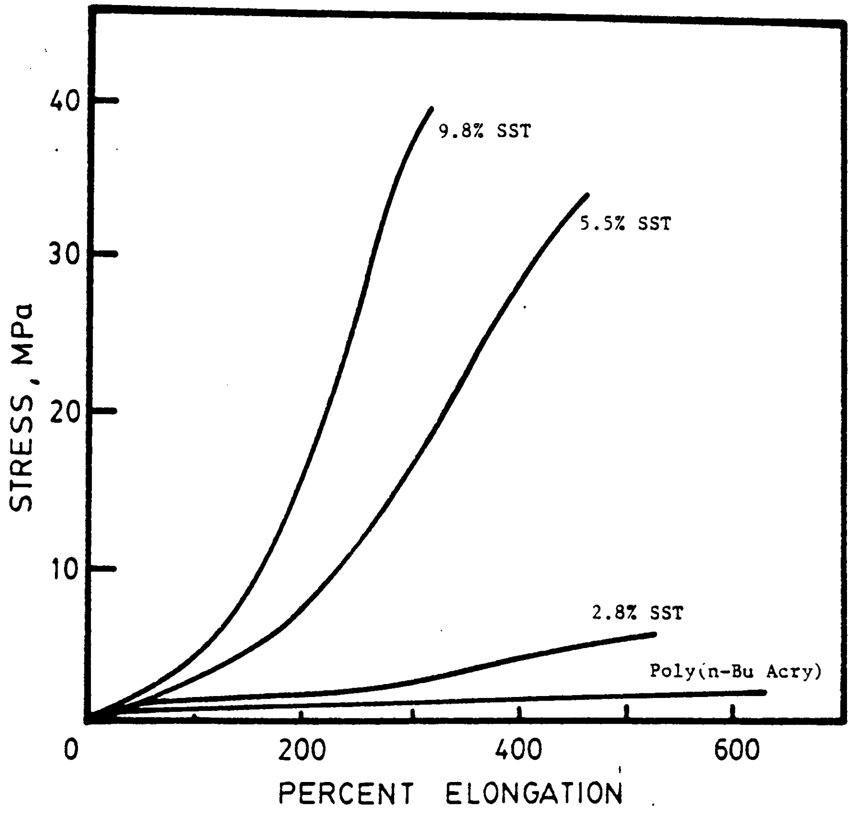


Figure 26. Stress-Strain Behavior of n-Butyl Acrylate/Sulfonated Styrene Ion-Containing Copolymers [161].

decided, therefore, to synthesize well defined block systems by anionic techniques which could be converted via post polymerization reactions to ionomers. Methacrylate polymerization and hydrolysis were thus chosen.

The novel reaction scheme which had been proposed for "blocky" ionomers through emulsion polymerization encouraged investigation into the synthesis and characteristics of very well defined ion containing block copolymers through anionic polymerization. The initial system chosen for synthesis, modification, and characterization was the polystyrene-poly(iso-butyl methacrylate) diblock (PS-PIBM DB) copolymer. This particular system was chosen for the following reasons:

1) The availability, ease of purification, and well established polymerization characteristics of styrene.

2) The large body of literature available on polystyrene based ionomers.

3) IBMA (Rohm and Haas) is a methacrylate monomer of high purity.

4) The methacrylate ester group may be converted, via hydrolysis, to a carboxylate ion.

These polystyrene-methacrylate copolymers are thus precursors to carboxylate ion containing block copolymers.

As is evident from the GPC chromatograms in Figure 27, both the diphenyl ethylene capped polystyrene and the PS-PIBM diblock copolymers have narrow molecular weight distributions. The polystyrene block molecular weight is $4x10^4$ g/mole, while the diblock molecular weight approaches $5x10^4$ g/mole. More importantly, no detectable homopolymer contamination is present in the very pure diblock. Cast films of the diblock polymer were also transparent. This high structural integrity was achieved by taking the following precautions.

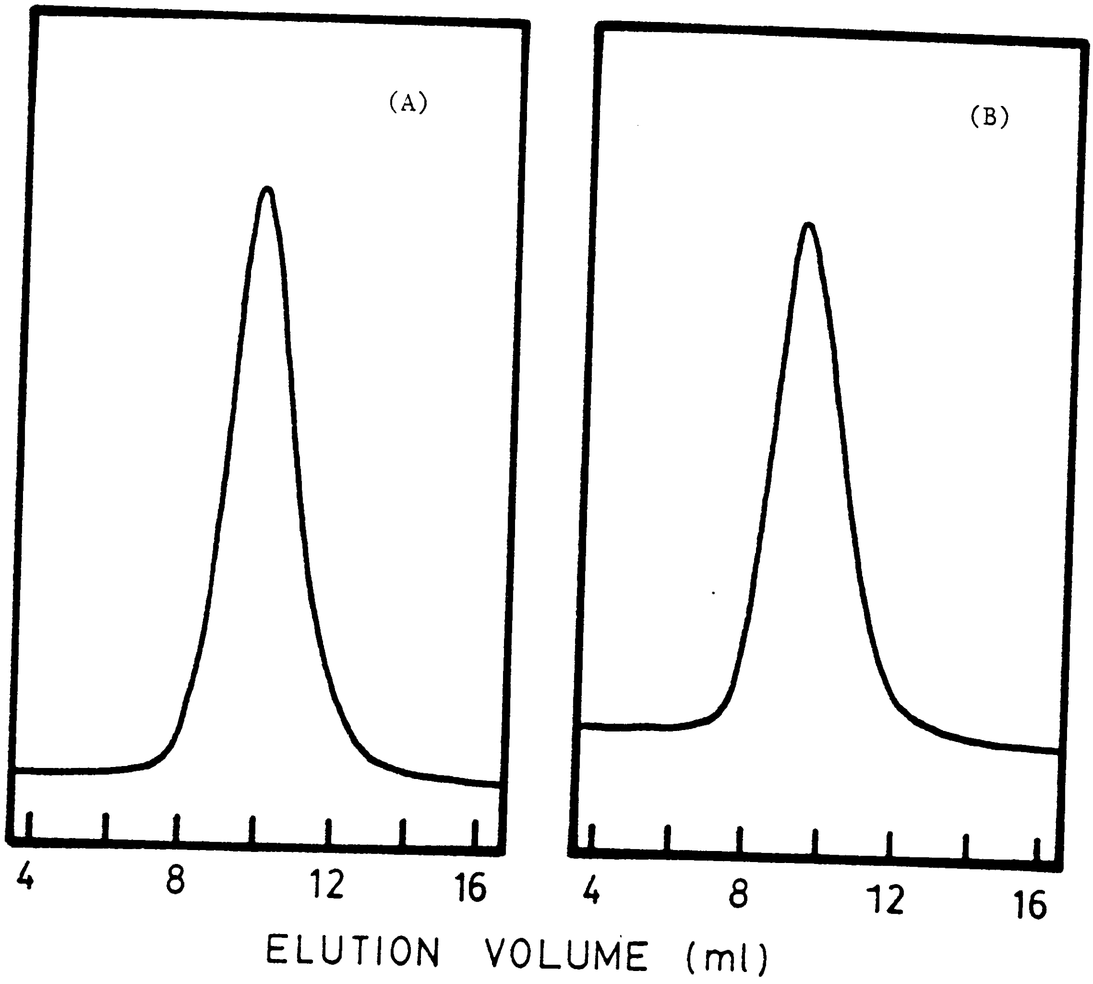


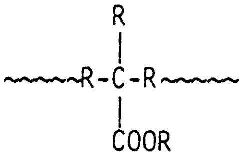
Figure 27. Size Exclusion Chromatograms of:

(A) Polystyrene Front Block

(B) Polystyrene/Poly(isobutyl methacrylate) Diblock Copolymer

1) Capping of the PS "Front Block" with 1,1-DPE to afford a highly hindered, less basic macromolecular initiator for methacrylate polymerization.
2) Slow addition at -78°C of IBMA to avoid thermal termination.
3) Utilization of high purity methacrylate monomers.

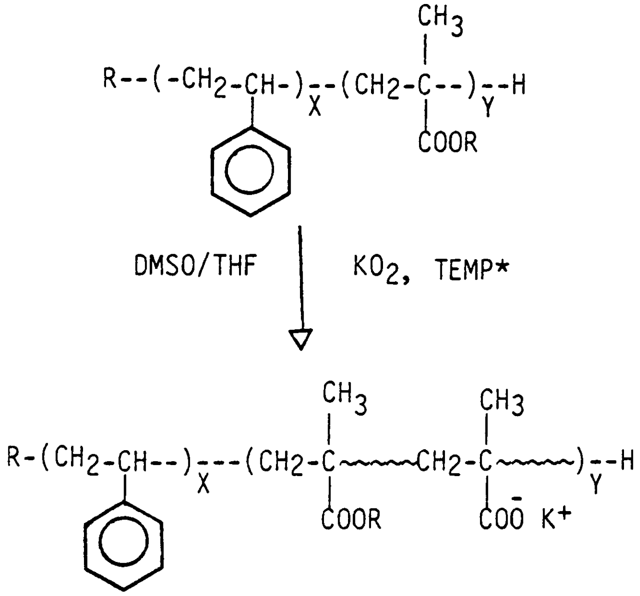
Hydrolysis of this well defined diblock material proved to be quite difficult. A variety of acidic and basic hydrolysis attempts were made, with little or no success. In retrospect, this hydrolysis resistance should have been anticipated, as it is known that esters of the structure R_3CCOOR' are difficult to hydrolyze [105]. An analysis of the structure of a methacrylate polymer reveals that it possesses the structure which helps explain its hydrolysis-resistant nature. Another



$$\sim\sim\sim R-\overset{\displaystyle R}{\underset{\displaystyle COOR}{C}}-R\sim\sim\sim$$

complicating variable is the bulky nature of the isobutyl group. As is seen in Table 24 early in this chapter, the isobutyl group can lower the rate of a nucleophilic reaction one hundred-fold over the methyl analogue. But, as these polymers were synthesized <u>before</u> the development of the aluminum alkyl purification approach, isobutyl methacrylate was the only available monomer with sufficient purity for clean block polymerization. A third factor is the hydrolysis-resistant nature of syndiotactic methacrylates (see literature review).

The work of Williams [103] with the KOH hydrolysis of butyl-methacrylate polymers discussed in the literature review sparked our interest in the KOH/Isopropanol hydrolysis route. Because of the high styrene content (80 wt. %) of the diblock materials in this study, no media could be found which would dissolve KOH and the PS-PIBM starting material, although a DMSO/Toluene 18-crown-6/KOH reaction did solubilize all the components. These vigorous reaction conditions resulted in little or no hydrolysis, presumably due to the steric bulk of the isobutyl group vs. the n-butyl group (see Table 24) as well as the syndiotactic nature of anionically prepared methacrylates. Evidence was found in the literature [164-165] for a facile new hydrolysis method which had achieved very fast hydrolysis of methyl laurate by using solid potassium superoxide (KO_2). This new method has successfully been employed in the hydrolysis of polymethyl methacrylate (PMMA). Elvacite 2041 (DuPont PMMA) was rendered water soluble by simply stirring over KO_2 at room temperature overnight. Scheme XXVI shows the hydrolysis route employed. As is indicated in the scheme, although PMMA is hydrolyzed at room temperature, the bulkier iso-butyl ester group is much more resistant to this hydrolysis reaction, and indeed, even at 80°C the hydrolysis is slow as judged by FT-IR. Figure 28 shows a typical FT-IR spectrum of the partially hydrolyzed diblock in the acid form. It is interesting to note that the location of the acid absorbance (1702 cm^{-1}) corresponds to acid dimers, while no acid monomer (1760-1780 cm^{-1}) is present. This may be a consequence of the grouping of the acid units into a small portion of the chain. The extent of hydrolysis vs. reaction time is shown in Table 36 where the absorbance ratio of acid to ester is given. As can be seen, there appears to be an induction period in this "sluggish" hydrolysis reaction. This may be due to the heterogeneous nature of KO_2 in THF/DMSO. These reactions



*R=Me, T=25°C
R=i-Butyl, T=85°C

SCHEME XXVI. Synthesis of Ion-Containing Block Copolymers via Superoxide Hydrolysis.

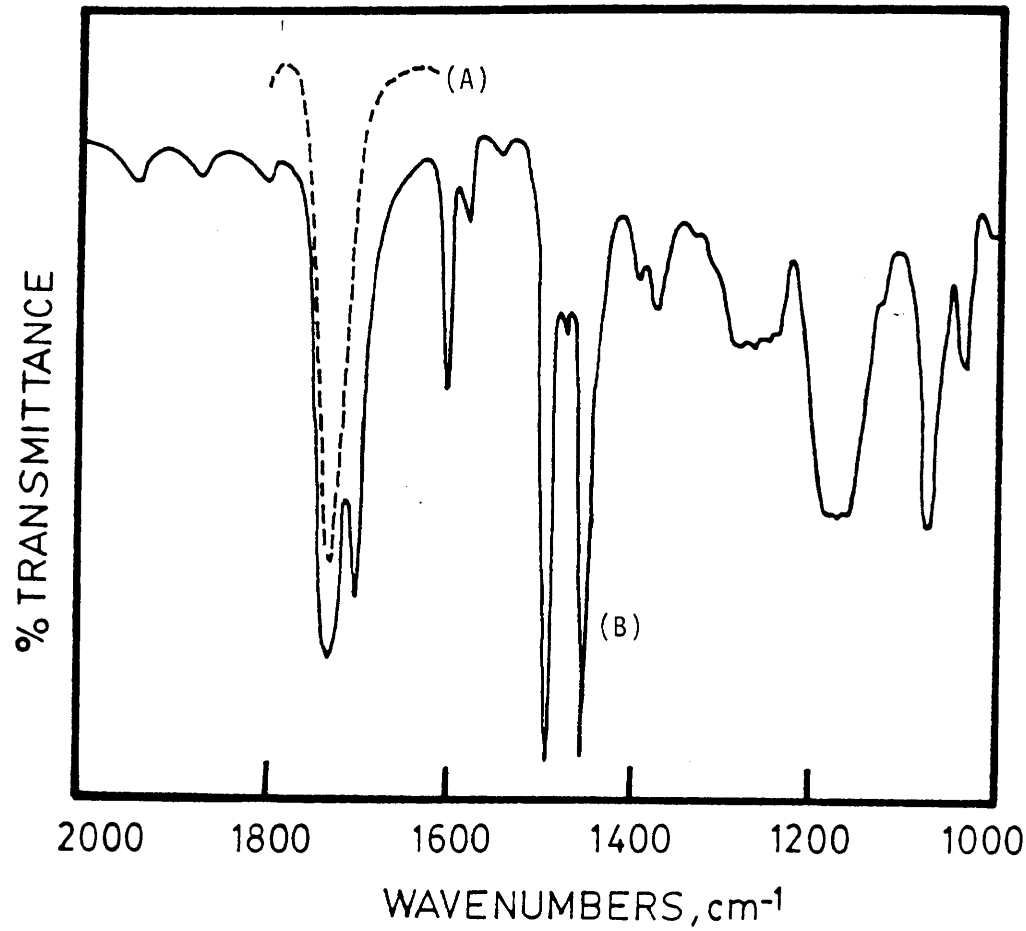


Figure 28. FT-IR Spectra of:

(A) Polystyrene/Poly(isobutyl methacrylate) Diblock Copolymer, and

(B) Carboxylated Block Ionomer obtained after Hydrolysis with KO_2

TABLE 36

Studies of Superoxide Hydrolysis in DMSO/THF at 83°C on Acidified Products

Sample No.	Rxn. Time (Hr.)	El. Vol. (GPC)	A_A/A_E (FT-IR)
I	0	28.8	0
II	1	28.7	0
III	2	28.8	0
IV	6	28.8	0.44
V	13	28.8	0.64
VI	17	29.3	1.15

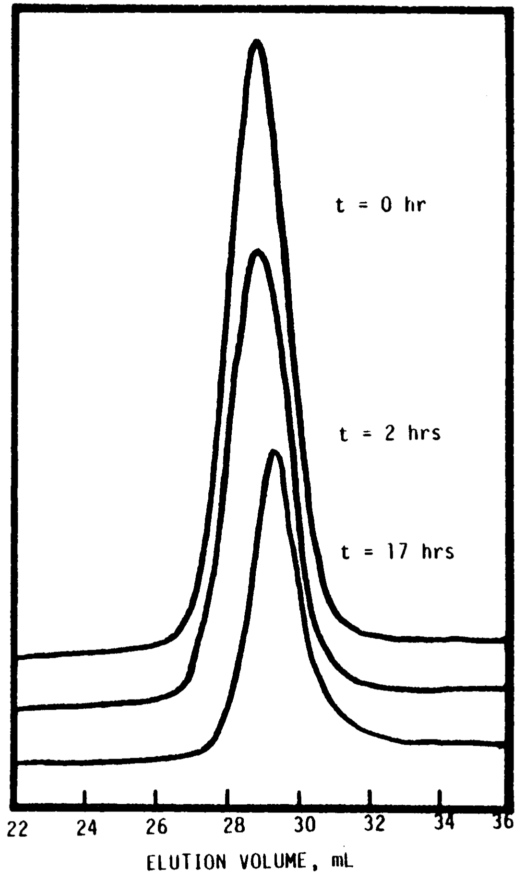
have also carried out in toluene/DMSO solvent mixture which quite surprisingly gives a much more homogeneous reaction mixture. These KO_2 reactions performed in toluene/DMSO solvent systems show no induction period, thus leading to much shorter reaction times. Table 37 shows the acid/ester absorbance values for the toluene/DMSO KO_2 hydrolysis of the PS-PIBM diblock. It should also be noted that no degredation of the polymer resulted from these reaction conditions as noted from GPC analysis on the acidified "ionomers". This can both be seen in Table 36 and Figure 29, where no peak shape change is observed with hydrolysis time. It is interesting to note that the peak elution (Table 36) volume stays constant until quite high degrees of hydrolysis. At 17 hours hydrolysis time (see Table 36) the elution changes due to the hydrodynamic differences of isobutylmethacrylate and methacrylic acid.

Characterization of the thermal and mechanical properties of these systems show several marked similarities with the poly(butyl acrylate-sulfonated styrene) emulsion polymers discussed earlier. Transparent films were produced by compression molding of the diblock hydrolyzed to the level of ca. 50% under high pressures at 250°C. These ion containing block copolymers were insoluble in all solvents tried, but dissolve quickly in THF when several drops of conc. HCl are added to convert the carboxylate ions to carboxylic acid groups. As seen in Figure 30, the block ionomer shows a very highly extended rubbery plateau (250°C) in the TMA experiment compared to the diblock precursor. The final probe penetration does not occur until temperatures approaching the decomposition temperature of PIBM. The temperature at which the ionic aggregates break down seems to be dramatically

Table 37

Studies of Superoxide Hydrolysis in DMSO/Toluene at 105°C on Acidified Products

Sample No.	Rxn. Time (Hr.)	A_A/A_E (FT-IR)
I	1	0.349
II	5	0.500
III	10	0.675



rotate 90°

Figure 29. GPC Behavior as a Function of Hydrolysis Time.

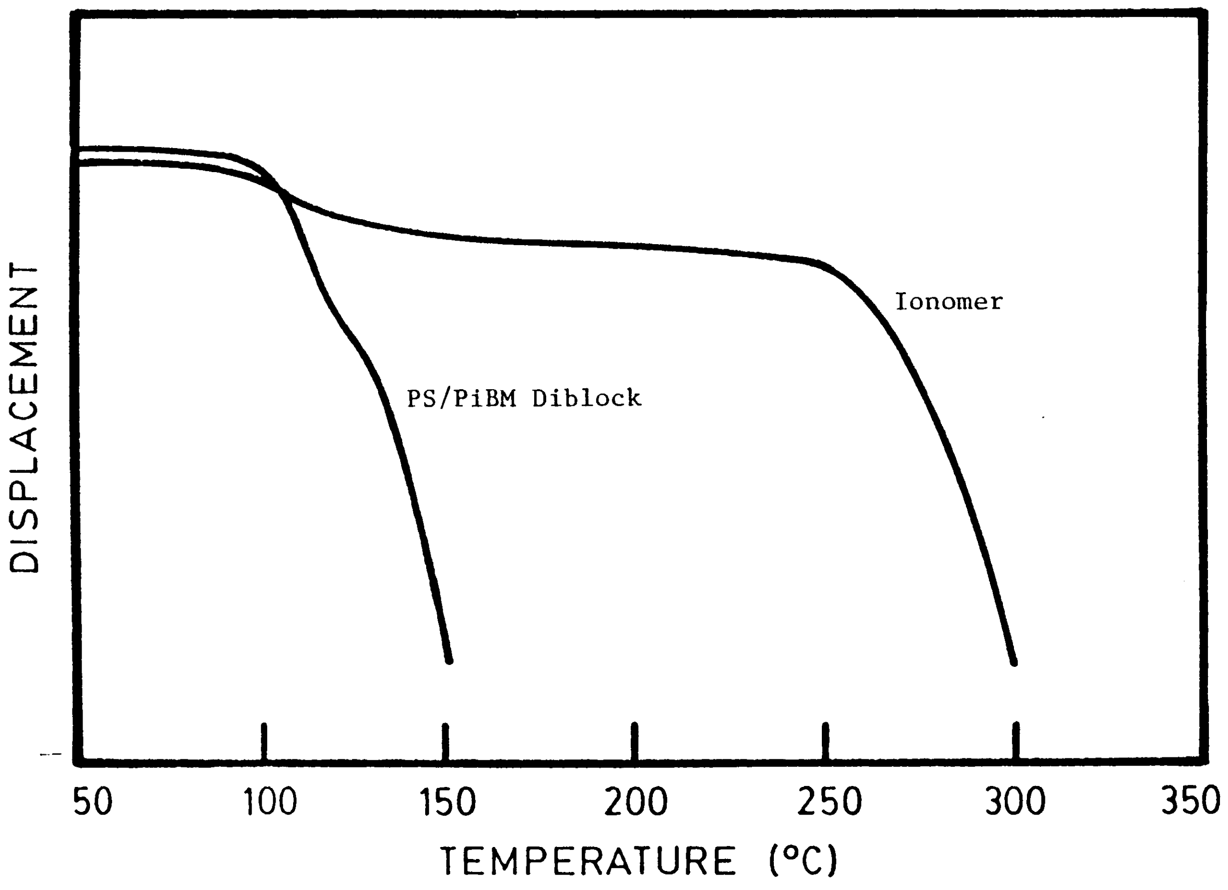


Figure 30. TMA Penetration Behavior of PS/PiBM Diblock Copolymer and Carboxylated Block Ionomer (K salt) Obtained after Hydrolysis.

influenced by the relative location of the ionic groups along the polymer backbone. The blocky nature of these ionic groups maximizes interaction to prevent this cluster decomposition from occuring. Comparison of the TMA spectra of a series of blocky vs. "random" ionomers would yield an interesting insight into this question.

Dynamic mechanical analysis (DMTA) as seen in Figure 31 shows no change in the glass transition behavior of the polystyrene matrix with ion content, as well as highly extended rubbery plateau behavior with a very high modulus. The storage moduli vs. temperature behavior for the PS-PIBM diblock precursor, the polystyrene diblock ionomer, and the polystyrene-isobutyl methacrylate-methacrylic acid diblock is shown in Figure 31. It is important to note that these three curves were offset for clarity, i.e., the modulus of the precursor is not higher than the ionomer. Two important features (as mentioned above) are the lack of Tg change of the polystyrene (as determined by the tan δ peak) before and after ionomer formation, and the extension of the rubbery plateau past 200°C. It should be noted that flow occurred in the precursor and acified versions immediately after Tg.

A further analysis of the tan δ behavior of these three Co- and ter-polymers reveals several salient features. The tan δ maxima for the three copolymers are shown in Table 38. Quite surprisingly, only one transition is evident for the diblock precursor, indicating a one phase system. The lack of microphase separation in this diblock can be explained by virtue of both the relatively small difference in solubility parameters between polystyrene (9.1) and poly(isobutyl methacrylate) (8.9), and the low block molecular weight of PIBM (ca.

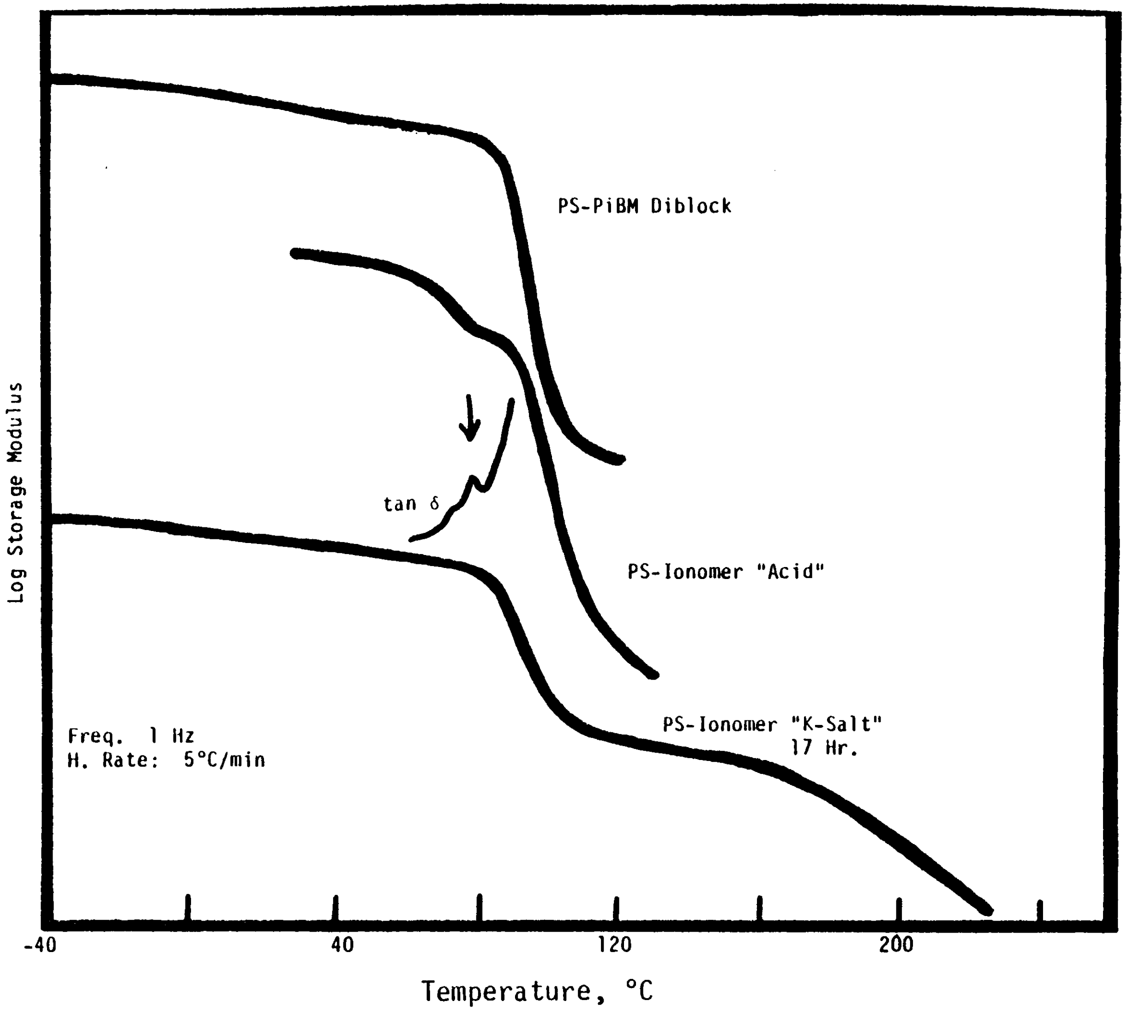


Figure 31. DMTA Behavior of:
A) Ps-PIBM Diblock
B) PS-"Ionomer" in Acid Form
C) PS-Ionomer (K-salt)

Table 38

Tan δ Maxima at 1 Hz

Polymer	tan δ maximum (°C)
PS-PIBM DB	103
PS-P(IBM-co-MAA)	106, 80
PS-IONOMER (PS-P(IBM-co-KMa)	103

5000-10,000 g/mole) in the copolymer. It would be of interest to synthesize a series of polystyrene-methacrylate diblocks varying the solubility parameter (MMA, EMA, BMA, Hexyl MA) and block molecular weight of the methacrylate block. This study is in fact already in its early stages. It is hoped that the role of block molecular weight and methacrylate solubility parameter on microphase separation of polystyrene-based diblocks will be elucidated.

The tan δ maximum temperature of the ion-containing block copolymer is the same as that of the PS-PIBM diblock precursor. This behavior is remarkably similar to the butyl acrylate-sulfonated styrene emulsion copolymers of Yilgor et. al. [98].

The behavior of the acidified ionomer, or more properly polystyrene-b-poly(isobutyl methacrylate-co-methacrylic acid) is quite interesting when compared to the PS-PIBM diblock precursor and the PS-ionomer diblock. The storage modulus drops at 80°C, while the tan δ also shows a small maximum at this temperature. The interpretation of this data involves the initiation of microphase separation by hydrolysis to the acid, which raises dramatically the solubility parameter of the methacrylate block. This solubility parameter increase results in microphase separation from the matrix. As the Tg of PIBM is ~55°C, it is not surprising that the tan δ value is slighly higher for the PIBM-co-PMAA block (80°C), due to an increase in intermolecular forces. The tan δ maximum for the polystyrene block is increased somewhat, probably due to the decrease in the plasticization of the polystyrene matrix by the PIBM block.

This investigation has provided insight into an ionomer molecular parameter largely ignored, the effect of ion location on ionomer properties. Well defined ionomer precursors are synthesized by anionic polymerization. Polystyrene-poly(isobutyl methacrylate) block copolymers are highly inert to most hydrolyzing agents. A new method for polymeric methacrylate hydrolysis was thus developed which involved potassium superoxide cleavage. The resulting potassium carboxylate block ionomers showed no polystyrene Tg change with ion content, insolubility in all solvent systems tried and highly extended rubbery plateau behavior as seen in a thermomechanical analysis study, properties different in varying degrees than conventional (random) ionomers.

Also discovered during the course of this study was the novel phase mixing character of certain "hydrocarbon"-methacrylate block copolymers. The level of phase mixing in these novel systems may be controlled by presumably altering the solubility parameter of both the styrenic block (styrene vs. p-methylstyrene vs. p-t-butylstyrene) and the methacrylate block (MMA vs. EMA vs BMA, etc.). In addition, phase separation may be promoted by controlled ester hydrolysis to form methacrylic acid units in pre-determined locations.

VI. CONCLUSIONS

This investigation of the anionic synthesis of novel methacrylate polymers has resulted in synthetic methodology which allows the chemical control over molecular weight, molecular weight distribution, stereochemistry and block polymer synthesis approaching that of the well established styrene-diene systems. The specific conclusion of this study are as follows:

1. High Purity Anionic Polymerization-Grade Methacrylate Monomers may be prepared by the use of trialkyl aluminum purification agents. This allows for the use of a wide range of methacrylate monomers.

2. Narrow MWD Poly(Alkyl Methacrylates) with predicted (low or high) M_N's have been synthesized in THF at low temperature with hindered alkyl lithium initiators.

3. Methacrylate-Methacrylate Block Copolymers with very narrow MDW and high structural integrity have been prepared.

4. Isotactic methacrylate polymers have been prpared in quanittative yields. These polymers have in some cases very low Tg's, but molecular weight control is lacking.

5. Styrene-Methacrylate block copolymers have been cleanly synthesized in THF at -78°C. The subtleties involved in polystyrene synthesis in these conditions have been addressed.

6. Methacrylate units have been controllably incorporated into well defined backbones. These materials produced ionomers of controlled structure upon hydrolysis.

VII. FUTURE WORK

An attempt was made to continually point out future directions and possible areas for fertile research throughout the text of this thesis. Several key areas will be reviewed below, however.

1. Further elucidation of monomer alkyl group effects in the BuLi initiated polymerization of alkyl methacrylate monomers.

2. All-Acrylic copolymer synthesis. This concerns both block and controlled sequence distribution stystems.

3. Model Ionomers. The utilization of t-butyl methacrylate and/or allyl methacrylate as a comonomer precursor to carboxylate and sulfonate ionic functionalities in highly controlled architectures. The major component can offer a range of dielectric contant matrices, e.g. MMA vs. styrene vs. t-butyl styrene.

4. Phase mixing in all acrylic and styrenic-acrylic block copolymers.

5. Diene-methacrylate copolymer synthesis; both monofunctional and difunctional systems are of interest.

6. Difunctional polymerization of MMA with DDPHL (double-diphenyl hexyl lithium).

7. Functional termination of methacrylate anions. As this is highly complex, a fundamental (model compound) study should precede any attempts at chain end-functional polymer synthesis.

8. Isotactic-Syndiotactic methacrylate polymer blends. It is well appreciated that i-PMMA and s-PMMA form a "stereocomplex" when blended which precipitates from common solvents and shows melting behavior. Largely ignored but highly important from both a fundamental as well as technological view, are blends of two different methacrylates of very different solubility and thermal behavior, where one polymer is highly syndiotactic and the other is highly isotactic. Preliminary work with s-PMMA and i-Poly(2-ethylhexyl methacrylate) show highly unusual results.

Transparent polymers are produced with no Tg change of either constituent (130°C and -28°C, respectively). This new concept in polymer blends offers the possibility of new materials ranging from rubber toughened plastics to high-strength adhesives.

9. Anionic methacrylate polymerization in the presence of trialkyl aluminum reagents. Early experiments, while somewhat conflicting, showed that methacrylate polymers could be synthesized quantitatively in the presence of these purification agents. This has both important technological ramifications and mechanistic complexity and thus should be further investigated.

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