SYNTHESIS OF NOVEL SILOXANE-CONTAINING BLOCK AND GRAFT COPOLYMERS BY ANIONIC POLYMERIZATION AND THE MACROMONOMER TECHNIQUE

by

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(ABSTRACT)

The synthesis of novel well defined graft copolymers is now possible with the recent advent of the macromonomer technique. Copolymers with narrow molecular weight distributions of the backbone as well as the grafts are possible.

The anionic alkyl- lithium initiated ring opening polymerization of the hexamethylcyclotrisiloxane has been investigated to prepare polymers of controlled molecular weights and narrow molecular weight distributions. This technique was extended to the preparation of macromonomers and from these macromonomers the synthesis of graft copolymers.

These siloxane macromonomers were then incorporated into acrylic and styrenic copolymers via free radical and anionic techniques. A series of graft copolymers were characterized by a variety of methods. The resulting copolymers exhibit interesting thermal properties dependent on graft molecular weight and composition. Well-defined morphologies were observed by TEM analysis, indicative of the unique structures prepared.

Graft copolymers offer unique possibilities of structure property relationships, often forming two phase morphologies that give rise to properties of both constituents. This allows the preparation of polymers designed to give optimal characteristics.

This thesis is dedicated to my wife and son for providing some sanity during the last months of this research as well as tremendous help in the preparation of this thesis.

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Dr. and Dr. at the Institute of Macromolecular Chemistry in Prague, Czechoslovokia provided much needed absolute molecular weight determinations and a theoretical basis on which to base the results of the CCD work.

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I. INTRODUCTION

Graft copolymers have been extensively studied for many years. The majority of these investigations have dealt with the synthesis and properties of these copolymers. The chemical architecture of these materials has been ill defined at best in most cases. Milkovich's development of the macromonomer method in the late 1970's has propelled the synthetic efforts forward significantly, and has allowed for more detailed analysis of the structure property relationships that exist in well defined copolymers.

Poly(dimethyl siloxanes) are an important class of polymers and have reportedly been anionically copolymerized with various styrenes. The preparation of block copolymers of siloxanes and methacrylates anionically is complicated by the mechanism of intiation and the hydrolytic instability of this linkage.

The architecture of block copolymers is controlled and therefore limited by the relationship between block molecular weight and composition. For example for the case of a diblock copolymer, with one block of 100,000 and a composition of 50 weight percent of each material, then the second block must also be 100,000 g/mole.

It will be shown that much greater variability exists with graft copolymers. A graft copolymer with backbone molecular weight of 100,000 g/mole may have many architectures which can have the same chemical composition. It is possible to have many short grafts, in the limiting case a random copolymer of two small monomers. It is also possible to have one long graft, resembling a diblock like material, or any possibility in between the two extremes. Any of these architectures can have the same overall average composition.

The variation of composition and architecture for graft copolymers will then have an effect on the morpholgy, surface properties and thermal and mechanical properties of the copolymers. Poly(dimethyl siloxane) grafts with molecular weights ranging from 300 to 20,000 were prepared and characterized. Graft copolymers with methyl methacrylate, styrene, p-methyl styrene and t-butyl styrene backbones were prepared and characterized. Diblock copolymers of the styrenes with poly(dimethyl siloxane) were also synthesized. Copolymerizations were carried out free radically and anionically in the synthesis of well defined graft copolymers.

II. REVIEW OF THE LITERATURE

A. GRAFT COPOLYMERS

1. Introduction

Graft copolymers represent a very important part of polymer chemistry. Their synthesis via radical processes is fairly easy and leads to several groups of multiphase polymers which display a wide range of properties. Unfortunately the lack of understanding of the detailed molecular structure of these graft copolymers is wide spread due to the complexity of the mixture of compositions obtained. Clearly developments leading to a better understanding of structures and structure-property relationships are therefore very important.

Conventionally, graft copolymers have been prepared by one of two methods "grafting from", and "grafting to" mechanisms. Within each of these techniques, the conventional mechanistic pathways were employed, namely free radical, anionic, cationic, and condensation methods.

2. Conventional Graft Copolymers

Many reviews have been published over the years on the synthesis and characterization of graft copolymers [1-17]. Typical uses for graft copolymers include impact modification and "compatabilization" or "emulsification" of blends of homopolymers. Recently other applications such as enhanced oil recovery has been reported [18]. Graft copolymers afford many of the same properties of block copolymers since both types of copolymers contain long sequences of two different types of macromolecular chains which are joined by at least one chemical bond. This linkage may provide the system properties characteristic of both homopolymers. A major advantage over simple physical blends is that phase separation occurs on a microphase level, instead of a macrophase level, thus permitting novel properties to be obtained. Conventional graft copolymers are complicated by the fact that they contain significant amounts of homopolymers due to the inefficiency of the grafting reactions. Therefore compositional heterogeneity is very significant and any characterization has to take this into consideration.

"Grafting from" mechanisms involve the initiation of polymerization of a monomer from the preformed backbone. Examples include the anionic initiation from metallated diene polymers, cationic initiation from poly(vinyl chloride) aluminum complexes, and free radical initiation from poly(vinyl alcohol) redox sites [19]. A summary of various reports in the literature is presented in Table 1.

Included in the above category are the commercially important impact poly(styrene) and ABS type of copolymers produced by ther free radical polymerization of styrene or styrene/acrylonitrile in the presence of poly(butadiene)

Table 1

Summary of Literature on "Grafting From" Mechanisms

Backbone	Comonomer	Mechanism	Reference
P(vinyl alcohol)		Free radical	19
P(butadiene)(bd)	Styrene Acrylonitrile	Free radical	20-22
P(bd-co-styrene)	Acrylonitrile	Free radical	20-22
P(butadiene)	Methylmethacrylate	Free radical	23
Acrylics		Free radical	24-29
P(propylene)	Styrene	Free radical	30
unsat'd P(urethanes)		Free radical	31-33
unsat'd P(esters)		Free radical	31-33
AZO contg PMMA	Styrene Methacrylonitrile	Free radical	34
Halogenated Polymers		Radiation	35-39
Natural rubbers		Radiation	35-39
P(butadiene)	Styrene	Anionic	42-44
DPE-co-DVB	Methacrylates	Anionic	45
PVC	Isobutylene i-Butylvinylether Styrene	Cationic	46-53
P(isoprene)	Acetylene	Ziegler-Natta	54

DPE-co-DVB = diphenylethylene-co-divinylbenzene

PVC = P(vinylchloride)

or poly(butadiene-co-styrene) backbones [20-22]. These reactions are typically carried out via an emulsion or suspension polymerization technique. Free radical abstraction of protons from the poly(butadiene) chain can then initiate polymerization and thus form graft copolymer. Nevertheless significant amounts of homopolymer are formed from radicals that never interact with the backbone. Other monomers such as the methacrylates have also been grafted onto poly(butadiene) by this similar mechanism, with similar levels of grafting efficiency [23].

The free radical polymerization of a monomer in the presence of saturated backbones can as well lead to graft copolymers by the free radical chain transfer to the backbone. Many reports have been published in the literature on various examples including acrylic and methacrylic polymers [24-29].

Another free radical technique resulting in graft copolymers is the initiation of styrene polymerization from hydroperoxides formed on the backbone of poly(propylene) [30]. Redox reactions on cellulosic polymers or poly(vinyl alcohol) in the presence of ceric ions have also been used to initiate graft polymerizations.

There has also been work done on the preparation of polymers containing free radical initiation sites. Azo or peroxide containing monomers have been polymerized into a polymer chain and were then used to initiate graft polymerization of another monomer [34].

Radiation methods have also been used to initiate monomers from backbones. Ultra-violet radiation will activate certain groups to form radicals, which can then be used to initiate polymerization [35-39]. The low absorption of energy can be overcome by using UV sensitivers or photoinitiators. Gamma radiation and electron beams are more useful due to their higher energy. [40-41]

The simplest technique involves the irradiation of a monomer swollen polymer, but it has the complication that irradiation can initiate the monomer directly and thus lead to homopolymer formation. A second technique in which the solid polymer is irradiated in the absence of oxygen to form trapped radicals with long lifetimes has also been used. Inhibitor free monomer is then swollen in and initiation from the living radicals leads to high yields of graft copolymer. A third technique in which the irradiation is done in the presence of oxygen leads to the formation of hydroperoxides. The polymer can then be dissolved and the hydroperoxide linkages degraded in a more controllable fashion such as thermally or by redox reactions at lower temperatures.

The first two techniques both share the problems of monomer-polymer miscibility and bulk reaction kinetics as versus the third technique which can be conducted in solution. For this reason the first two techniques employ aqueous suspension polymerizations to provide heat transfer.

Typical polymers include halogenated polymers in which halogen radicals are eliminated to form radicals on the backbone. Natural rubbers are easily ionized in the presence of oxygen to form hydroperoxides which have then been used to graft many monomers.

Step-growth or condensation methods can be used when backbones with pendant functional sites are present, such as amines or alcohols. Reactions onto these sites require the same conditions as typical step-growth reactions (eg. high puritiies and lack of side reactions). By this scheme polyamide branches have been prepared from poly(styrene) backbones containing amine functionalities.

Ionic polymerization techniques can lead to more well defined copolymers as well as less homopolymer contamination. If all initiation occurs from the backbone, then homopolymer levels can be reduced and grafts of controlled molecular weights and narrow molecular weight distributions can be prepared, since the initiator concentrations are controlled.

Anionic polymerization can reportedly be initiated from the metallated backbone of diene polymers such as poly(butadiene) [42-44]. Typically alkyl lithiums such as butyl lithium and a complexing agent such as tetramethyl ethylene diamine (TMEDA) are used to form anionic species on the poly(butadiene) backbone. These sites can then be used to initiate styrene monomer to form copolymers similar to impact polystyrene. Problems in this synthesis include the efficiency of formation of the lithiated backbone and side reactions that occur, insolubility of highly metallated backbones and efficiency of initiation from this backbone.

Another unsaturated backbone recently investigated is a copolymer of diphenylethylene and divinyl benzene, prepared anionically without the crosslinking side reaction often encountered in divinyl benzene polymerizations. The pendant vinyl groups are then useful for grafting [45].

Cationic polymerizations have been initiated from backbones such as poly(vinyl chloride) with aluminum catalysts. Lewis acids such as trialkyl aluminums complex with organic halides to form cationic initiators. Thus the allylic chloride sites in PVC were used to initiate the polymerization of isobutylene, iso-butyl vinyl ether, and styrene [46-53]. This approach has also been used to graft from unsaturated copolymers by first halogenating the unsaturated sites then forming the cationic initiator.

Coordination polymerizations have been accomplished from polymer backbones to prepare graft copolymers. The metallation of polymer backbones can also be used to prepare coordination type initiation sites. If these lithiated species are used to reduce the vanadium catalyst instead of alkyl aluminums, then coordination polymerization can be initiated from the backbone. Indeed, poly(isoprene-g-acetylene) copolymers have been prepared by this mechanism [54].

"Grafting to" mechanisms involve the attack of a reactive end group of one polymer chain onto the backbone of a second polymer chain [55]. Examples include the reaction of living anionic polymers onto polyesters or by halogen displacement reactions and the reaction of living cationic polymerizations onto phenoxide or carboxylate containing backbones. Table 2 summarizes various reports of "grafting to" type reactions.

Living anionic polymerizations have been used to form graft copolymers by the reaction of the living anion onto ester functionalities such as in poly alkyl methacrylates. Typically, living poly(styryl lithium) is reacted with preformed poly(methyl methacrylate) via attack on the

Table 2

Summary of Literature on "Grafting To" Mechanisms

Backbone	Copolymer	Mechanism	Reference
PMMA	P(styryl lithium)	Anionic	56
PS w/nitro grps	PEO	Nitro displacement	57
	P(styryl lithium)	Halide displcmnt	58-62
	PEO anion	Halide dsplmnt	58-62
P(p-vinylstyrene oxide)	PS lithium	Epoxide attack	63
Phenolic backbone	PTHF	Cationic pzn	64

ester linkage, and displacement of lithium methoxide and formation of a ketone moiety [56].

Also, nitro displacement reactions can also be used to graft an alkoxide functional polymer chain onto a backbone. Poly(ethylene oxide) anions have been used to displace the nitro group on nitro substituted poly(styrene) to form the graft copolymer PS-g-PEO [57].

Reactions of living anions in alkyl halide diplacements is another frequently tried "grafting to" reaction. Benzyl halides, or tosylates are most frequently used as all halides have a side reaction of metal-halide exchange instead of displacement and benzyl halides under the proper conditions have the highest efficiency. Displacements with living poly(styryl lithiums) or even living poly(ethylene oxide) anions have been reported [58-62].

The characterization of any of these graft copolymers include a determination of the average composition. From this and the knowledge of the initial backbone molecular weight estimates on the degree of branching can be calculated. Important variables include the number of branches per backbone, and spacing between grafts, length of grafts and polydispersity of graft molecular weights. [65-66] Also, the polydispersity of the original backbone causes another variable to be superimposed. Complicating the characterization of graft copolymers is the fact that hydrodynamic volume is a function of branching and thus interpretation of GPC measurments are often best treated with great care.

Model graft copolymers with well controlled structures and compositions would therefore be useful in learning how to characterize the more conventional graft copolymers. A recent advance in the polymer field has opened the door to the synthesis of much more well defined graft copolymers, namely the macromonomer method.

3. Macromonomer Methods

The term "MACROMER" was patented in 1974 [67] by the late Dr. Ralph Milkovich, even though, as early as 1958 literature can be found indicating that polymers with polymerizable head groups had been prepared [68]. A macromonomer can be defined as a polymeric or oligomeric chain with a polymerizable functionality at one or both termini. The context of this thesis will deal with only monofunctional macromonomers. Until the 1980's however, it was not a widely excepted hypothesis that these macromonomers would copolymerize in a well defined manner. In these last few years however much work has been reported on the preparation and copolymerization of macromonomers with other small monomers for the preparation of well defined graft copolymers which have a wide range of structures.

Several reviews and important papers have been published on the subject by authors such as Rempp[69-71], Kennedy[72], and Percec[73] on cationic polymerization methods, Corners [74] on free radical synthetic techniques, Asami [75], Franta[76], Cho[77], Chujo[78], Higashimura[79], Ito [80], Kawakami[81,82], Kobayashi[83], Nitadori[84], Oh[85], Penczek[86], Plate[87,88], Sageusa[89], Simionescu[90], Stanislaw[91], Vlegel[92], Yamshita[93-95] and Yang[96].

Many important variables need to be kept in mind when considering a paper on the synthesis and copolymerization of macromonomers. Characterization of the macromonomer structure and functionality is very important since end functionality is critical for incorporation. Many methods of macromonomer characterization will be demonstrated such as UV analysis of the end-group, and chromatographic techniques as well [97-99].

On the other hand certain structures can lead to branching along the macromonomer chain by chain transfer mechanisms. Also certain structures can degrade free radically and thus the macromonomer if incorporated could be of different structure than the original structure.

Alternate mechanisms of incorporation need to be considered since the architecture of the resulting copolymer would not be the same as if only end group incorporation were occuring.

Another important variable in the copolymerization of macromonomers is the copolymerizability as measured by the reactivity ratios, r_1 and r_2, of the macromonomer and comonomer. Appreciation of these numbers leads to an understanding of the "randomness" of the copolymers formed.

Characterization of these graft materials is still in its infancy as will be discussed later. Typical analysis such as by GPC needs to be interpreted cautiously due to the complications such as chain branching effects on hydrodynamic volume.

Compositional heterogeneity is another important variable to be considered in the characterization of graft copolymers [100,101]. There has been very little consideration in the literature of this heterogeneity by researchers synthesizing and copolymerizing macromonomers, which is unfortunate. One group in Czechoslovokia has, however, published extensively over the past twenty years on the heterogeneity of chemical compositions in many types of copolymers.

Starting with Stockmayers' theories [102] on the statistics of copolymerization, theories have been developed for the expected heterogeneities in not only random, block and graft copolymers, but also for graft copolymers prepared by the macromonomer method as well. Characterization of the heterogeneity by light scattering methods have also appeared in the literature [103-113].

Macromonomers can, in principal be prepared by any of the conventional modes of polymerization, such as free radical, condensation, anionic, cationic, coordination or group transfer polymerization techniques. Polymerizable groups may be fitted on the ends of the polymer by many methods, such as direct deactivation of the living polymer species or post reactions on preformed polymers.

The types of polymerizable groups that can be attached to these chains are also numerous, and include α-olefinic, styrenic, acrylic, vinylic, vinylic alkyl ethers, epoxides, or even difunctional species such as diacids, diamines, or diols. These macromonomers can then be copolymerized free radically, anionically, by a coordination or group transfer mechanism or by a step growth method, depending on the structures present.

Anionic polymerization is applicable to a smaller range of monomers than free radical polymerization, but allows for more well defined polymers. Polymers of controlled molecular weight and narrow molecular weight distributions are readily synthesized. Functionalization of anionically prepared polymers may be under taken by functional initiation or termination. Often times one must include a first step of anion deactivation, in order to prevent reactions of a strong anion with the termination agent, which could produce an undesired side reaction. Anionic preparation of macromonomers such as the styrenes, methacrylates, vinyl pyridines, cyclic ethers, cyclic lactams, and siloxanes, allow for controlled molecular weights, narrow molecular weight distributions and high yields of functionalization.

Cationic preparation of macromonomers is limited to only a few systems such as isobutylene, tetrahydrofuran, and vinyl ethers. These systems have been prepared by functional intiators, functional terminations and post reactions on preformed polymers as will be discussed in more depth later.

Macromonomers have also been prepared by free radical methods, typically by using functional chain transfer agents, such as alcohol functional thiols, which then result in alcohol terminally functional oligomers that can then be optionally esterified to form the macromonomer. Occasionally, the use of functional initiators has been reported, but only in cases where the active site will not under go polymerization or chain transfer during polymerization.

Condensation polymerizations have also been used to prepare macromonomers, with structures such as aromatic-poly(ether sulfones), poly(2,6dimethyl-1,4phenylene oxide) and polyesters.

4. Macromonomer Synthesis and Copolymerization

Perhaps the first report in the literature of the preparation of what are now defined as macromonomers was in 1958 when Rempp [68] pubished a method of terminating living polymerizations with allyl bromide, that was very efficient in functionalization.

Later, Waack used unsaturated organolithium initiators to initiate polymerization of styrene monomer[114]. The report was an attempt to investigate initiation efficiencies of various alkyllithiums, including vinyl, and allyl lithium. The initiation efficiencies were not high and thus Rempp's method would be more favorable. There was no attempt however to polymerize these macromonomers and considering the low reactivity of these type of end groups to free radical polymerization, poor reactivity would be expected. Waack later patented his method for preparing functional polymers [115].

Greber in 1962 published a report on the synthesis of p-vinylphenyl-polysiloxanes prepared from the reaction of p-vinylphenylmagnesiumchloride with chlorosilanes or 1-chloropolysiloxanes [116]. Oligomeric siloxanes of degree of polymerization of 1 to 4 were prepared. The homo- and copolymerization of these monomers with styrene were investigated and they were found to incorporate readily. Thus, the incorporation of siloxanes into styrenic graft copolymers was demonstrated.

In 1963 a second report by Greber appeared, on the preparation of oligomers bearing allylic, styrenic, and phenyl-CH2-CH=CH2 end groups by termination with the appropriate chlorosilanes [117]. Work was also done on intiation of vinyl monomers with grignard reagents bearing vinyl, and styrenic groups. Work with styrene, isoprene, vinyl pyridine, and methyl methacrylate was demonstrated.

In 1967 Gillman and coworkers made poly(methylmethacrylate) oligomeric macromonomers free radically and copolymerized these with styrene, acrylonitrile, and vinyl acetate [118]. Methylmethacrylate was polymerized free radically with an alcohol functional mercaptan to prepare PMMA oligomers bearing alcoholic end groups. These were then esterified with methacryloyl chloride to produce PMMA macromonomers with degrees of polymerization in the range of 8 to 12 corresponding to molecular weights of 800 to 1200.

Gillman also copolymerized his PMMA macromonomers to demonstrate the feasability of copolymerization with styrene, vinyl acetate, and acrylonitirile.

Milkovich's patent in 1974 [119] of the Macromer concept provided a giant scientific step forward from the scattered data to this date. A series of patents then followed in the next years detailing the preparation of functional groups on polymers [120]. Not until 1980 however did he publish in the literature on this work [121].

The review above provides a brief summary of the early work leading up to the present day research in the macromonomer field which is very complex. To adequately organize a discussion it is necessary to divide the subject of macromonomer synthesis into the various mechanisms of polymerization, such as anionic, cationic, free radical, and condensation methods. Tables 3 and 4 summarize the literature to date on the use of anionic polymerizations to prepare macromonomers.

Milkovich and Chiang are considered to be the founders of the field, having developed the idea and implemented it to demonstrate interesting copolymer properties resulting from the copolymerization of the macromonomers. They prepared macromonomers of styrene and isoprene, as well as diblock and triblock copolymers of styrene and isoprene.

Much of Milkovich's work involved the anionic synthesis of polystyrene and the deactivation of the

Table 3

Summary of the Synthesis and Copolymerization of Poly(styrene) Macromonomers Anionically

Author	End Group	Comonomer(s)	Reference
Milkovich	Methacrylate	Butyl acrylate	121
		Acrylonitrile	122
		Vinyl chloride	126
Asami	Styrenic	Styrene	129-132
		Methylmethacrylate	131
Hu	------	Methylmethacrylate	133-136
		Butylmethacrylate	
Ito	Methacrylate	2-Hydroxyethylmethacrylate	137
Ma	Norbornene	------	138-9
	Allyl	Ethylene-propylene	
Mancinelli	Epoxy	THF cationically	128
Nagasaki	Styrenic (FI)	Methylmethacrylate	140
Rempp	Vinyl silanes	------	141-5
	Methacrylate	Methacrylates	
	Styrenic		
Xie	Epoxy	Ethylene oxide	146-8
	Methacrylate	Butylacrylate	
Yamashita	CO2-glycidyl MA	Methylmethacrylate	149-52
		2-Hydroxyethylmethacrylate	
		Glycidyl MA	

Table 4

Summary of Macromonomers Prepared Anionically

Author	Macromer	EndGroup	Comonomer	Reference
Asami	P(isoprene)	Styrenic	Methylmethacrylate	130
	2-VPD, 4-VPD			
Hashimoto	VPD	------	------	154
Rempp	VPD	Styrenic	Styrene	155-6
		Methacrylate		
Severeni	4-VPD	Methacrlate	Butylacrylate	157
Rempp	PMMA	Styrenic	------	158
	P(isopropylideneglycerol)MA		------	
	P(2-trimethylsiloxyethyl)MA		------	
Hatada	PMMA	Styrenic(FI)	------	159
	P(triphenylmethylmethacrylate		------	160
Hamaide	PEO	Styrenic	Styrene	161-2
			Butyl Acrylate	
			Acrylonitrile	
Ito	PEO	Styrenic	Styrene	163,168
		Methacrylate	Styrene	
Rempp	PEO	Styrenic(FI)	------	164-5
		Methacrylate(FT)	------	
Kobayashi	PEO	Oxazoline(FI)	2-Ph-2-oxazoline	166
Mathias	PEO	Vinyl ether(PR)	Ethylvinylether	167

Table 4 (contd)

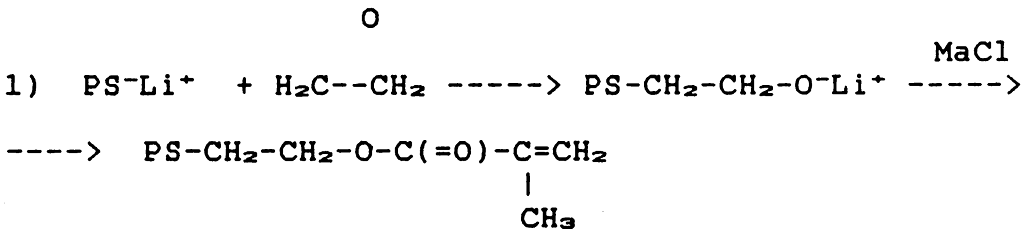
Summary of Macromonomers Prepared Anionically

Author	Macromer	EndGroup	Comonomer	Reference
Cameron	PSX	Methacrylate	Styrene	170,181-2
			Methylmethacrylate	
			Acrylonitrile	
Imai	PSX	Vinyl silane	Vinyl acetate	171
Matzurek	PSX	Methacrylate	Butylmethacrylate	172
Williams	PSX	Methacrylate	Isocyanoethyl MA	173
Yamashita	PSX	Methacrylate	Styrene	174-7,183
			Methylmethacrylate	
			Fluro acrylates	184
Smith	PSX	Methacrylate	Methylmethacrylate	178-80
			Styrene	
			t-Butylstyrene	

VPD= Vinylpyridine
PMMA= poly(methylmethacrylate)
MA= methacrylate
PEO= poly(ethyleneoxide)
PSX= poly(dimethylsiloxane)

(PR) = post reraction
(FI) = functional initiation
(FT) = functional termination

polystyryllithium anion with ethylene oxide to form the alkoxide, then reaction with methacryloyl chloride [122]. This reaction is outlined in Equation 1.



$$1)\quad PS^{-}Li^{+} + H_2\overset{O}{C\text{--}}CH_2 \xrightarrow{\quad} PS\text{-}CH_2\text{-}CH_2\text{-}O^{-}Li^{+} \xrightarrow{MaCl}$$

$$\xrightarrow{\quad} PS\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(=O)\text{-}\underset{\substack{|\\ CH_3}}{C}=CH_2$$

Also patented in 1974 and 1975 by Milkovich [123], but not reported in the literature until recently was the use of diblock macromonomers [124]. A patent dealing with tapered block macromonomers was also applied for in 1982. [125] Triblock copolymers of a styrenic monomer and a diene monomer were prepared, however the synthetic technique leads to tapered block copolymers. Initiation of styrene was followed by propagation and then by addition of the isoprene before propagation was complete. Theoretically the isoprene should incorporate as the second block followed by a short third block of styrene. Unequal reactivity of the two monomers leads to a tapering effect between the second and third blocks with mixed styrene isoprene copolymer instead of clean block copolymer. These triblock macromonomers with allyl or acrylic end groups were also copolymerized with ethylene, propene, or styrene, to give graft copolymers with good mechanical properties.

In their recent publication [124], block copolymers of styrene and isoprene, were prepared anionically with a methacrylate functionality present at the termini of the isoprene segment, by the same deactivation sequence. It was also reported that triblock copolymers of styrene-isoprene-styrene were also synthesized with very short blocks of styrene at the termini bearing the methacrylate functionality improved the copolymerization ability of the macromonomers.

The copolymerization of styrene macromonomers with butyl acrylate led to a thermoplastic elastomer. Phase mixing was a limiting factor and other comonomers, such as ethyl acrylate were used. This led to decreased phase mixing, but also adversely raised the soft phase Tg.

Copolymerizations of PS macromonomer with acrylonitrile and vinyl chloride were also reported. [122,126] Indeed copolymerizations with acrylonitrile and vinyl chloride lead to graft copolymers with improved processing over the homo polymers of the backbones.

Milkovich and Schultz were also one of the first groups to address the problem of macroscopic phase separation during polymerization as leading to the formation of homopolymers, instead of true graft copolymers. Miscibility of the graft copolymer formed early in the reaction with macromonomer and monomer is crucial since a phase separation early on will lead to incompatable homopolymer formation separately from the macromonomer phase. The presence of macromonomer rich and poor phases were predicted based on solution analogies, and the expected trends of incompatability were also demonstrated. Increasing macromonomer molecular weight and larger differences in solubility parameter between macromonomer and monomer increase the level of unreacted macromonomer due to this phase separation. Also increasing levels of macromonomer improve the compatability by decreasing the ratio of monomer to macromonomer phase volumes. Results of copolymerizations in suspension copolymerizations also bore out results that would indicate the above occurence, since much unreacted macromonomer was obtained in suspension copolymerizations. The addition of small amounts of benzene as a solvent decreased the amounts of unreacted macromonomer dramatically.

Diblock and triblock macromonomers of styrene-isoprene were copolymerized with styrene monomer to produce impact modified styrene [124]. By this method instead of direct copolymerization of an isoprene macromonomer they were able to change the morphology of the system to control physical properties. It was also found that having a short block of styrene at the termini bearing the methacrylate functionality increased incorporation efficiency due to better phase mixing in solution during the copolymerization. The chain scission characteristics of isoprene in a free radical process could also play a role in the reaction, and this was not addressed.

The presence of the styrene block on the graft as well as in the backbone limits both ends of the isoprene chain as compared to only one end in a pure isoprene graft case. This should decrease soft phase mobility and decrease domain sizes, however in their report it was found that the addition of pure styrene-isoprene diblock increased the impact properties of the copolymer assumably by increasing the soft segment domains and thus by passing the original intentions.

ARCO thus had many patents on the early macromonomer work and today a subsidiary of ARCO, Sartomer sells poly(styrene) macromonomers under the name Chemlink. Several papers have appeared in the literature wherein one of the Chemlink macromonomers was used in the preparartion of graft copolymers [127-128]. Recently, this technology was sold to an enterprise known as Horsehead Industries.

Several others have also used anionic polymerization to prepare mcromonomers of polystyrene including Asami[129-132], Hu [133-136], Ito[137], Ma [138-139], Mancinelli [128], Nagasaki[140], Rempp[141-145], Xie [146-148], and Yamashita [149-152]. Asami has reported on the use of anionic polymerization for not only polystyrene but also for isoprene and 2-vinylpyridine macromonomers [153]. Their attempts have involved the anionic polymerization followed by deactivation with p-vinylbenzylchloride or p-vinylbenzyltosylate, avoiding the deactivation step of ethylene oxide addition necessary with methacryoyl chloride as deactivator. It was found however that association of the polystyrl lithium in benzene solutions leads to some attack on the unsaturated site and addition of THF was necessary to get good yields of functional macromonomer.

Asami has copolymerized his styrene macromonomers by free radical, and anionic homo- and co-polymerizations of a styrenic end group and more recently group transfer polymerization of a methacrylate end group [131].

Homo- and co- polymerizations of PS macromonomer with styrene free radically and anionically were carried out in solution. They concluded that homopolymerizations were unaffected by macromonomer molecular weight and proceeded as solutions of very dilute monomer end groups would polymerize, with degrees of polymerization varying from 5 to 58 as estimated by GPC which as they point out underestimates the degree of polymerization, X_N, due to branching. They concluded therefore that the accesability of the macromonomer is the same as in the case of a small monomer.

Group transfer polymerization with methyl methacrylate monomer was carried out on a solution of monomer and macromonomer to produce a graft copolymer [131]. Asami was able to demonstrate that graft copolymers with relatively narrow distributions could be prepared in the case where the graft copolymer was about 70 weight precent poly(styrene) graft. The solution properties of this highly branched type structure are suspect especially under synthetic conditions which might lead to a random living copolymer with macromonomer remaining in solution that is then able to add to the living chain end. The addition of further macromonomer units all at the end of a copolymer can be likened to star block copolymer whose hydrodynamic volume is independent of molecular weight above a certain number of arms.

Poly(styrene) macromonomers prepared anionically were copolymerized with methyl methacrylate under free radical conditions by Hu and coworkers. They found that copolymerization rates were constant over a wide range of conversion, contrary to what some other workers have reported. A suggestion of a weak association of macromonomers is said to be supported by indirect evidence. Many workers reporting lowered reactivity at high conversions also report problems of macro phase separation in solution of the macromonomer, which probably explains their problems.

Copolymerizations of their macromonomers with butyl methacrylate or methyl methacrylate lead to graft copolymers which were characterized for microphase separation, optical, mechanical, and surface properties.

Ito and coworkwers compared random copolymers of styrene and 2-hydroxyethylmethacrylate with graft copolymers prepared by the copolymerization of anionically prepared poly(styrene) macromonomer and 2-hydroxyethylmethacrylate. Micellar behavior was observed for graft copolymers in methanol and in chloroform, with methanol preferentially solvating the methacrylate backbone around a core of insoluble PS. Chloroform formed a micelle with PS outwards around a core of methacrylate, as contrasted to the random copolymers which did not show any tendency to form micelles, due to the short statistical chain lengths. Evidence of micelle behavior was observed by NMR by noting that the insoluble fraction would act as a solid and not display any measurable resonances. Surface characterization of films of these copolymers by contact angles with water demonstrated that random copolymers show a gradual change in surface structure as a function of composition, while graft copolymers have surfaces dominated by the component of lower surface energy. The surface can be affected by casting solvent, for example casting from methanol (a solvent preferential for hydroxyethylmethacrylate) leads to films of high surface energy. However baking of the films above their Tg's returned all films to the thermodynamically favored low surface energy PS dominated surface structure.

Poly(styrene) macromonomers were prepared anionically and terminated with 5-bromomethylnorbornene by Ma and coworkers. Poly(styrene) macromonomers with allyl end groups were also prepared anionically and copolymerized with Vanadium catalysts with ethylene and propylene. Graft copolymers of structure EPR-g-PS were thus apparently synthesized succesfully having 1-4 branches per molecule with graft molecular weights from 10- 78,000.

Poly(styrene) macromonomers have also been synthesized by deactivation of the living styryl anion with ethylene sulfide followed by reaction with epichlorhydrin by Mancinelli. Cationic copolymerization with tertrahydrofuran led to a graft copolymer [128].

A novel method was developed by Nagasaki and Tsuruta where in, they metallated p-methylstyrene with lithium diisopropylamide to form 4-vinylbenzyllithium which will initiate styrene monomer. The growing anion does not attack the styrenic functionality of the p-methylstyrene head group thus leading to a poly(styrene) macromonomer with a styrenic type end group. Nagasaki demonstrated that his novel method of macromonomer preparation was valid by copolymerization experiments with MMA.

Chaumont and Rempp have reported the termination of polystyrl lithium with vinylchlorosilanes, showing results that would indicate that exclusive attack of the styrl lithium anion can be directed to the displacement of the chloride and not towards the vinylic or allylic silane structure. Attempts were made to deactivate the styrl lithium through use of ethylene oxide or diphenylethylene before addition of the chlorosilane. The carbon-oxygen-silicon bond formed from addition of ethylene oxide prior to the chlorosilane generally leads to a hydrolytically unstable bond. Deactivation of the styrl lithium by addition of diphenyl ethylene results in a sterically hindered anion of lower basicity that increases the favorable reaction towards chloride rather than vinyl attack.

Masson and Rempp have also investigated the termination of styrl lithium by Milkovich's method of ethylene oxide then methacryloyl chloride. Masson attempted the homopolymerization of poly(styrene) macromonomers free radically and anionically using diphenylmethyl potassium. Degrees of polymerization between 7 and 15 were reported with narrow molecular weight distributions as calculated by GPC being reported but weight average molecular weights by light scattering, indicated much higher distributions, probably due to the star-like characteristics.

Xie prepared poly(styrene) macromonomers anionically and terminated the living styryl anion with epichlorohydrin [146-8]. This macromonomer was then copolymerized with ethylene oxide cationically to form a graft copolymer that formed an emulsion in water and that swelled in water to form an elastomeric gellike mass. Crystalline poly(ethylene oxide) phases were observed.

Yamashita has also used anionically prepared styrene to prepare macromers by a different route [149-52]. In his reaction sequence living poly(styrl) lithium is deactivated by the addition of carbon dioxide. The carboxy terminal poly(styrene) is then reacted with glycidyl methacrylate to form the methacrylate functional poly(styrene).

The surface and micelle structures of copolymers with PS grafts with MMA, and hydroxyethylmethacrylate backbones. Similar to some of the work by Ito [137], micellar structures were demonstrated by NMR in selective solvent for one phase or the other, forming a core of insoluble material and a shell of soluble material. This type of morphology is carried on to films cast from preferential solvents as evidenced by contact angle analysis work on dry films. ESCA analysis also confirmed the surface domination of one phase depending on casting solvent.

Poly(styrene) macromonomers were copolymerized with hydrophilic comonomers and the hydrogels prepared from these copolymers were investigated. Glycidyl methacrylate backbones with poly(styrene) grafts were prepared and the hydrogels prepared from these copolymers by first casting films from a mixed (methanol/THF) solvent system and then by swelling the films in water. Polymer composition as well as cast morphology were shown to have strong influences on swelling which then affect oxygen diffusion through the hydrogel.

Copolymerizations with hydrophobic and hydrophilic comonomers was also undertaken to investigate the surface properties of blends with poly(styrene). Fluoroalkyl methacrylate graft copolymers exhibited dramatic domination of the air surface while the glass side surface was almost pure poly(styrene). Backbones of hydrophilic monomers produced an opposite affect with the surface being dominated by the lower surface energy poly(styrene), and the glass side was dominated by hydrophilic monomer. A change of structure was observed when the level of graft copolymer exceeded 0.1 weight percent in the blend and saturated at 0.5 weight percent. Above 0.5 weight percent graft copolymer in the blend analysis gave results identical to those of the pure graft copolymers. It was also shown that poly(styrene) branch length affected surface accumulation.

Macromonomers of poly(2-vinyl pyridine) and poly(4-vinyl pyridine) have been prepared by not only Asami [130], but also by Hashimoto[154], Rempp[155-156], and Severeni[157]. Asami prepared styrene terminated poly(2-vinyl pyridine) from the reaction of the living anion of poly(2-vinyl pyridine) and p-vinylbenzyl chloride. Copolymerization with methyl methacrylate was used as a test for functionality of the macromonomer.

Poly(methyl methacrylate) macromonomers have been prepared anionically by Lutz and Rempp[158] by terminating the living PMMA lithium anion at low temperatures with p-vinylbenzylbromide. The basicity of the methacrylate anion is low enough so that attack of the unsaturated styrenic double bond does not occur and displacement of the bromide is the favored reaction leading to the styrenic end functional poly(methylmethacrylate) macromonomer.

Other methacrylate macromonomers such as isopropylideneglycerol methacrylate and 2-(trimethylsiloxy)ethyl methacrylate were polymerized anionically and functionally terminated with p-vinylbenzyl bromide or p-isopropenylbenzyl bromide. Thus styrene functional methacrylate macromonomers were prepared anionically.

Poly(methylmethacrylate) macromonomers have also been prepared by Hatada [159] through the polymerization of methyl methacrylate with a functional grignard intiator. Vinyl benzyl magnesium chloride was prepared from vinyl benzyl chloride and magnesium then used to intiate methyl methacrylate. The PMMA chains then have styrenic end groups.

Poly(ethylene oxide) macromonomers have also been prepared by the anionic polymerization of ethylene oxide and deactivation with methacryloyl chloride. Hamaide [161-162], Ito[163], Rempp[164-165], Kobayashi[166], and Mathias[167] have all reported the synthesis of poly(ethylene oxide) macromonomers.

Hamaide prepared PEO macromonomers by the reaction of p-vinyl benzyl chloride with hydroxy end groups of commercially available PEO. These poly(oxyethylene) (PEO) macromonomers were then copolymerized with styrene, butylacrylate, and acrylonitrile. Reactivity data showed that the end group was similar to styrene and not affected by the polymeric structure.

Ito [168] prepared living PEO via anionic polymerization using potasium t-butoxide as initiator followed by termination with p-vinyl benzyl chloride or methacryloyl chloride. Another report investigated the solvent effects on the macromonomer reactivity with styrene monomer. Polymerizations were carried out in benzene, tertrahydrofuran, and methyl isobutyl ketone. Reactivity of the macromonomer dropped off as macromonomer molecular weight increased as has been found often in the literature. Secondly the effect of solvent was that good solvents for both phases were found to decrease reactivity as well.

Kobayashi also anionically polymerized ethylene oxide, but with a functional initiator. He prepared the lithium salt of an alcohol functional oxazoline which he then used to intiate the polymerization of ethylene oxide and terminated the polymerization with methyliodide. The macromonomers obtained then had oxazoline functional termini which can then be copolymerized cationically. The oxazoline end groups were then copolymerized with 2-phenyl-2-oxazoline to prepare the graft copolymer.

Masson and Rempp used two methods to prepare macromonomers of PEO, one being the functional termination and the other being a functional initiation of ethylene oxide. An α-Methyl styrene derivative bearing a benzyl alcohol site was used as the potassium salt to initiate ethylene oxide to prepare the α-methyl styrene functional material. The second method used to prepare macromonomers involved the functional termination of the growing potasium alkoxide with methacryloyl chloride.

Mathias used commercial PEO and a reaction with potasium metal at high temperature to which is then added acetylene to form a vinyl ether end group. Cationic copolymerizations with ethyl vinyl ether lead to graft copolymers which show activity as phase transfer catalysts. PEO copolymers typically with styrene are often used but other PEO copolymers offer different mixes of solubilities and possibly different activity as catalysts.

The anionic polymerization of lactams has also been used for the preparation of macromonomers by Hashimoto. [169] 8-oxa-6-azabicyclo[3.2.1]octan-7-one was polymerized anionically followed by reaction with p-vinylbenzylamine. Copolymerizations with styrene indicated a lower reactivity ratio than expected for small molecule analogs. Characterization of blends with poly(styrene) indicated that the hydrophilic polyamide was located on the glass side of cast films.

Macromonomers of poly(dimethyl siloxane) are also a very important area of study for reasons that will be discussed later. The anionic alkyl lithium initiated polymerization of D_3 may be used to prepare living siloxanolates of varying molecular weights, which are then terminated with a chlorosilane bearing polymerizable functionalities such as methacrylate or styrenic structures. Cameron[170], Greber[115-116], Imai [171], Matzurek [172], Williams [173], Kawakami and Yamahita [174-177] as well as Smith and McGrath [178-180] have all contributed to the literature on their synthesis of poly(dimethylsiloxane) macromonomers.

Cameron and Chisholm have reported careful investigations of the preparation and copolymerization of PSX macromonomers with styrene, methylmethacrylate, and acrylonitrile [181-182]. In their second paper, macromonomers of molecular weights 500, 1160, and 9750 were prepared and copolymerized with styrene to final copolymer molecular weights of 30-40,000 g/mole. It was theorized that in all cases, two phase morphologies existed based on DSC measurements, however significant lowering of the poly(styrene) Tg was evidenced with the two lower graft molecular weights.

Poly(vinyl alcohol)/poly(dimethylsiloxane) graft copolymers were prepared by the polymerization of vinyl silyl end group PSX macromonomers with vinyl acetate and the subsequent hydrolysis of the copolymers by Imai and coworkers [174]. Thus polymers with a mix of hydrophilic/ hydrophobic nature were prepared which might find many applications.

Mazurek and coworkers have presented work [172] on the preparation of poly(isobutylmethacrylate-g-PSX) intended for application as adhesive release agents. Unfortunately, the systems reported were not purified to remove free macromonomer and in fact the copolymerization conditions employed by these workers insured a macroscopic phase separation during polymerization. Thus free macromonomer or at least materials much higher in siloxane content than the average composition must have been generated. The characterization of these ill defined materials as release agents where it is well known that the highly surface active free siloxane will play a major role is questionable, at best.

Kawakami has investigated the surface properties of PMMA-g-PSX copolymers prepared from the copolymerization of PSX macromonomers [183]. Macromonomers varying in molecular weight from 3000 to 10,000 g/mole were prepared and copolymerized with methyl methacrylate. Films of these copolymers and blends with pure poly(methylmethacrylate) were then prepared and contact angle measurements taken. Surface domination of siloxane was found, even at low concentrations of siloxane. However it was found that low graft molecular weight coplymers were more efficient at dominating the surface which is opposite from expected and previously found data and very difficult to rationalize.

In a later report, copolymerizations with styrene and fluoroalkyl acrylates and methacrylates were carried out. [184] Again, blends of the PMMA-g-PSX copolymers with PMMA were initiated to show that even small amounts of siloxane in a blend tend to dominate the surface. Characterization by contact angle measurements, and ESCA were demonstrated. Oxygen permeation through polymers with siloxane branches was also studied [185-188]. Interestingly it was found that short oligosiloxane branches were more efficient in selctivity in permeation studies and also provided films with better mechanical strength. Fluoroalkyl methacrylates were not found to increase selctivity.

A method closely related to anionic polymerization known as Group Transfer Polymerization or GTP has also been used to prepare poly(methyl methacrylate) macromonomers. In this case living GTP polymerizations were terminated with vinyl benzyl bromide or tosylate, or initiation with vinylphenylketene methyl trimethylsilyl acetal were undertaken. Thus PMMA macromonomers with styryl end groups were prepared with narrow molecular weight distributions [189].

The use of cationic polymerizations to prepare macromonomers has resulted in the synthesis of poly(tetrahydrofuran), poly(isobutylene), poly(vinylether), poly(aziridines), poly(epichlorohydrin) and poly(styrene) macromonomers. Table 5 summarizes the reports in the literature on the preparation of macromonomers cationically.

Poly(tetrahydrofuran) macromonomers have been synthesized by Asami[190-191], Kreß[192], Rempp[193-194], and Takaki[195-196]. Asami has polymerized THF cationically and used functional termination with salts of methacrylic acid and p-ethenylbenzylalcohol. Characterization by UV spectroscopy indicated quantitative production of macromonomer which by GPC was of narrow molecular weight distribution. Copolymerizations of PTHF macromonomer with β-vinyl napthalene, and PS macromonomer with PTHF macromonomer were carried out [195].

Rempp and coworkers in many detailed studies have utilized a combination of functional termination as well as functional initiation [197]. They too have used the functional termination of the growing cationic chain with an α-Methyl styrene derivative that carries a benzyl alcohol functionality as well. A second method of using a

Table 5

Summary of Literature on Macromonomers Prepared Cationically

Author	Macromer	EndGroup	Comonomer	Reference
Asami	PTHF	Methacrylate(FT)	Styrene	190-1
		Styrenic (FT)	------	
Kreß	PTHF	Acrylic (FI)	------	192
Rempp	PTHF	Styrenic (FT)	------	193-4,197
		Methacrylate(FI)	------	
Takaki	PTHF	Methacrylate	Styrene	195-6
Kennedy	PIB	DCP (FI)	Ethylene-Propylene	198-209
		Methacrylate(PR)	Methylmethacrylate Styrene	
		Styrenic (FI)		
	PS	DCP	Ethylene-Propylene	199
Aoshima	PEVE	Methacrylate(FI)	Methylmethacrylate	210
Higashimura	PiBVE	Vinyl ether	i-Butylvinylether	211
Kobayashi	2-ME-2-Oxazoline	Styrenic(FI) Styrenic (FT)	Styrene	212-3
Goethals	t-butylaziridine	Methacrylic(FT)	-----	214
Yu	P(epichlorohydrin)	Allylic Acrylic	------	215

PTHF= poly(tetrahydrofuran)
PIB= poly(isobutylene)
PS= poly(styrene)
PEVE= poly(ethylvinylether)
PiBVE= poly(isobutylvinyl ether)

DCP = Dicyclopentadiene

(PR) = post reaction
(FI) = functional initiation
(FT) = functional termination

functional terminator was used as well. In the latter case, they made a cationic initiator from methacryloyl chloride and silver hexafluoroantiminate, which then can initiate the polymerization of THF. Termination of the polymerization was achieved with phenol.

Macromonomers of poly(isobutylene) have been prepared cationically by Kennedy and coworkers, using several techniques [198-209]. One method [198] used for the polymerization of styrene monomer is to use a functional initiator made from dicyclopentadienyl chloride and diethyl aluminum chloride. This cationic initiator (in the absence of chain transfer to monomer) produces chains which have a dicyclopentadienyl structure at one termini.

A second method of making macromonomers of poly(isobutylene) has been the preparation of hydroxy functional poly(isobutylenes) that are then esterified with methacryloyl chloride to prepare the methacrylate functional macromonomers. These PIB macromonomers were copolymerized with methyl methacrylate, and styrene [202-204,207,208].

Macromonomers of poly(isobutylene) are also prepared by the dehydrohalogenation of the chloro functional poly(isobutylene) prepolymers. This type of head group will under go cationic copolymerization or coordination copolymerization.

The final method of PIB synthesis that Kennedy's group has published is the use of a protected styrl initiator for isobutylene. 2-bromoethyl-p-cumyl chloride was used to initiate the polymerization of isobutylene. The polymer obtained from this is dehydrohalogenated with potassium t-butoxide to form the styrene end group.

Farona copolymerized poly(isobutylene) PIB macromonomers bearing dicyclopentadienyl end groups, with ethylene and propylene to prepare EPM-g-PIB copolymers.

Styrene can be polymerized cationically as well as anionically and thus Farona was able to initiate styrene monomer with dicyclopentadienyl chloride and diethyl aluminum chloride [199]. Styrene macromonomers with the dicyclopentadienyl end groups were copolymerized with ethylene and propylene to prepare EPM-g-PS terpolymers. The properties of this material having a rubbery backbone and hard branches were not reported however they would be expected to be of thermoplastic elastomeric structures if controlled properly.

An extension of the cationic polymerization of PIB to the block copolymerization PIB-b-α-methylstyrene was also reported [209]. In this report the PIB block with chloro end functionality was used to initiate polymerization of α-methyl styrene. Functionalization was accomplished by functional initiation.

Poly(vinyl ether) macromonomers have also been prepared cationically thru functional initiation and functional termination. Aoshima [210] has used the functional initiator formed by addition of 2-vinyloxyethyl methacrylate with hydrogen iodide to prepare poly(ethyl vinyl ether) macromonomers. These macromonomers were then homopolymerized and copolymerized with methyl methacrylate.

Higashimura[211] has functionally terminated the living cationic polymerization of vinyl ethers with the sodium salt of diethyl 2-vinyloxyethylmalonate to prepare vinyl ether end groups on his poly(vinyl ether) macromonomers. Macromonomers consisted of isobutylvinyl ether or benzoyloxyethyl vinyl ether polymers. It was shown that the macromonomers would copolymerize cationically with isobutylvinyl ether as well.

Kobayashi [212-213] has investigated the cationic polymerization of 2-methyl-2-oxazoline using both functional initiation and termination to provide macromonomers. His functional initiator consists of the halogenation reaction product of p-methyl styrene and iodine which will initiate oxazoline polymerization. The functional termination of oxazoline polymerizations with the amine functionality of 2-(N-2-Aminoethyl-N-methyl)aminoethylstyrene yields an oxazoline macromonomer with a styrenic end group.

Poly(epichlorohydrin) macromonomers were prepared by Yu via the cationic polymerization of epichlorohydrin with allyl alcohol or 2-hydroxyethyl acrylate, with Et_3OPF_6 under non-living conditions [215]. The macromonomers thus prepared have allyl or terminal functionality when terminated with allyl alcohol or acrylic terminal functionality when terminated with 2-hydroxyethyl acrylate.

The synthesis of macromonomers by a free radical process has also been reported in the synthesis of a few polymers which are largely unavailable by other techniques, as summarized in Table 6. The synthesis of a macromonomer by a free radical polymerization results in one less degree of control of the polymer structure than was obtained by the anionic or cationic synthesis. Either of the living techniques can lead to polymers of well defined molecular weight and molecular weight distribution, while free radical synthesis reults in a broader molecular weight distribution.

Another complicating feature of free radical polymerization is the method of chain termination. Chains can terminate by radical combination or disproportionation. In methods with large amounts of chain transfer agent this is less of a problem, however chain coupling by combination can lead to difunctional materials

Table 6

Summary of Literature on Free Radical Macromonomer Synthesis

Author	Macromonomer	End Group	Comonomer	Reference
Yamashita	P(styrene)	Methacrylate	2-HEMA	216
			MMA/2-HEMA	
Boutevin	Dodecylacrylate	Methacrylate	Acrylamide	217
Cacioli	PMMA	Methacrylate	Methylmethacrylate	218
			Ethylacrylate	
			Styrene	
			Vinyl Acetate	
			Acrylonitrile	
Yamashita	PMMA	Diol	Diisocyanate	219-21
	PMMA	Diacid	Diamine	
	PMMA	Methacrylate	DimethylammoniumMA	
	P(2-HEMA)	Diol	Diacid	
Ito	Sterayl MA	Methacrylate	Methylmethacrylate	222
Kawakami	P(2-HEMA)	Methacrylate	------	223
Nakashima	PMMA	Methacrylate	2-HEMA	224
Niwa	PMMA	Methacrylate	Styrene	225-6
		Styrenic/ MA	Methylmethacrylate	
Yamashita	PMMA	Methacrylate	Fluoromethacrylates	227-9
Boutevin	PVC, PVCl2	Acrylic	Acrylics	230-1

which are then capable of crosslinking the system. Radical disproportionation can lead to non-functional materials depending on the method being used.

Macromonomers of styrene, methacrylates, acrylates, vinyl pyrrolidone, and vinyl chloride and vinylidene chloride have been reportedly prepared free radically.

Yamashita [216] has investigated the synthesis of polystyrene macromonomers free radically by functionalizing the styrene chains with monoiodoacetic acid as a chain transfer agent. They were then able to react the terminal carboxylic acid structures with glycidyl methacrylate to produce polystyrene macromonomers with a terminal methacrylate functionality. Macromonomers were then copolymerized with 2-hydroxyethylmethacrylate (HEMA) or mixtures of HEMA with methyl methacrylate.

Boutevin polymerized dodecylacrylate in the presence of 2-mercaptoethanol which chain transfers to produce alcohol functional acrylate chains. The latter were then esterified with methacryloyl chloride to prepare methacrylate functional macromonomers which were then copolymerized with acrylamide [217].

Cacioli investigated the macromonomers formed during the polymerization of methylmethacrylate by the disproportionation of the growing methylmethacrylate radicals [218]. The unsaturated sites formed were shown to then under go further copolymerization with other monomers such as acrylonitrile. More importantly, however is the anticipated copolymerization of these macromonomers formed early on in a free radical reaction of MMA with chains growing later, which could lead to branching in PMMA. Fortunately, at high molecular weights this end group effect is small but should be a consideration at some point in the characterization of free radically prepared PMMA.

Chujo and Yamashita designed a difunctional alcohol at the termini of poly(methylmethacrylate) and poly(dimethylammonium ethyl methacrylate) through the use of the chain transfer agent α-thioglycerol [219-221].

PMMA macromonomers with dihydroxy end groups were copolymerized in a step growth reaction with 1,4-butanediol and 1,6-hexamethylene diisocyanate to produce polyurethane-g-PMMA.

Poly(methyl methacrylate) macromonomers with difunctional carboxylic acid functionalities were also prepared and copolymerized to prepare polyamide-g-poly(methyl methacrylate) copolymers. Thiomalic acid was used as a chain transfer agent for the free radical polymerization of methyl methacrylate producing a difunctional carboxylic acid end group. The macromonomers were then copolymerized with sebacic acid and diamines such as p,p'-diaminodiphenyl ether, p,p'-diaminodiphenylmethane, or m-phenylenediamine to produce the polyamide-g-poly(methyl methacrylate) copolymers. This was the first example of condensation reactions of macromonomers.

Chujo has also prepared poly(methyl methacrylate)-g-poly(dimethylethyl ammonium methyl methacrylate) and poly(dimethylethyl ammonium methyl methacrylate)-g-poly(methyl methacrylate) copolymers. Macromonomers were prepared by radical polymerization of a monomer in the presence of thioglycolic acid, affording carboxylic acid functional oligomers which were then capped with glycidyl methacrylate.

The solution properties of copolymers of similar composition were then investigated to elucidate the effect of structure on properties. Acetone/water mixtures were used since PMMA is hydrophobic. It was found that copolymers with PMMA backbones formed more "rigid" micelles than if the PMMA were present as a graft. Again, evidence was obtained by NMR analysis on the soluble portion.

Ito and Yamashita used thioglycolic acid as a chain transfer agent for the polymerization of stearyl methacrylate and reaction of the carboxy functional oligomers with glycidyl methacrylate to prepare the macromonomers [222]. Poly(methyl methacrylate)-g-poly(stearyl methacrylate) were synthesized and characterized by inverse gas chromatography. Inverse gas chromatography provides an indication of the surface and bulk properties of a copolymer.

Kawakami terminated poly(2-hydroxyethyl methacrylate) with a carboxy end group by using a chain transfer agent which was then reacted with a methacrylate functional isourea derivative to form a methacrylate end group [223].

Nakashima used the redox system of Fe/H2O2 to prepare poly(methyl methacrylate) macromonoers with hydroxy termination [224]. These oligomers were then esterfified with methacryoyl chloride to produce PMMA macromonomers. PMMA macromonomers were then copolymerized with 2-hydroxyethyl methacrylate. These copolymers exhibited interesting thromboresistance and improved mechanical properties over PHEMA homopolymers.

Methacrylate macromonomers have also been prepared by Niwa and coworkers [225-226]. Poly(methyl methacrylate) and poly(2-acetoxyethyl methacrylate) prepolymers were prepared by free radical polymerization in the presence of thioglycolic acid chain transfer agent. These carboxylic acid functional prepolymers were then functionalized by reaction with either glycidyl methacrylate or 1-ethenyl-4-oxiranylmethoxybenzene to produce methacrylate or styryl end groups, respectively.

Yamashita and Kawakami published several reports detailing their work on the synthesis of poly(methyl methacrylate) in the presence of thioglycolic acid which acts as a chain transfer agent [227-229]. The polymer chains then have carboxylic acid functionality at their termini which may be reacted with glycidyl methacrylate to produce methacrylate end groups. High functionality was demonstrated. In a second paper, copolymerization kinetics were determined.

These macromonomers were then copolymerized with perfluoroalkyl methacrylates and methyl methacrylate mixtures and the surface properties of copolymers and blends were investigated. Contact angle analysis with water showed that small amounts of the graft copolymer would modify the surface of blend films to repel water, indicating that the low surface energy fluoroalkyl methacrylates were dominating the surface, even when present in low levels in the bulk. Copolymers were also prepared with 2-hydroxyethyl methacrylate and methyl methacrylate mixtures, and fluoroalkyl methacrylates and 2-hydroxyethyl methacrylate mixtures. Again, contact angle studies were undertaken on films cast from THF onto glass. They were able to show a difference between glass and air sides, which was interpreted on the basis of surface accumulations during evaporation.

Boutevin prepared poly(vinyl chloride) and poly(vinylidene chloride) macromonomers by free radical polymerizations. Poly(vinylidene chloride) macromonomers were prepared from vinylidene chloride and carbon tertachloride, followed by post reaction with allyl acetate, hydrolysis to the alcohol, then esterification with acryloyl chloride [230-231].

Poly(vinyl chloride) macromonomers were prepared by free radical polymerization in the presence of thioglycolic acid or 2-mercaptoethanol. Reactions with acrylic acid, vinyl chloroformate, methacryloyl chloride, or 2,3-epoxypropyl methacrylate then lead to the desired macromonomers.

Styrene terminated poly(vinyl pyrrolidone) macromonomers were synthesized and copolymerized by Akashi and coworkers. Polymerizations of vinyl pyrrolidone were carried out in the presence of ß-mercaptopropionic acid chain transfer agent which leads to oligomers with carboxylic end groups. These prepolymers were then reacted with p-vinyl benzyl chloride to yield styryl end groups. [232]

Several reports have been published on the synthesis of macromonomers based on the mechanical scission of poly(styrene) or poly(methyl methacrylate) in the presence of an "end capper" such as diallylmalonic acid diethyl ester. This produces macromonomers of ill-defined nature and the polymerization of them has been described as producing "palm tree" like copolymers [233-235].

Several macromonomers have been reported to have been prepared by condensation methods, as summarized in Table 7. As with free radical polymerization, this method does have broad molecular weight distributions as compared to the living polymerization methods. By the nature of condensation methods however the materials are difunctional, and the preparation of monofunctional macromonomers is therefore complicated. The potential reward is the availability of macromonomers with structures and properties unobtainable by vinyl polymerization methods.

Macromonomers of poly(amines), poly(esters), poly(urethanes), and poly(aromatic ether sulfones) have been reported.

Goethals[214], Maeda and Inoue[236-237], and Tsuruta [238-243] have reported recently on the preparation of poly(amine) macromonomers by the lithium diisopropylamide catalyzed condensation of divinyl benzene with various diamines. Many possibilities of system properties exist as some diamines such as piperazine yield crystaline macromonomers. Copolymers were prepared of these amine

Table 7

Summary of Literature Reports on Condensation Synthesis of Macromonomers

Author	Macromonomer	EndGroup	Comonomer(s)	Reference
Goethals	P(amine)	Styrenic	Styrene	214
Inoue	P(amine)	Styrenic	Styrene Methylmethacrylate	236-7
Tsuruta	P(amine)	Styrenic	Styrene 2-Hydroxyethylmethacrylate	238-243
Hudecek	P(urethane)	Methacrylate	2-HEMA	247-8
Percec	P(ether sulfones)	Methacrylate	------	249-53
		Styrenic	------	
	P(2,6-dimethyl-1,4-phenyleneoxide)			
Kobayashi	P(amide)	Styrenic	------	254
	P(saccharides)	Styrenic	------	

macromonomers and styrene and characterized for their biomedical behavior. Morphology of the copolymers was shown to affect the mode of interaction with blood cells.

This work seems to follow reports over the past several years by Maeda and Tsuruta on the synthesis of new monomers synthesized by the same mechanism [244-246]. Apparently, the work would seem to be a natural extension of small molecule chemistry.

Maeda and Inoue have also reported on the preparation of poly(amino acid) macromonomers and their copolymerization with vinyl monomers. Macromonomers of Benzyl-L-glutamate-N-carboxyanhydride were prepared bearing styryl type end groups. Graft copolymers were prepared by radical copolymerizations with styrene and methyl methacrylate. The application of these type of materials to biomedical uses was suggested.

A second publication on similar copolymers detailed a second method of preparation. A copolymer of styrene and an amine functional styrene monomer was synthesized, and the polymerization of the amino acid initiated from the amine functionalities present on the backbone of the copolymer. N-carboxy amino acid anhydrides of L-alanine, benzyl-L-glutamate, or β-benzyl-L-aspartate were polymerized as grafts from the styrenic backbone to prepare the graft copolymers.

Hudecek has authored papers on the preparation of both poly(urethane) and poly(ester) macromonomers [247-248]. Copolymers prepared from the polymerization of 2-hydroxyethylmethacrylate and a polyurethane macromonomer were reported. NMR analysis of the copolymerization was followed to determine the kinetics of macromonomer incorporation.

Percec has published on the preparation of poly(aromatic ether sulfones) and poly(2,6-dimethyl-1,4-phenylene oxide) macromonomers [249-253]. Poly(aromatic ether sulfones reportedly bearing only one hydroxy group were prepared. Unfortunately the possibility of trans etherification was ignored however, and characterization indicating one hydroxy group per chain on the average was assumed to mean one per chain as an absolute value and is probably invalid. Poly(2,6-dimethyl-1,4-phenylene oxide) macromonomers were also prepared and in this case characterized to show one end group per molecule on the average, as expected. Copolymerizations with p-biphenyl acrylate or triethylene glycol p'-methoxy-p-biphenylyl ether methacrylate producing a graft copolymer with liquid crystaline backbone and amorphous grafts.

Copolymerization of the poly(2,6-dimethyl-1,4-phenylene oxide) macromonomer with methacrylate end group with p-vinylbenzyl methacrylate or terpolymerizations with methyl methacrylate via the group transfer polymerization mechanism were also carried out.

We have thus far seen the preparation and copolymerization of a wide range of macromonomer structures with an equally wide range of comonomers. The choice of structures and understanding of the ramifications of structure-property ralationships is very important. We therefore move on to a discussion of the history and properties of siloxanes, methacrylates, and styrenes which are the principal subject of this thesis.

II. B. SILOXANE POLYMERS

1. Introduction

Siloxane chemistry dates back to the early 1900's when Kipping investigated the synthesis of many organo silanes and oligomeric siloxanes. Many investigations of the reactivity of chlorosilanes towards hydrolysis have demonstrated the formation of cyclic or linear siloxane chains upon condensation of the intermediate silanols. Earlier investigators probably prepared similar materials, but misidentified them as ketone like structures [255].

Interest was regained in siloxane chemistry in the mid 1930's when Corning Glass Company, and General Electric Company began joint research and commercialization efforts. High molecular weight polymers were desired that would provide unusual properties relative to the materials then available. It is interesting that siloxanes are the only polymers prepared from mineral origin.

2. Cyclic Monomers

Cyclic monomers are typically prepared from the hydrolysis and condensation of chlorosilanes. The "direct process" of preparation of chlorosilanes from silicon and aliphatic or aromatic halides is as follows:

$$1) \quad Si + 2\,RCl \xrightarrow{\text{catalyst}} R_2SiCl_2$$

However,in pratice species of the general formula R_xSiCl_{4-x} are produced by interchange reactions. Reaction conditions have been developed to maximize the desired products. Hydrolysis of the dichlorosilanes to the silanols followed by condensation, then leads to mixtures of cyclics and linear oligomeric species. As can be imagined, varying the R group structure and mixing various types of R groups, can lead to a wide variety of properties. Process and product control is an ongoing research effort worldwide.

Work in the 1940's, by Rochow and Gilliam [256], led to the synthesis of methyl and phenyl chlorosilanes by the direct process. Higher alkyl chlorides react with silicon to form many by products as well as the desired dialkyldichlorosilanes. Catalysts such as copper and silver are used in the 250°- 500°C range. Free radical mechanisms are assumed to play a role in the synthetic scheme.

Other alkyl groups can be introduced by either Grignard reactions of alkylmagnesium halides with any of the chlorosilanes or by hydrosilylation of hydrosilanes with olefins. Also organo alkalis based on lithium, sodium, or potassium can be reacted with chlorosilanes to produce alkylchlorosilanes.

3. Polymer Synthesis and Characteristics

As mentioned polymerizations can be conducted directly from the hydrolysis and condensation of dichlorosilanes, or alternatively, either anionic or cationic initiation of the cyclic monomers produced from the hydrolysis of the dichlorosilanes can be pursued. Base and acid catalyzed ring opening polymerizations allow more control of polymer structure, and also permit different types of end group functionalization. Catalysts can be chosen to protect functional sites present in some monomers.

Reactions of dichlorodimethyl silane with water produce about a 50/50 mixture of cyclics and linear chains. Both cyclics and linear species are mixtures with a broad range of molecular weights. The relative ratios of products are strongly dependent on the nature of the solvents, and their concentration. Solvents for both the water and the siloxanes increases yields of siloxane cyclic polymers while water insoluble solvents increases the yield of small cyclics. Low temperatures also increase the yield of cyclics. Strong acids tend to increase the condensation reaction while silanols are stable in neutral solutions.

Addition of chain stoppers, such as trimethyl chlorosilane, changes the reaction significantly by terminating many active chains, thus decreasing the percentage of cyclics.

The formation of hydrochloric acid, from the hydrolysis of the chlorosilanes with water can and often does cause reequilibrations by a cationic method. Acid-catalyzed polymerizations can also be used to polymerize cyclics through the addition of an acid, such as sulfuric acid.

Base-catalyzed polymerizations are also used to polymerize cyclics to poly(siloxanes). The two mechanisms share many similarities: such as attack of the catalyst on either silicon or oxygen to ring open a cyclic monomer. An active species is thus formed which may attack either more monomer, or the backbone silicon-oxygen-silicon bond itself. Attack on a backbone forms a chain with much higher degree of polymerization (either cyclic or linear) and starts a new chain growing. This attack on the backbone leads to these reactions which are known as "equilibration" reactions, since backbiting of a reactive species to its own chain leads to cyclic formation. Typically about ten weight percent of the product of an equilibration polymerization might be cyclics with the remainder being linear polymeric species displaying a Gaussian molecular weight distribution.

Base catalyzed polymerizations proceed via pentavalent intermediate siloxanolate active species which are generated via attack on silicon. The mechanism of acid catalyzed polymerizations is less well understood, although widely practiced.

Basic catalysts utilized include potassium, sodium, rubidium, and cesium hydroxides, as well as "transient catalysts", such as tetravalent ammonium salts. The latter are known as transient since they degrade above a certain temperature to yield an inactive amine and an alkyl halide. Thus, the catalyst is no longer present and needs no special attention to remove it. This is unlike the alkali metal siloxanolates, which must be removed to prevent further equilibration with time.

Polymerization of the cyclic tertramer siloxane monomers appears to be driven by entropy with no enthalpy of polymerization. However lower cyclics such as D_3, and possibly higher cyclics such as those above D_6 are more strained than cyclics such as D_4, and are reportedly slightly exothermic. D_4 is the most common cyclic formed, probably because it is the most thermodynamically stable and most economically accessible.

Base catalyzed polymerizations are also affected by the nature of solvents. For example etheral solvents dissociate the siloxanolate ion pair and increase the rate of polymerization. An adverse affect of solvents (as a function of the their concentration) is that the amount of cyclics formed at equilibrium is increased. This fact can be used to advantage when preparation of the cyclics is desired.

Siloxanes have many interesting physical properties, which can often be related back to atomic structure. The silicon-oxygen bond length is about 1.64 Å, as compared to 1.83 Å for the sum of the silicon and oxygen atomic radii. Part of this might be explained on the basis of the silicon-oxygen bond polarization, since calculations have shown this bond to be about 50% ionic, on the Pauling scale. Back bonding between oxygen p orbitals and silicon d orbitals is indicated by several other properties such as bond angles, and acid-base properties.

The ease of rotation around the silicon- carbon and silicon-oxygen bonds explains the low glass transition temperatures of many of the polysiloxanes.

Surface tension of poly(dimethyl siloxane) is on the order of 19 dyn/cm., which is much lower than most conventional polymers and is attributable to weak intermolecular forces present in poly(dimethyl siloxane). This low surface energy allows siloxanes to spread on most surfaces, while repelling most liquids (including water) from their surface. The low surface energy also gives rise to a lubricating effect, since other materials will not stick to the siloxane surface. Many reviews and investigations have appeared on the surface properties of siloxane containing materials [257,258].

One important finding has been that surface domination of siloxane can be obtained even when the bulk composition of siloxane is 0.1 weight percent and less. Thus blending a homopolymer with its siloxane block or graft copolymer typically results in surface domination by siloxane, even when only very small amounts of siloxane are incorporated overall. The copolymer method is preferable to blending pure siloxane into the homopolymer because the organic segment anchors the siloxane into the blend. Thus, the copolymer blending method produces more stable blends and is less subject to siloxane "leaching". The type of copolymers blended may influence the surface morphology, due to restrictions on siloxane chain mobility [257-266].

Some other important properties include UV transparency and stability, biocompatability and high temperature stability.

Siloxanes are also known to have high oxygen permeabilities. High gas permeability is probably due to the large free volume present in a structure where chain flexibility keeps chains at a distance from each other. Solubility of the gas also plays a role in gas permeation through rubbers.

Siloxanes are quite thermally stable, but when exposed to high temperatures, atomic oxygen or oxygen plasmas, are observed to degrade to organosilicates, and eventually silicon dioxide. Silicon dioxide forms a barrier layer on the surface of the polymer which may often protect the bulk from further degradation. This is important in the aerospace industry where exposure to atomic oxygen, in outer space, quickly degrades organic adhesives. Copolymers with siloxanes can protect the surface and thus retard degradation. Lithographic applications also come to mind since oxygen ion etch development of designs requires the formation of a barrier layer of a non-volatile metal oxide. This works especially well with poly(siloxanes) since they tend to be at the surface, due to their low surface energy.

Siloxanes are very sensitive to e-beams or x-rays and are cross linked by these hig energy sources. This fact may be used to develop negative resists from siloxane copolymers. Many reviews have been published on the radiation sensitivity of poly(siloxanes) [267-270]. Investigations of the substituent effects have also been important. For example this has led to the knowledge that small amounts of phenyl substituted siloxanes can stabilize dimethyl siloxanes [271-275]. One characteristic of the dimethyl siloxanes is their low glass transition temperatures which may be increased by incorporation of diphenyl siloxanes.

Work with copolymers where the second polymer has a Tg above room temperature allows the glassy matrix to minimize flow [276]. In lithography, it has been found that about nine weight percent silicon is needed in the matrix to provide ion etch resistance by formation of the SiO_2 layer. This corresponds to about 27 weight percent poly(dimethyl siloxane) in a copolymer. Depending on composition and radiation source the lithographic properties of the second polymer or those of the siloxane may predominate. This is advantageous when the second polymer also works as a negative resist. Chlorostyrene block copolymers with siloxanes are an example, since the crosslink density will be even higher. However when the second polymer is positive working, such as with poly(methyl methacrylate) the two mechanisms could be working against each other, depending on the energy source.

4. Anionic Polymerization

Lithium siloxanolates form such a tight ion pair that polymerization does not easily proceed for any monomer except D_3. Even for the polymerization of D_3, propagation does not proceed without addition of a promoting solvent, such as THF.

Fessler [277], and Frye [278] studied the reactivity of alkyl lithiums with siloxanes and the subsequent reactivities of the siloxanolates in solvated and unsolvated media. Under the proper conditions, the preparation of well defined poly(siloxanes) with narrow molecular weight distributions, was possible. With the correct solvent conditions, the reactivity of the ion pair of the lithium siloxanolates can be such that attack on the backbone is prohibited while attack on the very strained cyclic structure of D_3 is allowed. In this way reequilibrations do not occur and a well defined anionic polymerization proceeds leading to controlled molecular weights, narrow molecular weight distributions, and functional termination at one or both ends depending on initiation method. This is in contrast with equilibration techniques which produce only difunctional species and Gaussian molecular weight distributions.

Other workers have also studied the polymerization and copolymerizations of various cyclic siloxane monomers [279-282].

5. Block Copolymerizations

Block copolymerizations can be undertaken through the initiation of D_3 with a polymeric lithium species instead of butyl lithium directly. Again, propagation proceeds only upon addition of a promoting solvent, such as THF. Many reports have appeared in the literature over the past twenty years on this subject.

Polymers with elastomeric properties similar to styrene-butadiene-styrene triblock copolymers were desired since diene coopolymers have undesirable side reactions, such as degradation of the unsaturated linkages. Aging of these elastomers, therfore, leads to either brittleness with crosslinking, or softening with chain scission reactions. The surface properties of siloxane containing copolymers are also of interest.

Triblock copolymers of styrene-siloxane were synthesized by many workers [283-290], via the anionic polymerization of D_3 initiated from the polystyryl lithium chain ends. Crossover to the siloxanolate proceeds quantitatively, However the siloxanolate anion is too weak to reinitiate styrene. Therefore to form a triblock copolymer, coupling of two growing siloxanolate anions with dichlorodimethyl silane is carried out. The economics and mechanical properties of copolymers prepared in this manner were not sufficient for commercialization.

Styrene-siloxane alternating block copolymers, where the block molecular weights were much lower also provide elastomeric properties and are of interest. Difunctional initiators are used to initiate styrene, which after complete propagation then initiates the siloxane monomer. The difunctional chains are coupled with dichlorodimethyl silane or some other dichlorosilane, to form the alternating copolymer. Blocks of approximately 10,000 g/mole are used with at least 20 repeat units of AB structure to get optimum properties [291-292].

Another innovative synthetic scheme has appeared recently from the General Electric Labs by Crivello and coworkers. A free radical mechanism was used to initiate the polymerization of styrene and other monomers from linkages between blocks of poly(dimethylsiloxane). An alternating copolymer structure of styrene-siloxane blocks was thus proposed. However, further characterization has shown the structure to be of much higher molecular weights than previously believed [293-295].

The chemistry is based on the decomposition of pinacolates or carbon-carbon bonds with tetra phenyl substitution. These linkages are introduced into siloxane chains by end capping oligomeric siloxanes with Si-H functionalities and hydrosilylation to the pinacolate containing moieties. Thus polymers are prepared with pinacolate functionalities between siloxane segments.

Degradation of these pinacolates in the presence of styrene or other monomers, should then lead to alternating styrene-siloxane copolymers. Linkages formed after propagation and recombination of the radicals with styrene monomer still have three phenyl substituents and will reinitiate. Unequal reactivity, however, seems to lead to a small number of very large styrene blocks. Therfore many siloxane segments are separated by little more than the pinacolate functionalities. Still copolymers with good mechanical properties were reported.

II. C. POLY(ALKYL METHACRYLATES)

1. Introduction

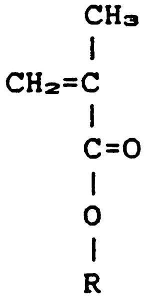
Methacrylate polymers have long been valuable, since they have a wide range of properties and applications, depending on structure. Copolymers with controllable properties can be prepared from a large number of acrylic monomers and also from copolymerization with other vinyl monomers. Polymers ranging from tough, rigid film forming plastics to soft, adhesives are possible [296-298].

Otto Rohm's doctoral thesis in 1901 was the first work published on methacrylates. He studied the synthesis and characterization of polymers derived from methyl methacrylate. Later he and a partner formed the company Rohm and Haas. One of the early applications was safety glass sheets, and during World War II, cockpit canopies on fighter planes. Methacrylate polymers today find uses in plastics, constant viscosity oil additives, adhesives, sealants, floor polishes, and surface coatings.

2. Monomers

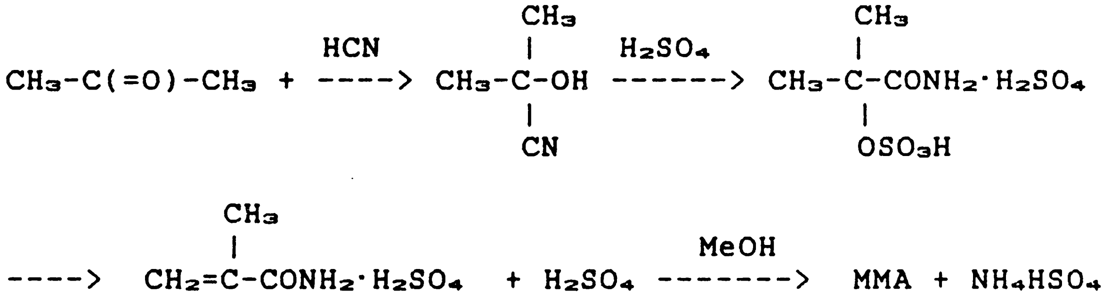
There are several routes to the preparation of methacrylate monomers, primary routes starting from petrochemicals, and secondary processes involving conversions of the methacrylic functionality. Methacrylates are α,ß-unsaturated esters of the general structure in equation 2. These secondary processes are used largely for laboratory scale preparation of specialty monomers while commercially the primary route is used.

2)



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

The primary route presently has two major schemes which are used. Historically the most used route for methyl methacrylate synthesis is known as the acetone cyanohydrin route, and is shown in Scheme I. Acetone is reacted with HCN to form a cyano alcohol, which is then reacted with 98% sulfuric acid, to give the methacrylamide sulfate salt. This salt is then reacted with an alcohol to form the corresponding methacrylate ester. The monomers are then fractionally distilled removing most of the water and alcohol impurities.

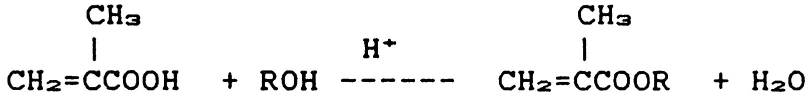


$$CH_3\text{-}C(=O)\text{-}CH_3 + \xrightarrow{HCN} CH_3\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}OH \xrightarrow{H_2SO_4} CH_3\text{-}\overset{CH_3}{\underset{OSO_3H}{C}}\text{-}CONH_2\cdot H_2SO_4$$

$$\longrightarrow CH_2{=}\overset{CH_3}{C}\text{-}CONH_2\cdot H_2SO_4 + H_2SO_4 \xrightarrow{MeOH} MMA + NH_4HSO_4$$

Scheme I. HCN Process MMA Synthesis

A second method is sometimes used to avoid the problems of waste created in the first method. This route involves the catalytic oxidation of isobutylene to methacrylic acid. Esterification of methacrylic acid with the appropriate alcohol again yields the desired methacrylate ester, as indicated in Scheme II. Catalyst developments now allow yields of over 90% based on isobutylene by this method with 99% purity of product.

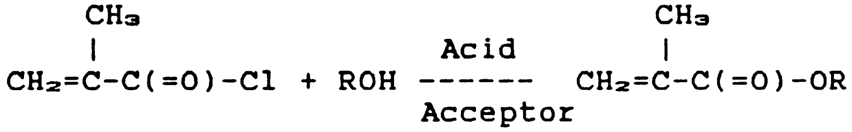


$$\mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}COOH + ROH \xrightarrow{H^+} CH_2{=}\overset{\overset{CH_3}{|}}{C}COOR + H_2O}$$

Scheme II. Synthesis of Methacrylates Via Esterification of Methacrylic Acid

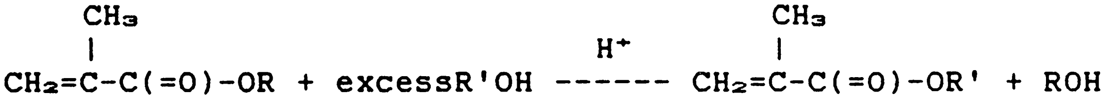
Dow has developed a process based on the reaction of vinyl halides such as 2-bromopropene with carbon monoxide and an organic carbonate such as dimethyl carbonate [299].

Secondary routes involve esterification of an excess of the desired alcohol with methacrylic acid or methacryloyl chloride or transesterification with methyl methacrylate, by acid catalysts, as follows in Schemes III and IV.



$$\mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}C({=}O){-}Cl + ROH \xrightarrow[Acceptor]{Acid} CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}C({=}O){-}OR}$$

Scheme III. Synthesis of Alkyl Methacrylates Via Reaction of Alcohols with Methacryloyl Chloride



$$\mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}C({=}O){-}OR + excess R'OH \xrightarrow{H^+} CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}C({=}O){-}OR' + ROH}$$

Scheme IV. Ester Interchange Synthesis of Alkyl Methacrylates

Tertiary alcohols tend to dehydrate under strongly acid conditions. Thus, monomers such as t-butyl methacrylate are most often prepared from methacryloyl chloride and t-butanol with a tertiary amine acid acceptor.

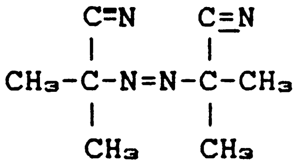
In any of these routes driving the reaction to the right involves removing the produced water or alcohol. Purification of the methacrylate ester is complicated by the fact that most alcohols have boiling points very similar to their methacrylic ester. Also azetropes often form between the alcohol and methacrylate ester [300].

3. Polymer Synthesis and Characterization

Alkyl methacrylates are most widely polymerized via free radical mechanisms to high conversions and high molecular weights. Reactivities of the various methacrylate monomers and other vinyl monomers allows preparation of fairly random, short-sequenced homogeneous copolymers. Copolymers of various methacrylates, acrylates, methacrylic and acrylic acids and styrenic monomers are possible [301].

Azo initiators are commonly used due to their high efficiency and lack of oxidation reactions that can cause yellowing of the resultant polymers with aging [302]. Azoisobutyronitrile or AIBN is the most important example of these initiators and has the structure shown in equation 3. Commercially, one important trade-name is VAZO-64 (DuPont). The 64 refers to the fact that it has a 10 hour half life at 64°C.

3)



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

AIBN

Block copolymers have been reportedly prepared under free radical conditions, especially if relatively high viscosity enhances the lifetime of the radicals. Under these conditions addition of a second monomer results in at least partial growth of the second block [303].

A more controlled mechanism of polymerization utilizes the anionic homo- and copolymerization of methacrylates [304]. Under the proper conditions, polymer molecular weight, molecular weight distribution, stereochemistry, and end group functionality can be controlled. The possibility of block copolymer formation exists if the enolate anion maintain thier chain end stability.

Anionic polymerization investigations over the last several years have pointed to a number of requirements for the living polymerization of methylmethacrylate [305-313].

One requirement is that it must be conducted in an etheral solvent, such as THF at low temperatures (<-65°C) and preferably lower. Above -65°C side reactions of attack on the carbonyl group occur. Clealy exotherms during the polymerization can easily elevate the reaction temperature above this critical value of -65°C. For this reason, slow addition of highly purified monomer, at -78°C, has been recommended. However, addition of monomer to a living polymerization must be carefully controlled to obtain controlled molecular weights and narrow molecular weight distributions. Monomer purity is crucial to avoid killing active chain ends. Allen and coworkers in our laboratories developed the method of distillation from trialkyl aluminums to remove all traces of impurities. Classical techniques such as Calcium hydride do not remove alcohols [314-318]. If one achieves a living anionic polymerization of alkyl methacrylates, simple termination with a protonic source yields a relatively stable saturated polymer end group.

Classically PMMA GPC standards have been prepared by the addition of an anionic initiator to a mixture of methyl methacrylate in solution. A portion of the initiator is consumed by impurities, but the remaining initiator produces polymer of narrow molecular weight distribution.

A clean and controllable polymerization also requires the use of an initiator which minimizes side reactions, on the carbonyl group. Investigations by Rempp et. al. have shown that the adduct of s-BuLi and 1,1-diphenylethylene or diphenylhexyl lithium works well at -78°C. The bulkiness and lowered basicity of this carbanion allows it to initiate anionic polymerization with no measurable carbonyl attack [311].

The use of diphenyl ethylene has also been extended to the synthesis of styrenic- methacrylate block copolymers. Living poly(styryl lithium) also attacks the carbonyl MMA monomer. However, by first end capping the styryl lithium chain end with diphenyl ethylene, this new anion was shown to cleanly initiate polymerization of MMA at -78°C, which permitted the formation of pure diblock copolymers.

Poly(alkyl methacrylate) properties are dependent on the structure of the ester-alkyl group and tacticity. Polymer glass transition temperatures generally decrease with increasing linear ester group length. This trend is explained by free volume arguments and intermolecular forces. Branching raises the glass transition temperature which is explained by intramolecular forces, and the energy barrier to carbon- carbon bond rotation in the backbone. Tacticity effects also play a role in determining glass transition temperature, for alpha methyl substituted macromolecules [319].

Table 8 lists glass transition temperatures for a series of alkyl methacrylates as a function of tacticity. Typical glass transition temperatures in the literature are for atactic materials although tacticity may change even as a function of reaction temperature. For example moderately high syndiotactic PMMA has a Tg of 115-120°C, but PMMA synthesized anionically in THF at -78°C has a Tg of 130°C with approximately 80% syndiotacticity. Purely syndiotactic PMMA has been calculated to have a Tg of perhaps 160°C [320]. Isotactic PMMA has been reported to have a Tg of as low as 43°C depending on the method of preparation and therefore isotactic content [321]. The average Tg difference between syndiotactic and isotactic poly(alkyl methacrylates) has been reported to be 50-60°C [322].

Literature data for any given "stereochemistry" is not representative of pure "100 %" sterochemistry. For example, syndiotactic data is often reported for materials prepared in THF at -78°C, while atactic is reported for materials made free radically. Isotactic materials are those made in toluene anionically.

However, none of these materials is of a pure tacticity. For example atactic t-butyl methacrylate has a

Table 8

Glass Transition Temperatures (°C) of Poly(alkyl methacrylate)'s

ESTER	ISO	ATACTIC	SYNDIO
Methyl	44	105	105
Ethyl	12	65	66
n-Propyl		35	
i-Propyl	27	81	85
n-Butyl	-24	20	
i-Butyl	8	53	
s-Butyl		60	
t-Butyl	7	118	114

higher Tg than syndiotactic t-butyl methacrylate, and tacticity measurements confirm that the free radical material is of higher syndiotacticity than the anionic material.

While most ester polymers show instability to acids or bases, the steric hinderance of the ester group (R3C-COOR) makes PMMA resistant to hydrolysis. PMMA is also resistant to hydrocarbon solvents, but is soluble in many polar solvents.

An interesting property of poly(methyl methacrylate) is its miscibility with poly(vinyl chloride), poly(vinyl fluoride) and poly(vinylidene fluoride). Miscibility is however only true for the syndiotactic and atactic forms, since the isotactic PMMA is immiscible. Blends are also only miscible over relatively narrow ranges of composition. PVC/ PMMA blends for instance are miscible only up to 50 weight percent PMMA. Above this level of PMMA, the blend consists of the 50/50 phase in equlibrium with a pure PMMA phase [323-325].

Miscible blends allow the mixing of properties of the two systems without the preparation of statistical copolymers. Blending of block or graft copolymers with one phase "anchoring" allows for even more benefits since this allows the incorporation of a third polymer into the blend that would not be compatible on its own [326].

Many review papers have dealt with the theory of miscible and immiscible polymer blends [327-329].

4. Degradation Behavior and Applications

PMMA depolymerizes above 300°C to monomer, producing greater than 95% yields of MMA. This approach has been used to reclaim PMMA scrap monomer again.

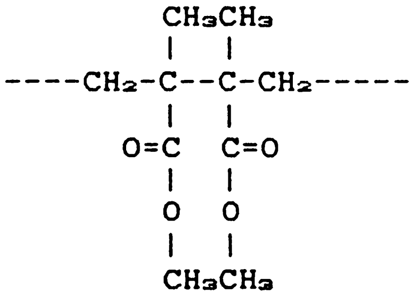
Australian workers have investigated the thermal degradation of PMMA and found that it occurs in two steps. Approximately 50% degrades in the 170-250°C range while the remainder is stable past 300°C. This was largely explained by invoking end group effects. PMMA radicals terminate predominantly by a disproportionation mechanism, which produces one saturated and one unsaturated end group from two interacting radicals. A small amount of head to head linkages may also be formed at lower temperatures from combination type termination reactions. Model oligomers were prepared to mimic the possible end group structures, and characterized. These type of groups are shown in Scheme V.

TGA analysis was then performed, and it was observed that head to head linkages decomposed at 195°C, unsaturated end groups and the saturated end group structures decomposed at 225°C and 300°C respectively. These temperatures were independent of molecular weight up to 10,000 g/mole. Typical processing temperatures for PMMA would thus have to be around 200°C. Indeed the presence of these linkages thus prevents thermal processing of PMMA homopolymer [330,331].

Other workers have confirmed these conclusions recently by a different route in which chain transfer agents were used to control end groups. The amount of chain transfer agent used allows one to control the percentage of chains that would have unsaturated end groups. Thermal stability measurements were reported that confirmed the earlier findings [332].

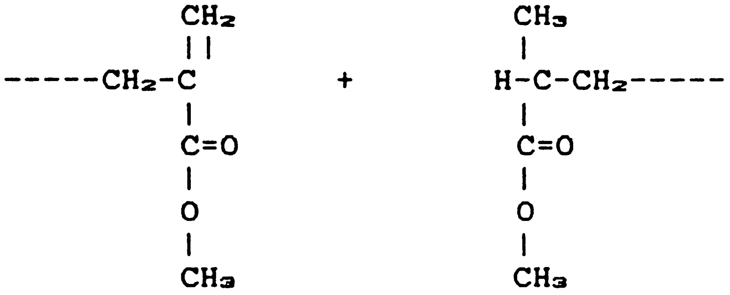
Synthetic schemes producing polymers with only saturated end groups, such as living anionic polymerizations or group transfer polymerizations would thus be capable of preparing PMMA with thermal stabilities of over 300°C. This could possibly allow wider applications for an already large volume industry.

Methacrylates in general and PMMA in particular are known to degrade and depolymerize under high energy irradiation such as UV (215 nm) and electron beams, as shown in equation 4 [333-336].



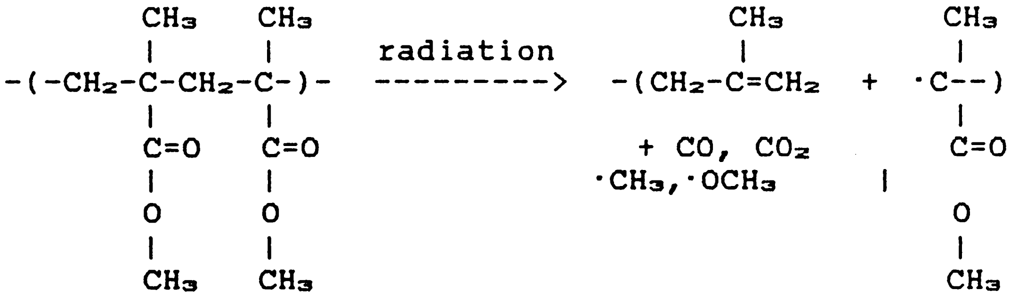
$$\text{----}CH_2\text{-}\underset{\underset{\underset{\large CH_3}{|}}{\underset{O}{|}}}{\underset{O=\overset{|}{C}}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{--}\underset{\underset{\underset{\large CH_3}{|}}{\underset{O}{|}}}{\underset{\overset{|}{C}=O}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2\text{-----}$$

Head to Head Linkage Formed by Combination of Radicals



$$\text{-----}CH_2\text{-}\underset{\underset{\underset{\underset{\large CH_3}{|}}{\underset{O}{|}}}{\underset{C=O}{|}}}{\overset{\overset{CH_2}{\|}}{C}} \quad + \quad H\text{-}\underset{\underset{\underset{\underset{\large CH_3}{|}}{\underset{O}{|}}}{\underset{C=O}{|}}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2\text{-----}$$

Scheme V. Unsaturated and Saturated End Groups Formed in Disproportionation Reactions



$$-(-CH_2-\underset{\substack{|\\C=O\\|\\O\\|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-CH_2-\underset{\substack{|\\C=O\\|\\O\\|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-)- \xrightarrow{\text{radiation}} -(CH_2-\overset{\substack{CH_3\\|}}{C}=CH_2 + \cdot\underset{\substack{|\\C=O\\|\\O\\|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}--) \quad + CO,\ CO_2\ \cdot CH_3, \cdot OCH_3$$

-----> Depolymerization

Equation 4)

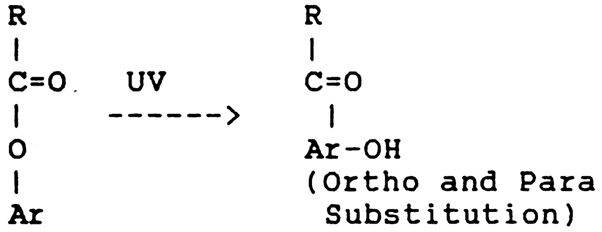
Microlithography has taken advantage of the positive resist properties of PMMA such as availabilty, high resolution, and handling ease [33$_7$-339]. One very important property is that it does not swell before it dissolves which would cause a decrease in resolution. Limitations include its low sensitivity and thermal instability. High temperatures are often used in metal vapor depositions, which would degrade classical PMMA [340-344].

As mentioned previously, incorporation of metals that form non-volatile oxides allows for reactive ion etching of resists. Several reports have appeared in the literature on efforts along these lines. Monomers with silicon or tin moieties, have been copolymerized with MMA for this purpose [345-348]. Thus, reactive ion etch resistance should be gained along with the properties of PMMA. However, incorporation of enough of these monomers to have nine weight percent metal in the system required that most of the MMA be replaced and thus the properties of MMA were lost. Glass transition temperatures are reduced in agreement with the ease of rotation of carbon-silicon bonds. The extension to phase separated block and graft copolymers has received much less attention. This route does offer, one to have significant amounts of siloxane incorporated without changing the fundamental PMMA characteristics.

PMMA is a fairly UV stable polymer due to the low, far UV, intensity of the spectrum in natural light. PMMA has an initial transmittance of 92%, and after 3 years of exposure to light shows no decrease in transmittance. Other typical glassy materials such as polycarbonate lose transmittance and increase their haze with far less exposure.

Another interesting area of research is the stabilization of polymers to UV light and the use of the stabilized polymers as coatings to protect substrates. Much effort has gone into adding stabilizers to polymers although often the long range effectiveness is lost due to vaporization or "leaching" of the stabilizer. Thus, polymer bound stabilizers are desirable and have received much attention. Several classes of UV absorbing moities have been introduced, including benzotriazoles, and ortho-hydroxy aromatic compounds [349-374].

The Photo-Fries rearrangement of aromatic esters to ortho hydroxy compounds is a much used route to even better UV stabilizers. The six membered ring formed has hydrogen bonding between the phenolic proton and carbonyl group. This extends the UV absorbance further towards the visible range. Also a certain amount of antioxidant effect may be possible by the phenolic structure. Compounds such as phenyl acrylate, and acrylic benzophenone derivatives have been used which polymerize readily, but can then be converted to the ortho hydroxy substituted derivative by UV irradiation,as shown in Scheme VI.



$$\begin{array}{l} R \\ | \\ C{=}O \\ | \\ O \\ | \\ Ar \end{array} \xrightarrow{UV} \begin{array}{l} R \\ | \\ C{=}O \\ | \\ Ar{-}OH \\ \text{(Ortho and Para} \\ \text{ Substitution)} \end{array}$$

Scheme VI.Photo Fries Rearrangement of Aromatic Esters

Incorporation of UV absorbing groups has been achieved by direct copolymerization and by reacting the moiety onto a preformed backbone.

II. D. STYRENIC POLYMERS

1. <u>Introduction</u>

Styrenic polymers and copolymers have been a commercially important part of the polymer industry since 1930. Dow was the first company to successfully produce styrene monomer. World War II, later, cut off the supply of natural rubber and forced synthetic efforts to prepare styrene-butadiene rubbers.

Styrene monomer was first isolated in the 1800's from the distillation of balsam. Polymerizations produced only brittle materials and so it was not commercially applied until much later. Dow developed a process, simultaneously with BASF, for the manufacture of styrene monomer via the dehydrogenation of ethyl benzene. Post-war developments have continued the efforts of rubber modified copolymers.

2. Monomers

Styrene can be produced by several techniques, of which, the most commercially important is the dehydrogenation of ethyl benzene. The two processes developed by Dow and BASF differ principally in how heat is added to the system.

The Dow process involves the addition of super heated steam to ethyl benzene and then contact with the catalyst, at a temperature of approximately 630°C. These high temperatures result in some thermal cracking. The BASF technique does not involve premixing with steam, but rather uses steam to heat a tubular reactor. Temperatures can be maintained more evenly at about 580-610°C, with little thermal cracking taking place.

Other important styrene derivatives such as p-Methyl styrene, p-t-butyl styrene, and p-chlorostyrene are also of interest.

p-Methyl styrene is the para form of a monomer also known as vinyl toluene. The synthesis of the para product by Mobil corporation is also a carried out by a cracking method. Cracking of p-methyl ethyl benzene under controlled catalytic conditions leads to the formation of p-methyl styrene.

p-t-Butyl styrene is another interesting styrenic derivative that might be an important product at some point. The synthesis of this monomer via a cracking method has been done as well. The cracking of p-t-butyl ethyl benzene must be carefully done to proceed predominantly at the ethyl functionality.

3. Polymer Synthesis and Characteristics

Styrene is polymerizable by free radicals, anions, cations and by coordination catalysts. Commercial homo- and copolymers are most typically produced free radically as in the case of styrene-butadiene rubbers, impact polystyrene, and SAN. Kraton thermoplastic elastomer by contrast is a commerical product which is produced by the anionic block copolymerization of styrene and butadiene.

Highly isotactic poly(styrene) is available by the

Ziegler-Natta catalyzed polymerization of styrene. These materials are crystallizable, showing a melting point of 240°C. The isotactic materials otherwise have many properties similar to atactic poly(styrene). Once crystalized, the materials are insoluble in common solvents. Crystalization rates are very slow and there has been no major commercial development.

Styrene polymers have a Tg of approximately 100°-105°C, independent of the stereochemistry. Homopolymers form clear, glassy films if of sufficient molecular weight, typically >100-150,000 g/mole. Solubility parameters for poly(styrene) have been estimated to be about 9.1- 9.2 cal/gm½.

Substituted styrenes such as p-methyl styrene, and p-t-butyl styrene have higher Tg's and lower solubility parameters. Polymers based on p-Methyl styrene have a Tg of approximately 115°C, and a solubility parameter of ~8.6 cal/gm½, while p-t-butyl styrene has a Tg of 145°C and a solubility parameter of ~8.1cal/gm½.

Free radical polymerizations were the only important route for styrene polymerization until 1956, with Szwarc's discovery of the living anionic polymerization. In hydrocarbon solvents, living polymers are stable at room temperature almost indefinitely, assuming the absence of terminating impurities. Side reactions occur only slowly at room temperature, typically by elimination of metal-hydrides and formation of unsaturated end groups. Often the metal hydride abstracts a proton from an adjacent carbon atom and conjugated allylic anions are formed.

Styryl anions have also been found to initiate the anionic polymerization of many other monomers such as butadiene, isoprene, methacrylates, and siloxanes. As mentioned in the section on siloxanes, diblock, triblock, and multiblock styrene-siloxane copolymers have been prepared anionically.

Systematic studies of analogous copolymers with varying styrenic phases should therefore be of interest to the scientific community. Effects of Tg and solubility parameter on the properties of the copolymers can then be investigated.

III. RESEARCH INTRODUCTION

In order to meet the final goals, this research had several objectives to fulfill, the first of which was the investigation of the living nature of the anionic ring opening polymerization of hexamethylcyclotrisiloxane. Once the techniques for this process had been extablished the extension to block copolymerizations with styrenic monomers was desired.

The next step was the preparation and characterization of poly(dimethyl siloxane) macromonomers with methacrylate end groups. These were then free radically copolymerized with various methacrylic and styrenic comonomers. Investigations into the efficiency of copolymerizations were undertaken.

Copolymers with overall molecular weights of at least 100,000 g/mole were desired for optimal properties. It was desired that molecular weights be above a critical value where "properties" such as Tg become relatively constant. Thus variations in "properties" that were experimentally determined were assumed to be dependent on the system architecture alone and not a combination of variations.

Copolymers with varying backbones and varying graft molecular weights and compositions were synthesized and characterized. Clear trends were found between system architecture and properties.

Copolymers of PMMA-g-PSX were also prepared anionically to investigate the effects of molecular weight and compositions distributions on the properties of the system. Molecular weight and composition distributions for the two polymerization mechanisms were determined and used as explanation of the properties found for the copolymers.

IV. EXPERIMENTAL

A. Reagents and their Purification

An emphasis on purification routes that not only produce highly pure reagents for anionic reactions but also that lead to their use with minimal contact with the atmosphere after their purification is important. Typical purification schemes involved the handling of materials by syringe or double ended needles after purification to avoid contamination.

Crucial to the above techniques is the ability to provide a system that can alternately apply vacuum and purified nitrogen. A useful system with a dual manifold is outlined in Figure 1. Important features include the use of teflon rotaflow stopcocks to preclude the need for silicone grease, which can terminate anionic polymerizations. This system is capable of a vacuum of approximately 10^{-2} torr. The nitogen manifold was kept at 8- 12 psi of prepurified nitrogen that was passed through columns containing Calcium Hydride, molecular sieves and alumina. The columns were designed to remove moisture and other protic impurities that might terminate an anionic polymerization. The vacuum manifold was attached to a vacuum pump with an inline liquid nitrogen cold trap, and attached to the distillation apparatus via hoses.

1. Polymerization Solvents

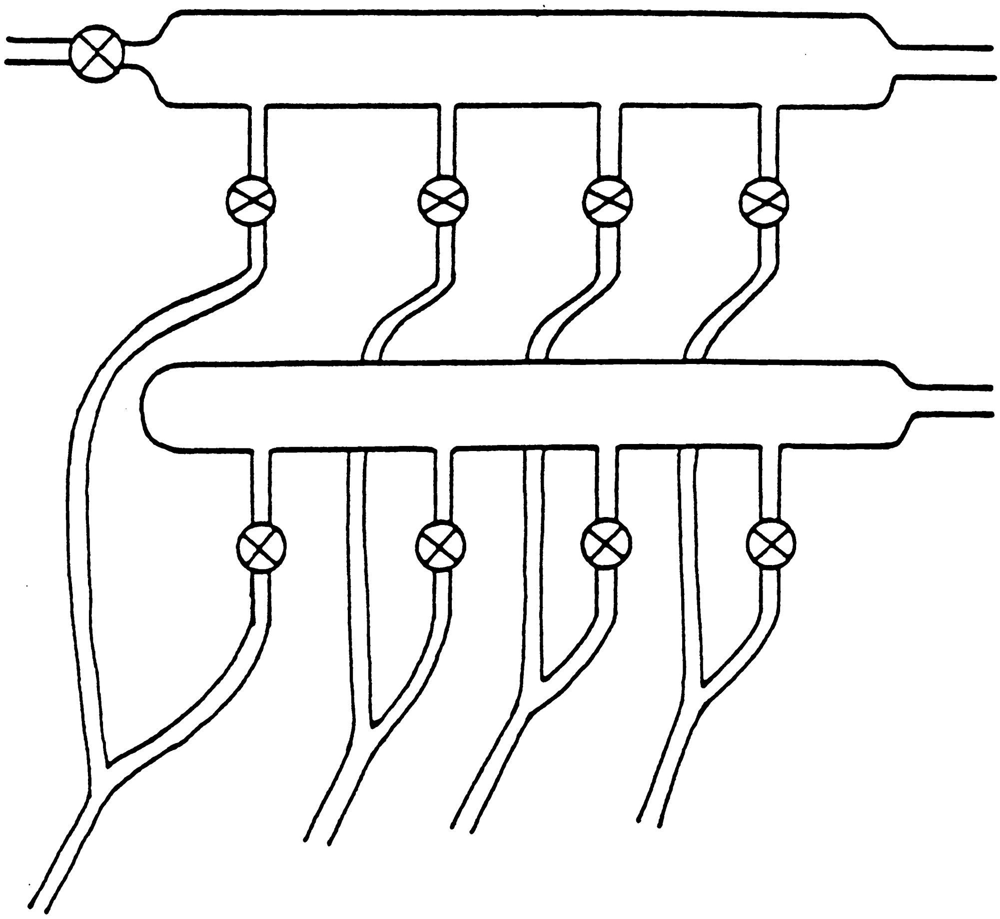


Figure 1. Dual Manifold Vacuum-Nitrogen System

a) Cyclohexane (Fisher Reagent Grade) was stirred over concentrated sulfuric acid for one to two weeks. The darkening color of the sulfuric acid layer was an indication of the reaction with olefinic impurities to form sulfonated materials. The cyclohexane was then either passed through a column of basic alumina to remove acidic impurities, or added to a round bottom flask containing a teflon stir bar and several small pieces of sodium dispersion in paraffin. A fine dispersion of metallic sodium developed with dissolution of the original wax coating. The resulting dispersion has a large surface area. No reaction is usually noted, if adequate time is given for separation of the acid and organic layers. This mixture was then placed on a nitrogen flushed distillation apparatus and refluxed for several hours, followed by distillation.

If extremely pure cyclohexane is desired, a further step can be taken. The above distillate was introduced into a flask containing the living anion formed by reaction of butyl lithium and diphenyl ethylene. The red color of this anion can be used as an indicator of anionic purity of the cyclohexane. Finally, the cyclohexane can be distilled from this red solution to produce an extremely pure cyclohexane.

b) Tetrahydrofuran (THF) (Fisher, Certified

Grade) was placed in a round bottom flask with teflon stir bar and several small pieces of a sodium dispersion in paraffin wax were added. With stirring, the wax dissolved, forming a fine dispersion of higher surface area than sodium metal. After refluxing under nitrogen for 1 hour in a distillation apparatus, a small amount of benzophenone was added to the cooled solution. A highly colored sodium dianion formed, as indicated by a purple color. This color was used as an indicator of solvent purity, since the complex is only stable in the absence of proton sources and oxygen. The reaction often turns green with oxidation of the complex, but it can then be reformed by further addition of sodium dispersion and/or benzophenone and degassing. After stirring and refluxing for several hours the THF was then distilled, taking care not to expose the THF to air or other contaminants. The distilled THF was then used directly in anionic polymerizations, by transfer into reactors via syringe or canula.

c) Toluene (Fisher Certifed Grade) was purified for free radical reactions by degassing and storing under nitrogen. Degassing was accomplished by pulling a vacuum on a round bottom flask containing toluene while stirring, and cooling, which prevented distillation of the toluene.

d) Triethylamine (Fisher) was purified by a vacuum distillation after having been stirred over Calcium hydride for one week.

2. Purification Agents

a) Calcium Hydride (Fisher) was crushed to a fine powder to maximize surface area. Since this is a hetrogeneous drying agent, maximum efficiency is only achieved with very high surface areas.

b) Triethyl Aluminum (TEA) (Ethyl Corporation) was supplied as 25 wt.% solutions in hexanes and used as received.

c) Dibutyl Magnesium (DBM) (Lithium Corporation) was used as a 15 wt% solutions in ISOPAR E (hydrocarbon mixture) as received.

d) n-Butyl Lithium (BuLi) (Lithium Corporation) was supplied as a 1.6 Molar solution in hexanes. It was used as received.

e) Alumina (Fisher) was activated by drying in a vacuum oven for 24 hours at 100°C.

3. Monomers

a) Hexamethylcyclotrisiloxane (D_3) (Petrarch) was first melted and stirred with calcium hydride then sublimed under vacuum in an apparatus as shown in Figure

2. After complete sublimation cyclohexane was admitted to the sublimed crystals and warmed to dissolve the D_3 to form solutions of about fifty wt.% solids. This solution was then transfered under nitrogen to a bottle that was cleaned, dried, and contained some ground calcium hydride. These solutions were stable and can be handled by syringe techniques for monomer addition.

b) Methyl Methacrylate(MMA) (Rohm Tech.) A large batch of MMA (~1 liter) was stirred over finely ground calcium hydride (CaH2) under a nitrogen atmosphere for several days. Next, the monomer was vacuum distilled and transferred to a clean dry septume capped bottle under nitrogen. By this method, we have a continual supply of monomer that is as pure as conventional techniques would require. Monomer of this purity can be stored for extended periods of time in a freezer without significant amounts of polymerization. This monomer is adequate for free radical polymerizations however, since it is largely inhibitor and oxygen free.

For anionic grade MMA, a further step is required which involves a second distillation step in a setup as outlined in Figure 3. The glassware was typically washed with soap and water then etched with hydrofluoric acid if necessary. It was then rinsed with acetone and dried at 120°C overnight. The glassware was best set up while hot,

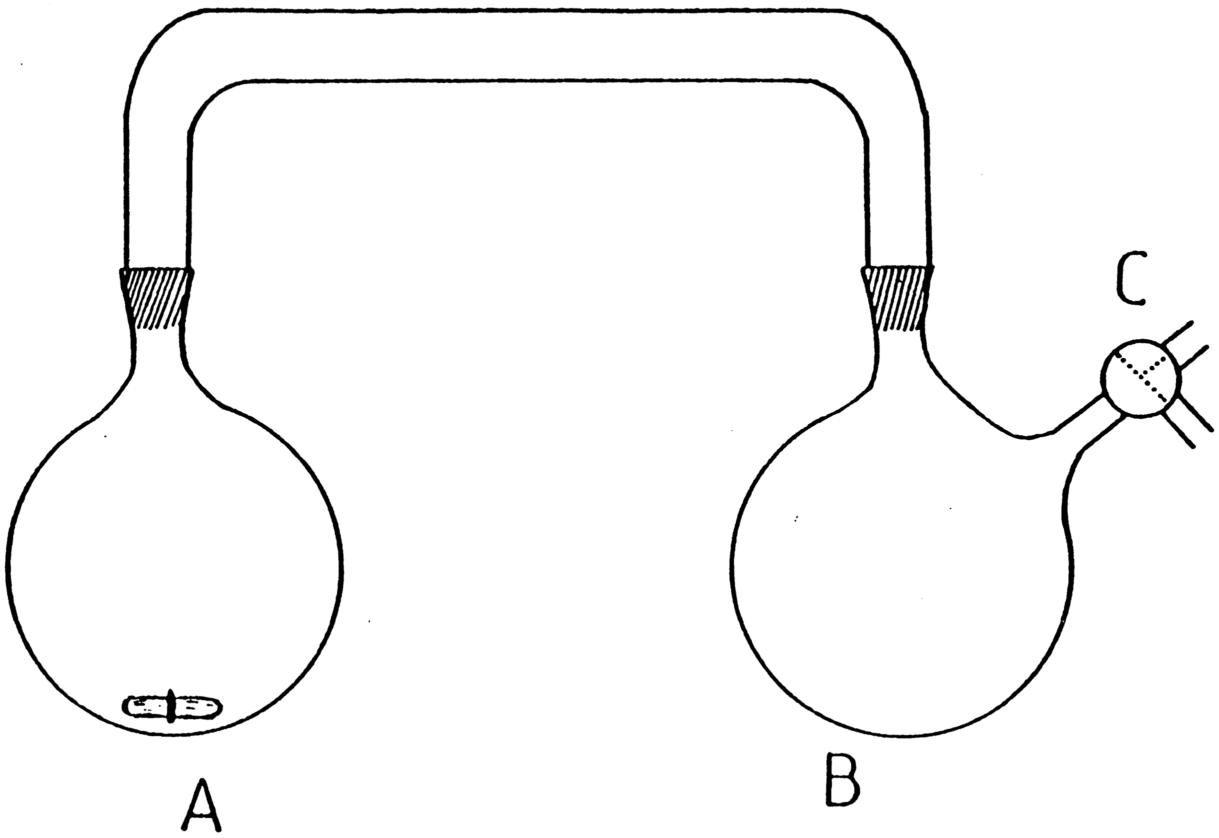


Figure 2. Distillation Apparatus

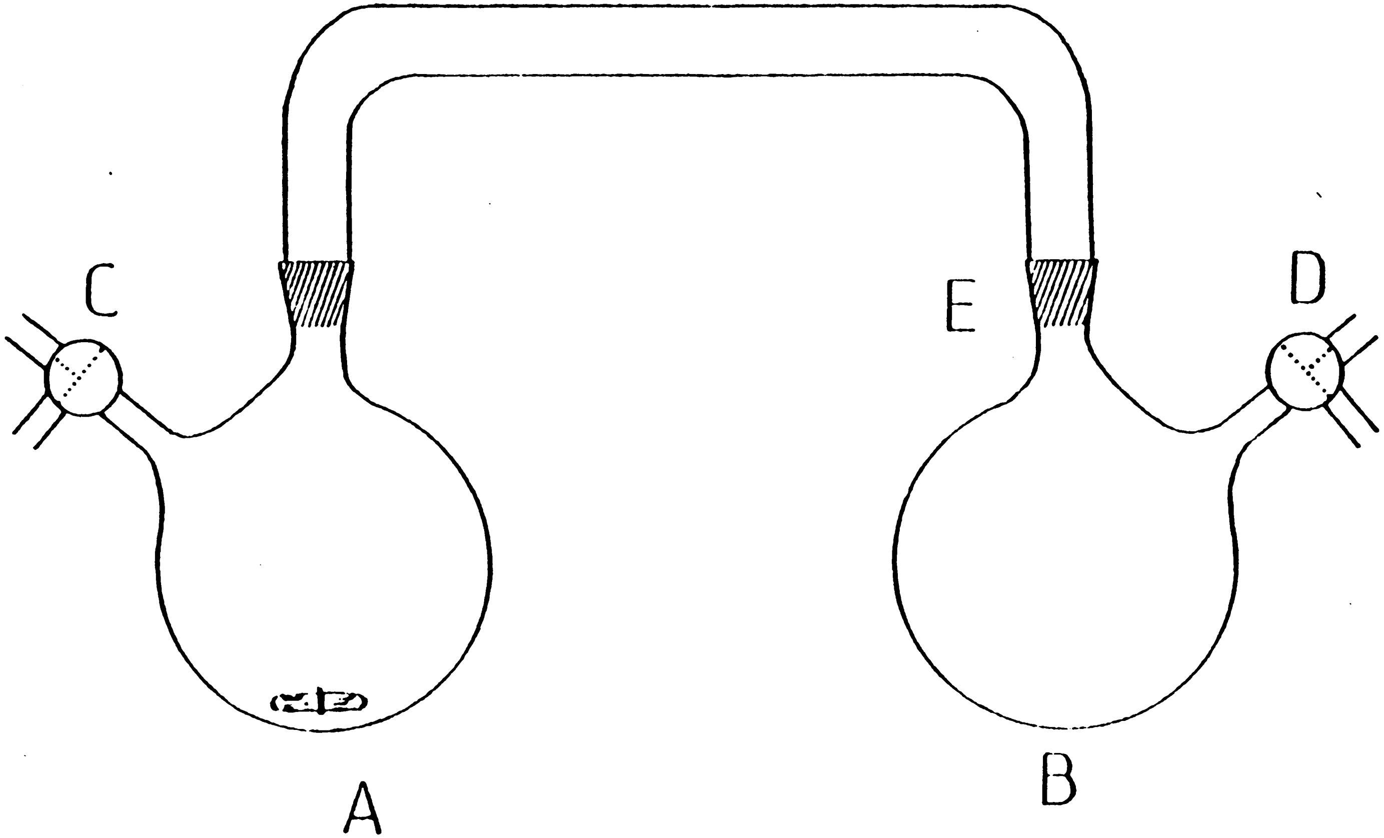


Figure 3. Distillation Apparatus

with nitrogen purging through the system. Once set up and clamped together, a vacuum can be applied and the system flamed to remove most of the moisture associated with the walls of the glassware. Upon cooling, nitrogen can be readmitted to the system and MMA was transferred into the flask on the left via a two ended needle or canula. In general, emphasis was placed on monomer and solvent handling techniques, so that exposure to the atmosphere was minimal. A solution of trialkyl aluminum in hexanes was then added dropwise to the stirring monomer. A yellow colored complex forms only when all other impurities have been removed via reaction. In this way it is possible to titrate impurities, forming species such as aluminum alkoxides etc. An additional 0.5 -1 ml of trialkyl aluminum is then added in excess to insure reaction with impurities. The monomer solution was then covered with a black cloth and allowed to stir for approximately 30 minutes. Next, vacuum was slowly applied to remove hydrocarbons present as diluent for the trialkyl aluminum, as well as though formed upon reaction with protonic impurities. As vacuum was increased cooling was also applied, to prevent distillation of the monomer. Finally, the monmer was frozen down to - 78°C and a high vacuum applied. Next the monomer was allowed to warm with vacuum open to remove any last traces of hydrocarbons. This freeze-thaw cycle can be repeated if necessary to remove the relatively large amounts of hydrocarbon present. If proper care is taken, a vacuum which will cause MMA to distill at less than 10°C can be obtained. The monomer as distilled is extremely pure and care must now be taken to keep it frozen until use. It is best if the monomer is used immediately, since lack of all inhibitors will result in premature polymerization.

c) i-Butyl Methacrylate (Polymer Sciences) was passed through an alumina column then distilled from Calcium hydride in the same method as described for methyl methacrylate. The purifies monomer was stored in a brown glass bottle under nitrogen.

d) t-Butyl Methacrylate (Rohm) was passed through an alumina column then distilled from Calcium hydride similarly to methyl methacrylate. Of course higher temperatures are needed and premature polymerization of monomer can be a problem, if the temperature exceeded ~ 35°C.

e) N,N-Dimethyl Acrylamide (Polymer Sciences) was distilled from Calcium hydride and stored in a refrigerator under nitrogen until use.

f) Styrene(Fisher) B.P. 145°C was also passed through a column of activated alumina to remove inhibitors and was collected into a round bottom flask. A three way valve was fitted in the neck of the flask and a vacuum was applied with stirring and cooling to remove dissolved oxygen. With dry ice/ isopropanol mixtures at approximately -78°C, styrene will freeze and it is important to apply vacuum early in the sequence to prevent the trapping of oxygen in the frozen monomer. The mixture was frozen again and vacuum was applied for an additional 10 - 15 minutes. Then the monomer was allowed to thaw. Vacuum was left open for the first few minutes of thawing to remove any traces of dissolved gases. This sequence can be repeated several times, if desired, to thoroughly remove all dissolved gases. At this stage the monomer is ready for free radical polymerizations.

Anionic grade styrene can be prepared by the distillation of monomer from dibutyl magnesium under vacuum. A set up as shown in Figure 3, was flamed under vacuum to remove surface water and gases. The monomer previously passed through a column was added to the set up via a canula under a nitrogen atmosphere. The freeze-thaw cycle mentioned previously for styrene was then undertaken in the distillation set up in an attempt to remove all oxygen. Next, a solution of dibutyl magnesium was added via a syringe, while watching for the characteristic yellow-green complex of the pure system. Once this has been obtained a small excess of dibutyl magnesium was added (~0.5 -1 ml) and the monomer was allowed to stir for about 1/2 hour to ensure complete reaction with all impurities. The system was then evacuated while freezing the monomer down, and again a high vacuum was applied on the frozen monomer. With a good vacuum, the system can be isolated and allowed to warm, with cooling of the flask on the right, distillation will take place with minimal heating of the monomer solution on the left.

This monomer is extremely pure and is best used immediately. Alternatively it was kept frozen until use to prevent premature polymerization.

g) p-Methyl Styrene(Mobil) was purified similarly to styrene.

h) p-tert-Butyl Styrene(DOW Chemical) B.P. 219°C was purified simalrly to the above styrene monomers, except more care needs to be taken in the distillation, since its boiling point is much higher and polymerization occurs readily in the distillation flask with heating. Leaving the vacuum open creates the danger of bumping of the monomer, but lowers the boiling point by increasing the vacuum applied to the system.

i) 4-Methacryloxy-Benzophenone was prepared from 4-Hydroxy Benzophenone and methacryloylchloride by the following synthetic scheme. To a solution of 50 grams (0.5

mole) of triethylamine which was distilled from calcium hydride and 150 ml of diethyl ether was added 20g (0.1 mole) of 4-hydroxy-benzophenone. After dissolution of the 4-hydroxybenzophenone the mixture is cooled to 0°C and 11.5 grams of methacryloylchloride (vacuum distilled) was added dropwise to 10% excess. This solution was then allowed to warm to room temperature and was then heated at 40°C for 1 hour to ensure complete reaction.

Workup of the reaction involves the addition of 100 ml. diethyl ether, and repeated extraction with dilute HCl to remove salts and the excess of triethyl amine. Next, extraction with an aqueous solution of sodium bicarbonate was used to remove any excess methacrylic acid that will have been formed by the hydrolysis of excess methacryloylchloride. Final extractions with deionized water to remove any remaining base were done and the ether layer was dried with magnesium sulfate and filtered. The ether layer can then be removed by rotoevaporation and the crystals recovered are recrystalized from hexanes. The appropriate FTIR and NMR of the expected material was obtained. Figures 4 and 5 show the FTIR and NMR respectively of the recovered monomer. One notes the absorbances at $1740cm^{-1}$ and $1660cm^{-1}$ corresponding to the ester and ketone carbonyls, repsectively. The peaks from 7.2 to 7.9 ppm in the NMR correspond to the aromatic

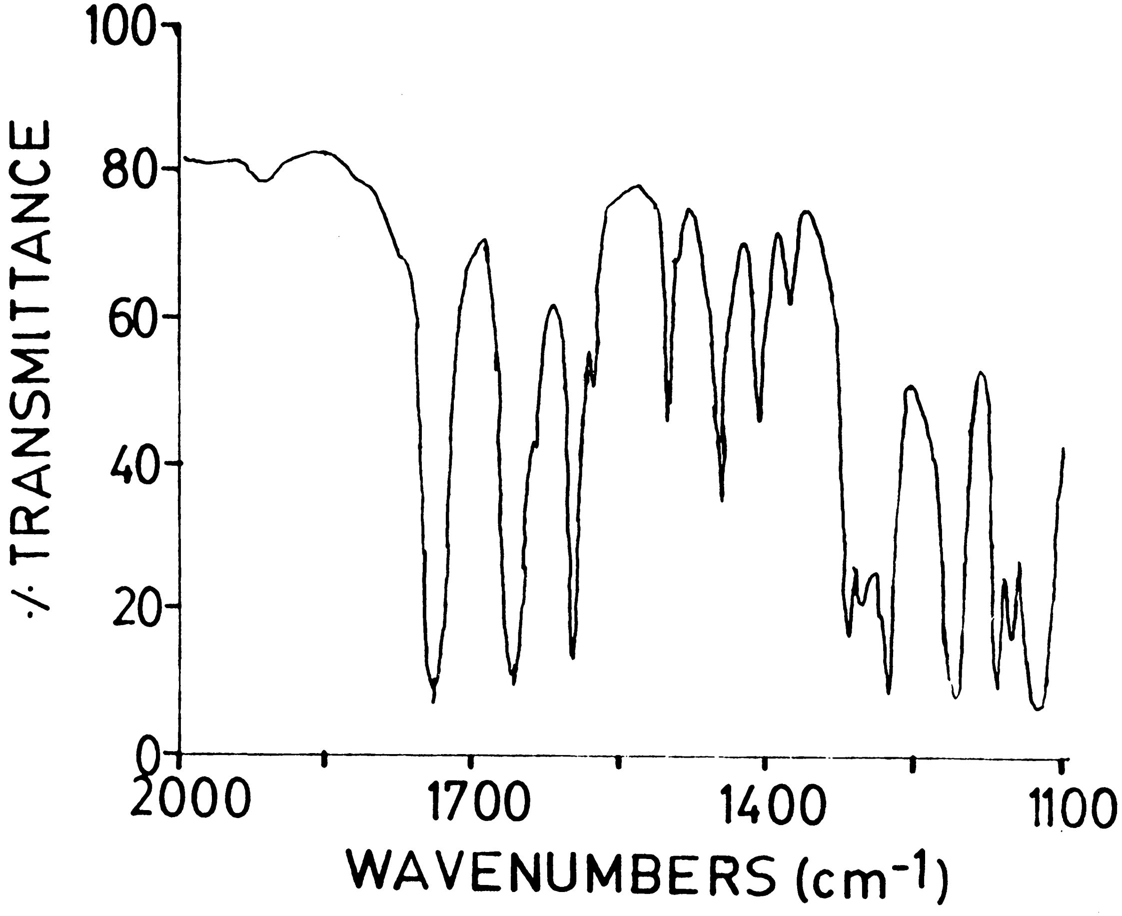


Figure 4. FTIR Spectra of 4-Methacryloxy benzophenone

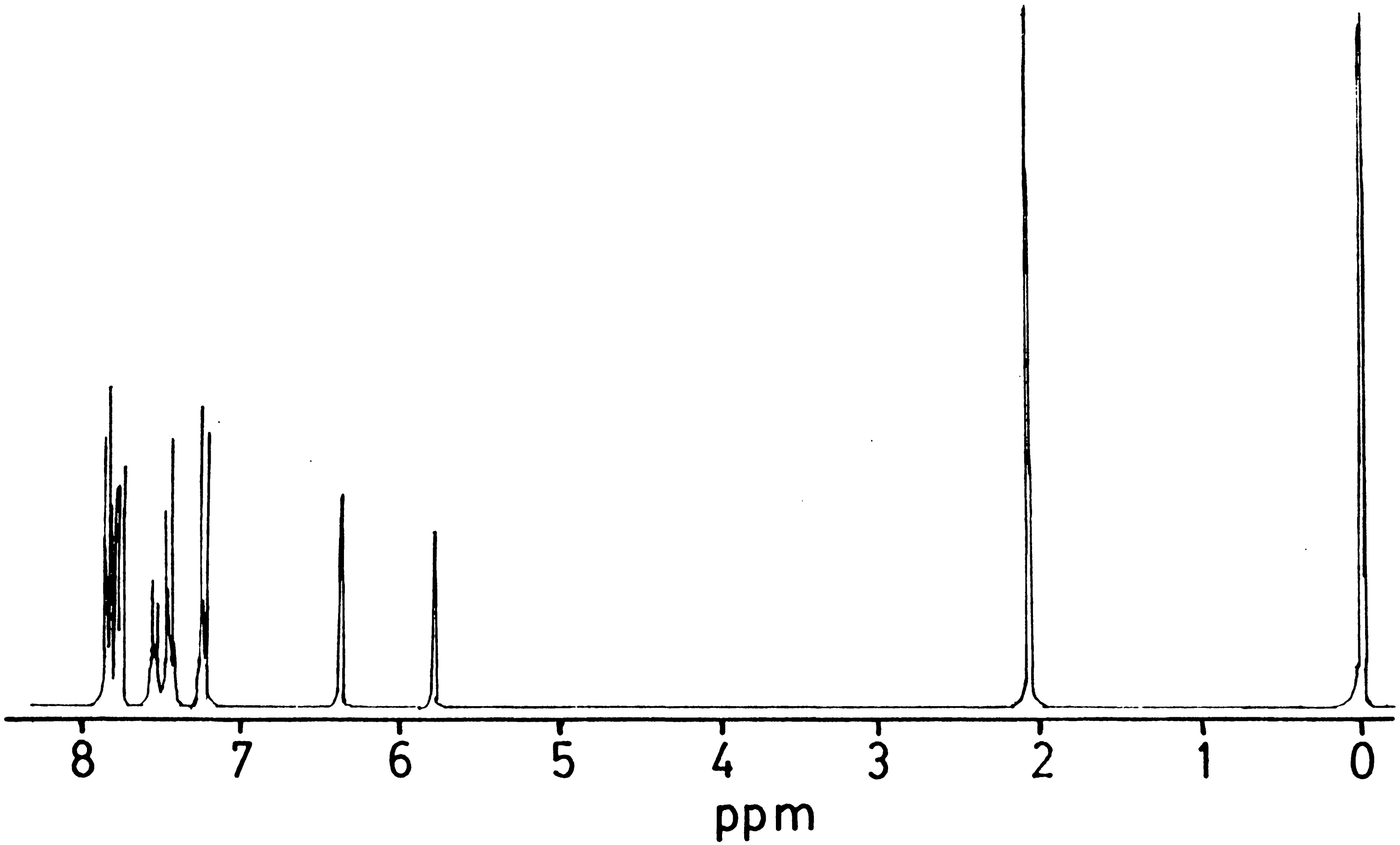


Figure 5. Proton NMR Spectra of 4-Methacryloxy-benzophenone

protons of one para substituted ring and one mono substituted ring. The two vinyl protons are split into a doublet at 6.4 and 5.8 ppm, and the α-methyl protons are observed as a singlet at 2.1 ppm.

4. Initiators

a) s-Butyl Lithium (s-BuLi)(Lithium Corporation)(1.35M in hexanes) was used as received for general reactions, although for critical purity s-BuLi was distilled on a high vacuum line at 60- 100°C at 10^{-6} torr.

b) 1,1-Diphenylhexyl lithium was prepared from 1,1-diphenyl ethylene (DPE) and s-BuLi. Diphenyl ethylene (Eastman) B.P. 270°C was distilled under vacuum from a reaction of DPE and s-BuLi. A typical distillation apparatus as shown in Figure 3 was set up and flamed under vacuum. After cooling and filling with nitrogen DPE was admitted to the left flask and with stirring, s-BuLi was added slowly, with observation of the color of the stirring solution. The reaction desired when all impurities have reacted is the addition of s-BuLi across the double bond of DPE which formed an intensely colored deep cherry red to black colored solution. Impurities found in DPE include the oxidation products such as benzophenone which readily react with s-BuLi to form greenish colored products. During the titration with s- BuLi, a series of colors may be evidenced with the final color often being a deep red to black. At this point, a vacuum was pulled to remove the hexanes added with the s-BuLi. After sufficient time to remove all hexanes the reaction mixture was cooled with increasing vacuum until the mixture was frozen Full vacuum was applied and the mixture was warmed. The vacuum path remained open and the flask on the right was cooled. The cross path was warmed with electrical heating tape. High temperatures are needed on the left side to distill the reagent. Finally DPE was stored in a brown bottle under nirogen for short periods of time until use. Polymerization was not a problem with this species however oxidation to epoxide and ketone structures must be avoided.

Anionic copolymerizations of methyl methacrylate and macromonomer were intiated with a preformed diphenylhexyl lithium. Solutions of DPHL were prepared as follows; to 30 ml of THF at -78°C were added 2.2 ml (0.012 mole) of diphenyl ethylene, followed by 10 mmole (7.5ml) of s-BuLi. This produced a solution of diphenylhexyllithium (DPHL) that is approximately 0.25 Molar.

c) <u>Azoisobutyronitrile</u> (AIBN)(VAZO 64 from Du Pont) was recrystalized from methanol as reported in the literature. Solutions of known concentrations in solvents suitable for the polymerization of the desired monomers, were then prepared and refrigerated until use. In this way very small amounts can be measured and added to reaction flasks easily by syringe techniques.

B. Polymer Synthesis

Polymerizations by anionic mechanisms requires purity levels beyond the scope of normal purification and handling techniques. The preparation of these reactors involved the scrupulous cleaning of a round bottom flask with soap and water and rinsing with hydrofluoric acid, dilute aqueous base, distilled water and finally a rinse with acetone. These flasks were then dried in a forced air oven at 120°C overnight, removed and fitted with a septa and purged with nitrogen. The septa were attached with copper wire to counterbalance the nitrogen pressure. Flaming of the flask with continual purging removed any last traces of moisture from the surface of the glass. These flasks were then filled with nitrogen to a positive pressure of 8 psi. and allowed to cool. Once cool, these flasks were then ready to be charged with solvents, initiators and monomers with minimal contamination.

1. Siloxane Homopolymers

Polydimethylsiloxane homopolymers were prepared by the anionic polymerization of D_3 or hexamethylcyclotrisiloxane with alkyl lithium initiators. Typically, a round bottom flask that has been cleaned and dried as stated earlier was charged with the desired amount of D_3/cyclohexane mixture. The calculated amount of s-BuLi was added with stirring to produce the desired molecular weight. A sample calculation of molecular weight for an anionic polymerization is given in Scheme 6. The initiation reaction was allowed approximately 15 minutes to go to completion. Next, purified THF was added to partially dissociate the ion pair and promote polymerization of the cyclic siloxane trimer. The amount of THF was not crucial, but will control the kinetics of polymerization. Larger amounts will increase the rate of polymerization, but it has also been reported that this can lead to equilibration reactions as well, which is obviously undesired. By adding about 10% by volume THF/Polymerization volume, the polymerization will proceed at room temperature in about 24 hours to molecular weights of less than 50,000 g/mole. With higher molecular weights (lower initiator concentrations), times approaching 48 hours were allowed to complete the polymerization. Also, since the mixture of D_3 and cyclohexane is about 45 weight

Scheme 6

Molecular Weight Calculation for Anionic Polymerization

M theory = g monomer/ moles initiator

M theory = 10,000 g/mole

10 g of monomer

thus

moles of initiator = 10g/10,000 g/mole = .001 mole initiator percent solids it is advisable to dilute with either cyclohexane or THF to avoid exteremely high viscosities in high molecular weight polymerizations.

Termination of these living polymerizations was accomplished by adding a small excess of a chlorosilane such as trimethylchlorosilane, which reacts with the siloxanolate to produce the terminated siloxane chain. The lithium chloride by product precipitates from solution after a short induction period as a colloidal dispersion.

Polydimethylsiloxanes are best recovered by adding adequate sodium bicarbonate to neutralize the HCl which forms from the excess of chlorosilane added. If this step is not taken HCl can lead to backbone degradation later in the isolation of the polymer. A second step was then the precipitation of this solution into rapidly stirring methanol to produce an oily dispersion. This dispersion settled to the bottom upon stopping the stirrer. The rate of settling will be dependent on siloxane molecular weight. Materials above 10,000g/mole settled within minutes, and materials around 1000 g/mole take several hours to completely separate. The methanol was then decanted off and the siloxane polymer recovered and vacuum dried.

2. Siloxane Macromonomers

Macromonomers of polydimethylsiloxane were prepared similarly to the above homopolymers except that termination was accomplished by adding the hydrosilation adduct of dimethylchlorosilane and allylmethacrylate, (3-Methacryloxypropyldimethylchlorosilane). Characterization of this compound by proton NMR, Figure 6, indicated the structure was as described. Resonances at 5.8 and 6.4 ppm were assigned to the two vinylic protons. A triplet centered at 4.4 ppm was assigned to the two methylenic ester protons. The α-methyl protons appeared at 2.2 ppm. The β-methylenic protons appeared as a complicated set of resonances from 1.9 to 2.1 ppm. The methylenic protons on the carbon adjacent to the silicon were found at 1.1 ppm, however they were not a triplet as expected. A large triplet was found with a small amount of other peaks, which were interpretted as resulting from Markonikov type hydrosilation across the allylic double bond. This small amount (<5 %) would also explain some of the complexity of the peaks at 2 ppm. The six protons present on the two silicon methyls resonate at .65 ppm. Integration agreed with the assignments.

This compounds reacts similarly to other chlorosilanes. The siloxanolate is too weakly basic to attack the conjugated methacrylate functionality and desirably displaces the silylchloride at silicon.

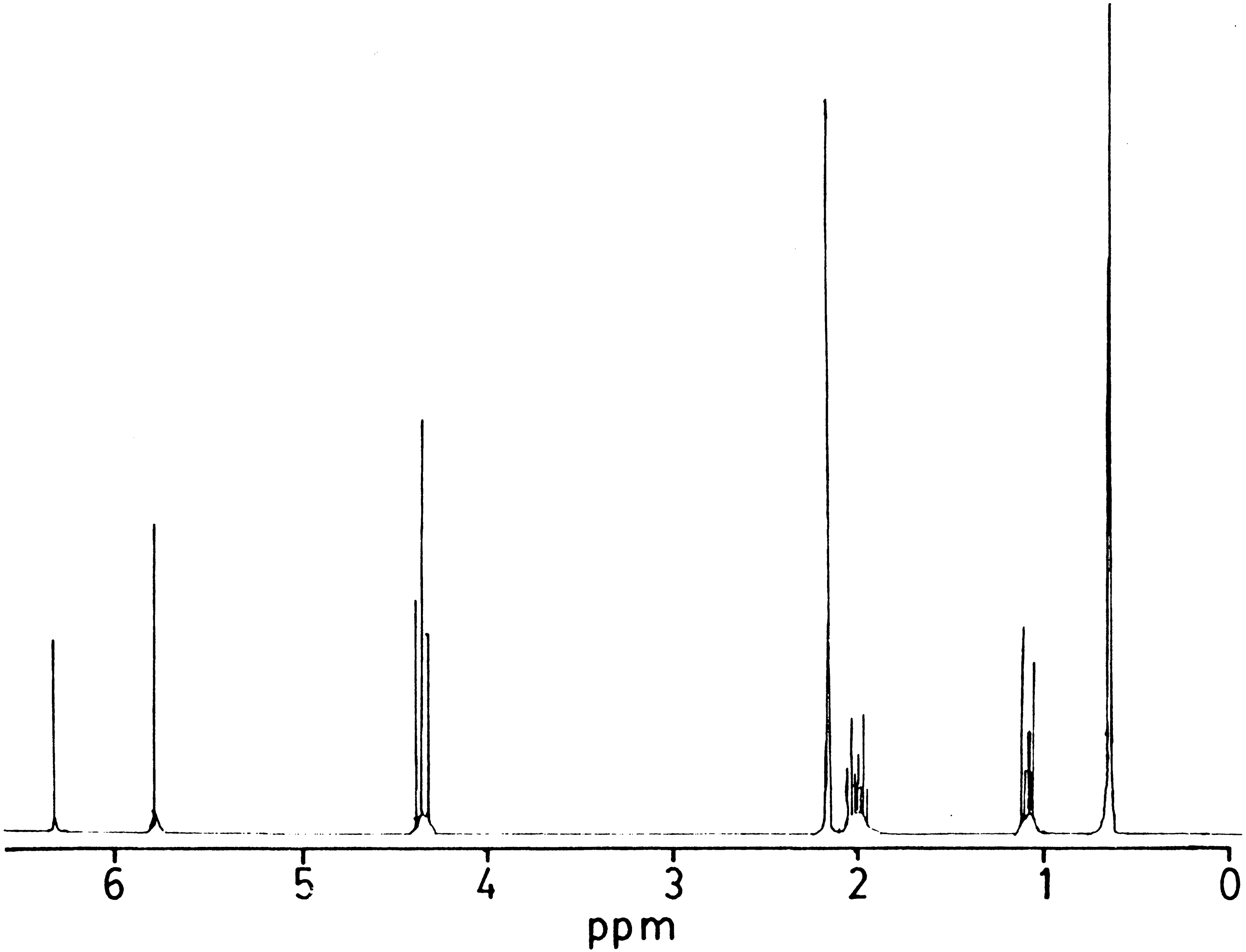


Figure 6. NMR Spectra of 3-Methacryloxy Propyl Dimethyl Chloro Silane

The isolation of these polymers was similar, except that more care needs to be taken in the purification of the macromonomers to ensure that difunctional materials are removed from the product. The self condensation disiloxane product formed from the hydrolysis of excess 3-Methacryloxypropyl-dimethylchlorosilane has solubility in the low molecular weight siloxane macromonomers and is present in a larger molar quantity than in higher molecular weight samples. For these reasons, the low molecular weight macromonomers are best precipitated twice to ensure complete removal of difunctional methacrylate species.

3. Free Radical Synthesis of Methacrylate-Siloxane Graft Copolymers

Graft copolymers were prepared by the free radical solution copolymerization of methacrylate monomers and polydimethylsiloxane macromonomers. Copolymers with molecular weights of approximately 100,000 g/mole were desired for optimal film forming properties. To prepare polymers of this molecular weight, it is necessary to have minimal chain transfer, a low concentration of initiator, and high concentrations of monomer in solution.

Experimentally, phase separation of macromonomer from graft copolymer occured under some conditions and further dilution with solvent must be done to prevent formation of homopolymers.

Methacrylate copolymerizations were typically run at 20-30 percent solids in toluene at 64°C with 0.1 weight percent (based on monomer) Vazo 64 as initiator. Macromonomers were weighed into the flask on a balance and then septums were attached and wired on. Next nitrogen was purged through the system for several minutes to remove air. The solvent, monomer(s) and initiator, all of which exist as degassed solutions, were then charged via syringe.

Lower molecular weights macromonomers and lower siloxane composition copolymers can be run at the high end of concentrations while copolymerizations involving macromonomers of 10,000 or 20,000 g/mole must be run at lower concentrations especially with increasing copolymer siloxane composition. Phase separation typically started to occur at about 15 percent conversion and dilution was started to maintain a homogeneous solution.

After 24-48 hours, no odor of monomer was detected and the samples were diluted if necessary and then precipitated by pouring into an appropriate non-solvent, typically methanol. After vacuum drying, the samples were extracted in a soxhlet with a solvent for polydimethylsiloxane. For methyl methacrylate copolymers hexanes or petroleum ether was a good solvent for polydimethylsiloxane but a non-solvent for the graft copolymer. Samples were then extracted for 24 hours, and redried and were then ready for analysis.

4. Anionic Synthesis of Methacrylate- Siloxane Graft Copolymers

The anionic copolymerization of methyl methacrylate and polydimethylsiloxane macromonomer was carried out in tetrahydrofuran at -78°C by a different method than is typically used for the homopolymerizations of methylmethacrylate. It is however, similar to that used for the preparation of GPC standards of methyl methacrylate.

Macromonomers were first degassed by a series of alternating nitrogen, vacuum purges. They were then charged via syringe to a clean and dry round bottom flask which had been fitted with a septum. Again, the septum had been wired on and the flask was purged with nitrogen to remove the air. Next, purified THF and methylmethacrylate monomer were charged to form a 2-3 % solution (weight/volume). A cleaned and flamed thermocouple was passed through the septum into the solution in order to monitor the reaction temperature. The solution was cooled to -78°C in a dry ice/isopropanol bath, and allowed to come to equilibrium with vigorous stirring.

In a separate round bottom flask at -78°C, a solution of diphenylhexyl lithium in THF was prepared as described previously.

0.2 ml aliquots (.1 mmole) of the DPHL solution were then charged into the monomer/macromonomer solution while watching the temperature carefully. The frequency of aliquot addition was crucial in the preparation of narrow molecular weight distribution polymers. Materials with the narrowest molecular weight distribution were prepared when aliquots are added at 1 minute intervals. When all impurities had been titrated away by the DPHL anion then polymerization will proceed. A slight exotherm of 2-3°C will be noticed within 10 -20 seconds.

At these concentrations of monomers and initiator, an exotherm of no more than 10°C was noticed which was critical for the preparation of narrow molecular weight distribution polymers as will be discussed in the results and discussion section. This also complicated the use of the thermocouple as a detector of polymerization since only small changes will be noticed. The maximum in exotherm occurered at about 2-3 minutes and then the temperature started to fall again. After the temperature reequilibrated at - 78°C in about 3-4 minutes, the reaction was stopped by addition of methanol.

Precipitation of the copolymers was carried out immediately to minimize any possible side reactions between alkoxides present in the system and the polydimethylsiloxane grafts. Precipitation into methanol, followed by drying, and extraction in a soxhlet for 24 hours to remove free polydimethylsiloxane was carried out.

5. Styrenic- Siloxane Graft Copolymers

Graft copolymers with styrenic backbone were prepared by techniques similar to the methacrylate polymerizations. Macromonomers were weighed directly into round bottom flasks and then septums are attached and wired on. Monomers were then syringed in as was the solvent cyclohexane. The initiator (Vazo-64) was also added by syringe as a solution in benzene. Toluene is to be avoided since it has a much higher chain transfer constant to styrenes than to methacrylates. Also styrenic copolymerizations must be started at about 50 weight percent solids to obtain the molecular weights desired. This caused phase separation to occur much earlier and dilution with more cyclohexane is necessary.

Phase separation was a function of macromonomer molecular weight and styrenic monomer structure. Monomers such as p-tert-Butyl styrene are much more aliphatic-like, have lower solubility parameters and phase separated to a much smaller extent.

Polymerizations were allowed to proceed 24- 48 hours for complete conversion and then were worked up by precipitation into methanol, vacuum drying, and extraction in a soxhlet with isopropanol. Again the solubility parameters of the backbone play a role in the clean up procedure. Styrenic copolymer of up to 40 weight percent siloxane can be extracted in a soxhlet with hot isopropanol. Above this level the copolymer also had limited solubility in hot isopropanol and must therefore be washed with cold isopropanol. Para-tert-Butyl styrene copolymers on the other hand have complete solubility in hot isopropanol above about 25- 30 weight percent siloxane compositions. The t-Butylstyrne copolymers were also prone to plasticization by hot isopropanol and were often recovered from the soxhlet as swollen spheres. Polymers with p-Methyl styrene as the backbone were also somewhat different, since the free siloxane was not removed by repeated washings and the copolymer seems to somehow adsorb the free siloxane homopolymer strongly.

6. Styrenic- Siloxane Diblock Copolymers

To a clean, dry, round bottom flask under a nitrogen atmosphere is charged purified THF and anionic purity styrene monomer to form a 5 weight percent solids solution. This mixture was then cooled to - 78°C, and with vigorous stirring s-BuLi was added dropwise until a slight yellow color is persistent. The calculated amount of s-BuLi was then charged very quickly with a corresponding increase in the intensity of the color to a yellow to red color, depending on the molarity of anion formed and its structure. After giving the reaction five minutes for complete polymerization, a 300% excess of the amount of D_3/cyclohexane solution was added as would be needed to achieve crossover of all of the styryl lithium chain ends. Also the cooling bath can be taken away and the solution allowed to warm to room temperature. In a matter of 1- 2 minutes the color of the living anion faded as the "transparent" siloxanolate anion is formed by the ring opening reaction. In this way minimal termination occurs, and the remaining amount of D_3 can be added to form the polymer of desired composition.

A further calculation on the relative amount of s-Buli needed to titrate away impurities as a fraction of the total amount of s-BuLi was needed to calculate the amount of excess D_3 that should be added. The alkoxides formed by titration of impurities will initiate D_3 to form homopolydimethylsiloxane as well as the block copolymer. At extremely high styrenic molecular weights the amount used to titrate can be a considerable portion of the total s-BuLi charged and would throw off the copolymer composition considerably if not accounted for.

Polymerizations were given 24- 48 hours depending on the molecular weight. Termination with trimethylchlorosilane yielded a block copolymer with a stable end group. Workup with a small amount of sodium bicarbonate to neutralize hydrochloric acid formed from reaction of excess chlorotrimethylsilane with moisture, then precipitation into methanol yielded the polymer. Extraction with isopropanol either hot with a soxhlet or cold by slurrying was under taken as described for the graft copolymers to remove any free polydimethylsiloxane.

7. Styrenic-Siloxane Diblock Macromonomers

Diblock macromonomers of polystyrene and poly(t-butylstyrene) with polydimethylsioxane were prepared as previously described for styrenic-siloxane diblock copolymers. The living styrenic block was prepared in THF at -78°C and to which was added D_3. Upon crossover the reaction was allowed to warm to room temperature and propagation took place over a 24 hour period. Termination was accomplished by the addition of 3-Methacryloxy-propyldimethylchlorosilane. Precipitation of the polymer solution into methanol yielded a powdery polymer, that was vacuum dried and extracted with cold isopropanol to remove any free siloxane. The diblock macromonomers prepared were of approximately 60-70 weight percent siloxane and were soluble in hot isopropanol.

8. Methylmethacrylate Graft Copolymers of Diblock Macromonomers

Copolymers prepared with diblock macromonomers were prepared in a similar fashion to copolymers with polydimethylsiloxane macromonomers. Polymerizations were run in toluene at about 20-30 weight percent solids at 64°C with AIBN as initiator. Reactions were complete after 24- 48 hours and workup into methanol followed by vacuum drying and soxhlet extraction with isopropanol yielded clean graft copolymers.

9. Styrenic Graft Copolymers of Diblock Macromonomers

Copolymers of PS-g-(PS-b-PSX) and PTBS-g-(PTBS-b-PSX) were prepared by the solution copolymerization of the diblock macromonomers with styrene and t-butylstyrene monomers. Conditions were similar to those used for the copolymerizations with polydimethylsiloxane macromonomers. Cyclohexane was used as a solvent, starting at about 50 weight percent solids and diluting with reaction conversion to maintain a homogeneous solution. Extraction with hot isopropanol removed any free siloxane and also unreacted diblock macromonomer.

10. Polymer Bound UV Stabilizers

Methacrylate copolymers with 4-Methacryloxy-Benzophenone at varying weight percent (1-10) benzophenone monomer were prepared by a radical copolymerization. Copolymerizations were run in toluene at 64°C with AIBN as initiator at about 25 weight percent solids.

C. Blending Studies

1. Poly(Methylmethacrylate)/ Poly(Vinyl chloride)

Blends of PMMA with PVC were prepared by a solution casting technique to investigate the compatability of the two polymers. Both atactic (free radical) and moderately high syndiotactic (anionic) PMMA were used along with chromatographic grade PVC from Aldrich. THF was found to be a common solvent for both polymers. Samples were weighed out in compositions from 1/9 to 4/6 PMMA/PVC and dissolved in THF then cast onto metal plates and covered tightly to allow the atmosphere to become saturated with THF vapors, which produced a very slow evaporation rate. With faster evaporation rates surface roughness leads to hazy films. Characterization by DSC and TEM were then conducted.

2. Poly(Methylmethacrylate-g-Poly(dimethylsiloxane))/ Poly(vinylchloride)

Blends of PMMA-g-PSX with PVC were also prepared by the slow evaporation of THF solutions with compositions ranging from 3/7 to 1/9 PMMA-g-PSX/PVC. These films were analyzed by DSC, contact angles, and TEM.

3. PMMA-g-PSX/PMMA

Blends of the graft copolymer with homopolymer of the backbone were prepared by dissolution in chloroform and slowly evaporating the solution on metal plates. Characterization by contact angles, ESCA, and TEM were then performed.

D. Structural and Compositional Analysis of Macromonomers and Copolymers

Structural characterization of homo- and copolymers involves several steps to determine that the polymer is of the composition and architecture that was desired. GPC analysis provides an idea of number and weight average molecular weights as well as evidence of mono- or bimodality of the molecular weight distribution. NMR is very useful in the determination of polymer composition and microstructure, where it exists. FTIR is useful qualitatively to determine the presence or absence of certain functional groups.

DSC and DMTA were employed to investigate the nature of phase mixing or separation in copolymers. Surface studies involed the use of contact angles and ESCA analysis. Microphase separation can be further investigated by TEM and SAXS to provide a quantitative value on phase separation.

1. FTIR Characterization

a) Instrumentation

A Nicolet MX-1 FTIR was used to obtain infrared spectra. Samples were prepared by casting dilute solutions onto NaCl salt plates. Solvents were removed by heating on a hot plate.

b) End- Capping Studies

This study was carried out by taking samples from a polymerization of D3 with time and capping these samples with chlorodimethylsilane. The Si-H absorption at around 2125 cm-1 was then measured and compared to a peak due to Si-CH3 at 1413 cm-1, which should be independent of molecular weight. By ratioing the aborptions as a function of time, it was possible to estimate the degree of polymerization. As molecular weight increases the ratio of

Si-H endgroups to Si-CH3 along the backbone should decrease, then finally level off when the final molecular weight is reached.

2. Proton NMR

1H NMR analysis were performed with a IBM 270 MHz SL instrument.

a) Macromonomer Functionality

A functional number average molecular weight was determined for macromonomers of molecular weight less than 2000, by ratioing the integration of the alpha methyl protons present on the end group to the integration of the silicon methyls along the backbone. The number obtained was the molecular weight per end group, which for perfectly functional macromonomers should agree with the absolute number average molecular weights as determined by VPO.

b) Copolymer Composition

Ratioing the intergrations of the silicon methyls to the alpha methyl protons in methacrylates or the aromatic protons in styrenic copolymers allowed for a determination of the mole or weight percent siloxane in the block or graft copolymers by the following type of calculation.

Weight % Monommer B= Weight B/(Weight A + Weight B)

Weight B= Molecular Weight B * # moles B

Weight% B = MW B* moles B/(MW A * moles A + MW B* moles B)

moles B = integration B/ number of protons integrated in B

With integrations from the NMR analysis of the copolymer and knowledge of repeat unit molecular weight and structure, weight percentages were determined. Terpolymers were also analyzed given adequate resolution of the various peaks and all of this was fitted to a computer program for ease of calculation when a number of samples are to be analyzed, as is shown in Appendix 1.

c) PMMA Tacticity

The tacticity of poly(methylmethacrylate) can be determined by H^1NMR analysis of the alpha methyl resonances. Three stereochemical triads exist leading to three resonances in the range of 0.8 to 1.3 ppm relative to tetramethylsilane. Table 9 lists shifts and their assignments, and in Figures 7 and 8, typical spectrum are shown for free radical and anionic PMMA respectively.

3. UV Spectroscopy

UV spectra were run on a Perkin Elmer 552 instrument, typically scanning from 350nm to 190nm at 20nm/min.

A wavelength maximum of 214nm was established for the unsaturated methacrylate group. Methyl methacrylate was

Table 9

α-Methyl Proton Shift Assignments

Shift ppm	Tacticity
0.8 ppm	Syndio
1.0 ppm	Atactic
1.25 ppm	Iso

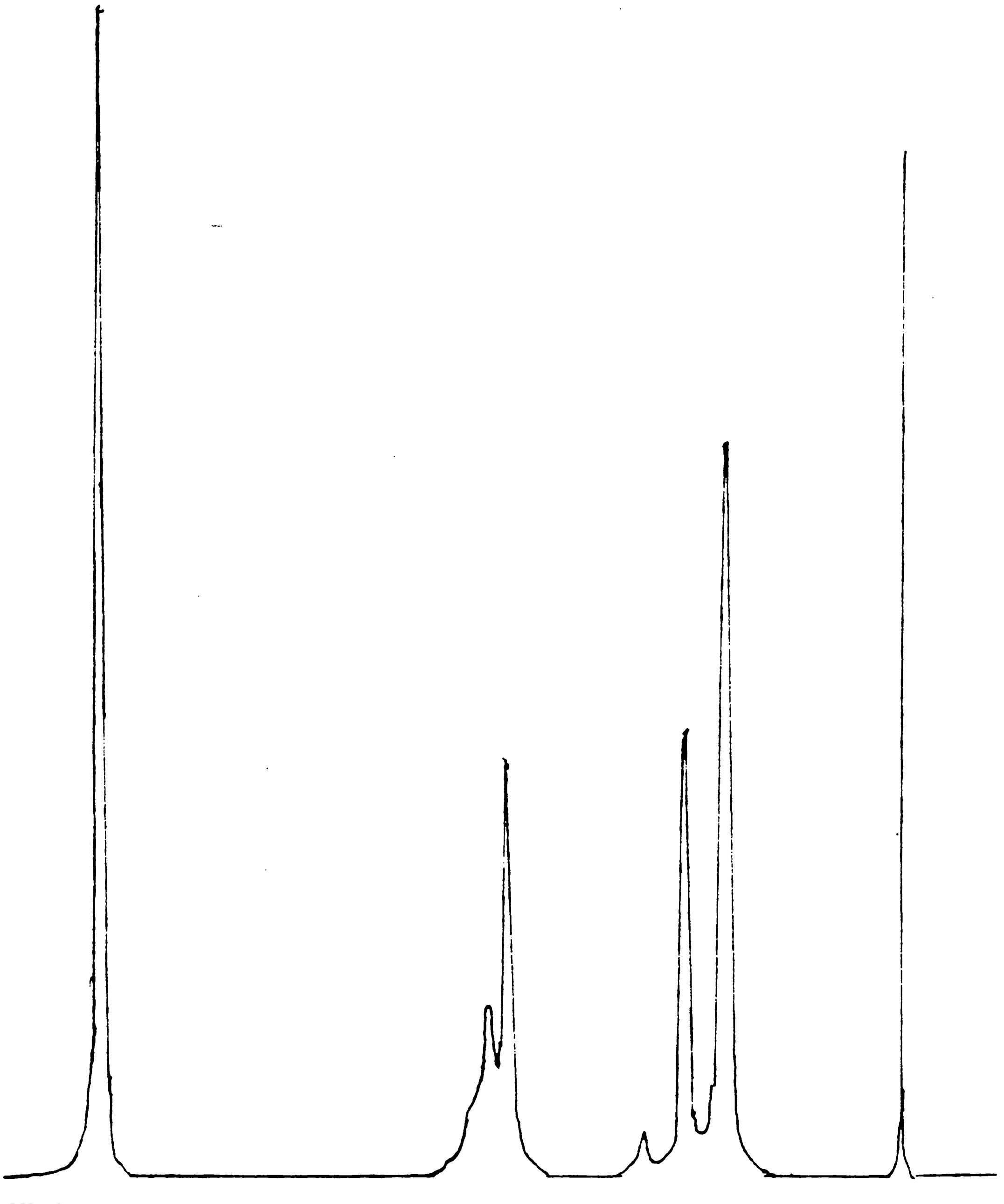


Figure 7. NMR Spectra of Atactic PMMA

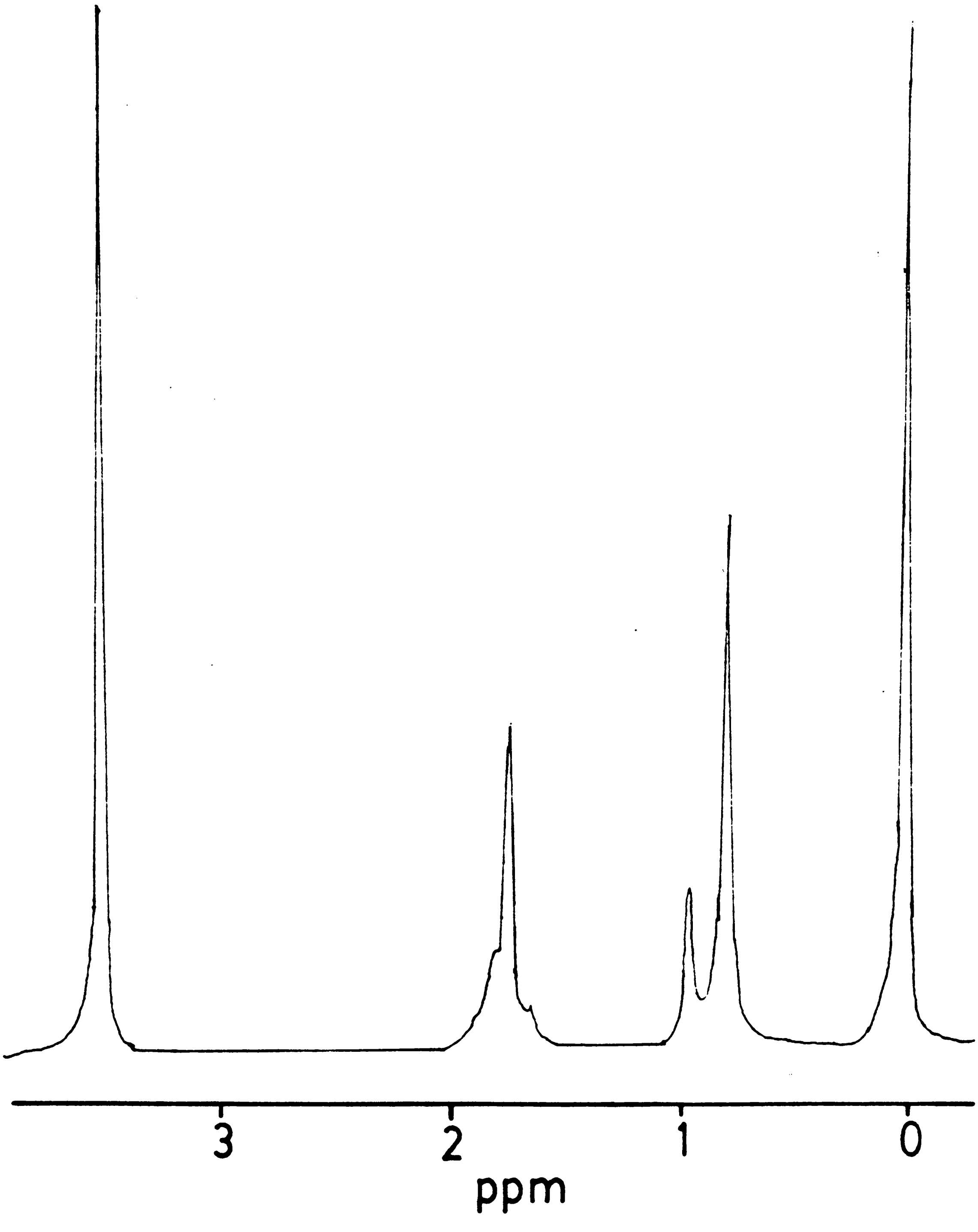


Figure 8. NMR Spectra of Syndiotactic PMMA

used as a standard in THF solutions to prepare a Beers Law plot with slope of 5110 Abs. liter/mole and a correlation coeeficient of 0.999. Macromonomer solutions of known concentration in THF were then prepared and analyzed. We then extrapolated the absorbance back on the Beer's law plot to a methylmethacrylate concentration. One could then divide the macromonomer concentration in terms of grams/liter, by the methyl methacrylate concentration in terms of moles/liter and the number obtained is the functional molecular weight in terms of grams of polymer per mole of end functional methacrylate group. Again, this functional molecular weight can be compared to an absolute number average mlecular weight for a determination of functionality. The UV technique seems appropriate for molecular weights as high as 30- 50,000 grams/mole.

4. Vapor Phase Osmometry (VPO)

Vapor phase osmometry was run in toluene using sucrose octaacetate as a standard.

Solutions of macromonomer in toluene were analyzed by VPO to determine their number average molecular weight as a comparison to the functional molecular weights as determined by UV and NMR techniques.

5. Size Exclusion Chromatography

Polymers were analyzed by Gel Permeation Chromatography (GPC) in a Waters 150-C with ultra styragel columns of 500A, 1000, 10,000, 100,000, and 1,000,000 A porosities with THF solvent. PMMA and Polystyrene standards(Polysciences) were used to determine number average molecular weights. A refractive index detector and a UV detector were used.

a) Polydimethylsiloxane Analysis

The refractive index of polydimethylsiloxane is very close to that of THF and it has no significant UV absorption of its own. Pure polydimethyl siloxane was hard to analyze, except by overloading the solution with sample. However macromonomers were easily analyzed by using a UV detector set at 214nm to monitor the methacrylate head group.

b) Molecular Weight Distributions

Analysis of polymers by GPC results in a trace of concentration versus elution volume. A further step in the analysis is the use of a computer program to analyze the slice data and compare it to standards from which a linear and or cubic fit can be obtained. This allows the generation of number and weight average molecular weights as well as accurate molecular weight distributions. A program was written to analyze the data by both linear and cubic fits which is given in Appendix 2.

It was typically found that the cubic fit was better and gave narrower distributions, due to errors occuring in the linear fit.

c) Macromonomer Incorporation Studies

Samples were taken with time from a macromonomer copolymerization and analyzed by GPC to show the dissappearance of macromonomer and formation of copolymer. One difficulty was in finding an appropriate detector to measure both components. As mentioned earlier, the macromonomer provides no response to the refractive index detector. Monitoring of the 214nm band by the UV detector fortunately allowed for an easy analysis. It was important to be able to use a single wavelength to detect both species throughout the range of conversions at a constant detector sensitivity. The absorptivity of the macromonomer is approximately 5000 Abs. liter/mole, while the backbone is of the order of 30 Abs. liter/mole. Thus small amounts of macromonomer can be detected and large amounts of copolymer do not "swamp out" the measurement at high conversions.

d) Molecular Weight Calculation Methods

As mentioned, PMMA and PS standards were used to give number and weight average molecular weights which can only be considered equivalent molecular weights for copolymers.

A complicating factor is that branching in graft copolymers leads to changes in hydrodynamic volume.

By a combination of the above mentioned GPC techniques with a differential viscometer detector, absolute molecular weights can be obtained. Computer analysis of the two detectors response as compared to standards used to set up a universal calibration curve generate absolute values of number average molecular weight for each "slice" and can therefore generate number and weight average molecular weights of the entire copolymer. Also, higher orders of molecular weight can be generated as well as intrinsic viscosity and Mark-Houwink constants.

6. Super Critical Fluid Extractions (SCFE)

Super Critical Fluid Extractions were performed on some PMMA-g-PSX copolymers as a method of compositional separation for heterogeneity determination. SCFE's were performed by Dr. Val Krukonis and coworkers at Pasex Corporation using butane as a carrier.

A temperature of approximately 150- 160°C was used with a pressure starting at 1500 psi. Increasing pressure was used to extract out less soluble materials.

Ten gram samples were typically fractionated into 5 or 6 fractions and analyzed by NMR and GPC for composition and molecular weight.

7. Membrane Osmometry

Diblock copolymers of the styrenic-siloxane copolymers and PMMA-g-PSX copolymers were analyzed by membrane osmometry to confirm their molecular weights as estimated by other techniques, since no standards are available for such block or graft copolymers for GPC.

Toluene was used as a solvent in a Wescan Model 231 membrane osmometer, for analysis of diblock copolymers. Graft copolymers were analyzed by Dr. Stejskal at the Institute of Makromolecular Chemistry.

8. Intrinsic Viscosities

Viscosity measurements were obtained with a Canon model 100 viscometer in methylene chloride and or THF at 25°C. Concentrations used ranged from 0.2 to 0.5 g/dl.

9. Light Scattering

Measurements were done at the Institute of Makromolecular Chemistry in Prague, Czechoslovokia, at low angles, (< 10 degrees), typically 6-7 degrees in the forward direction. A series of solvents (Methyl ethyl ketone, THF, Dioxane, Toluene, tetralin, p-dichlorobenzene and trichlorobenzene) were used. A plot of the apparent weight average molecular weight versus refractive index increment was prepared. At zero refractive index increment this should be the true weight average molecular weight.

Solvents having the same refractive index as one component of a copolymer are said to be isorefractive with that component. These solvents can then be used to determine the weight average molecular weight of the other copolymer component since the isorefractive component does not contribute to the scattering. Thus, toluene is isorefractive for poly(methyl methacrylate) and tertrahydrofuran is isorefractive for poly(dimethyl siloxane). Weight average molecular weights were determined for the overall copolymers as well as the entire copolymer. Number average molecular weights of the individual components can be determined by multiplying the number average molecular weight obtained by membrane osmometry by the weight percent of that component in the copolymer. Therefore, it was possible to determine the absolute molecular weight distributions of not only the copolymer as a whole but also of each of the components.

Heterogeneity factors were determined, for PMMA-g-PSX copolymers, as well. Homogeneous copolymers and homopolymers show no variation of apparent weight average molecular weight as a function of solvent refractive index. The parabolic curvature found in a plot of apparent weight average molecular weight versus refractive index increment was then used to determine the heterogeneity factors P, P/<Mw>, Q and also Q/<Mw>.

10. Thermal Analysis

a) Differential Scanning Calorimetry (DSC) Tg's

DSC thermograms were obtained on a Perkin Elmer DSC-2 run at 10°C per minute. Glass transition temperatures were measured at the midpoint of the transition. High and low temperature transitions were measured.

b) DSC Mixing Studies Delta Cp

The measurements obtained above were also used to investigate the degree of mixing by measuring the delta Cp of the transition. These values were then compared since mixing should lower the Cp of transition.

c) Dynamic Mechanical Thermal Analysis (DMTA)

DMTA spectrum were obtained on a Polymer Labs DMTA at a frequency of 1 Hz. with a temperature range of -150°C to +150°C at a scan rate of 5°C per minute.

d) Thermal Gravimetric Analysis (TGA)

TGA data was obtained on a Perkin-Elmer System 2 instrument, under nitrogen and air atmospheres at a heating rate of 10°C / minute.

11. Transmission Electron Microscopy (TEM)

TEM analysis were carried out on a Phillips IL 520 STEM at 100kv in the TEM mode by Greg York. Films were either cast as a dilute solution in chloroform onto a water surface or allowed to dry slowly to thick films then ultracryomicrotomed at -100°C.

12. Scanning Electron Microscopy (SEM)

SEM analysis was also carried out on the Phillips IL 520 STEM in the SEM mode. Samples were first coated with a film of platinum/palladium which were approximately 100 angstroms thick by Stephen McCartney.

13. X-Ray Photon Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA analysis was carried out on a Kratos XSAM-800 instrument with Mg anode, 200 watts at a vacuum of 10^{-9} torr by Stephen McCartney.

Variable angle work was done to determine the composition as a function of depth of the surface over the top 70- 100 A. More information on this type of work can be found in the Master thesis' of N. Patel and G. York [379].

14. Contact Angles

Films of various homo- and copolymers were prepared by casting dilute solutions onto metal plates and allowing the slow evaporation of solvent. Drops of water were then applied to the surface in increments of 2 microliters to 20 microliter total dropsize. This advancing angle measurement obtained by the use of a goniometer is repeated in 2 to 3 spots across the film. Typically the angle increases with drop size until the drop size reaches about 6- 8 microliters then levels off. The measurements from 3 spots are averaged. The difference in reults is approximately plus or minus one degree.

15. Small- Angle X-Ray Scattering (SAXS) were obtained by G. L. Wilkes and Hao Hsim Huang with a Siemens Kratky camera system in conjuction with an M. Braun position sensitive detector from Innovative Technology Inc. Optimal slit widths of 100µm were used. Invariant calculations were performed to determine levels of phase mixing.

V. RESULTS AND DISCUSSION

A. Synthesis of Siloxane Homopolymers

The anionic ring opening polymerization of D_3 or hexamethylcyclotrisiloxane is, somewhat surprisingly, not very well characterized in the literature. Alkyl lithium initiated polymerizations theoretically should allow the preparation of well defined living polymers, without equilibration side reactions that typically occur with most catalysts. The lithium siloxanolate anion is a relatively unreactive ion pair that does not propagate in hydrocarbon solvents. However, addition of polar promoting solvents such as ethers activates the ion pair and attack on monomer occurs. The highly strained cyclic trimer readily reacts with the promoted siloxanolate ion and under the proper conditions the ion pair will attack the strained cyclic, but will not induce equlibration by reaction with the preformed polysiloxane chain. The lack of reaction is therefore based on the kinetics of the two reaction steps (propagation vs. redistribution).

Many reports have indicated that these polymerizations are best terminated at 70-90% conversion if one wishes to obtain the narrowest molecular weight distributions and avoid equilibration reactions [174-177]. Their logic is based on kinetic arguments that the monomer is attacked at a much higher rate than the linear chain.

Thus, in the presence of monomer, backbone attack should be minimal.

A question remains to be answered therefore, whether the polymerization and side reactions are thermodynamically or kinetically controlled. Unfortunately no data has been published to clarify up this question, other than the advice that better results are obtained with short stopping of the reaction.

Initial research reported herein was therefore directed at characterization of the polymerization of hexamethylcyclo-trisiloxane. Monomer was purified as described in the experimental section and characterized by DSC analysis of the melting points before and after sublimation. Monomer purification was principally intended to remove higher cyclics and oligomeric siloxanes, since it is a very hydrophobic compound.

The melting point was rather broad before sublimation, as shown in Figure 9. However, the post sublimation product showed a very narrow melting range indicating high purity. Liquid chromatography analysis (HPLC) also showed the sublimed monomer to be pure.

The solvent chosen for monomer dilution, storage and polymerizations was cyclohexane, since much work has already been done on polymerization of styrenic monomers in cyclohexane. Thus, cyclohexane was known to be

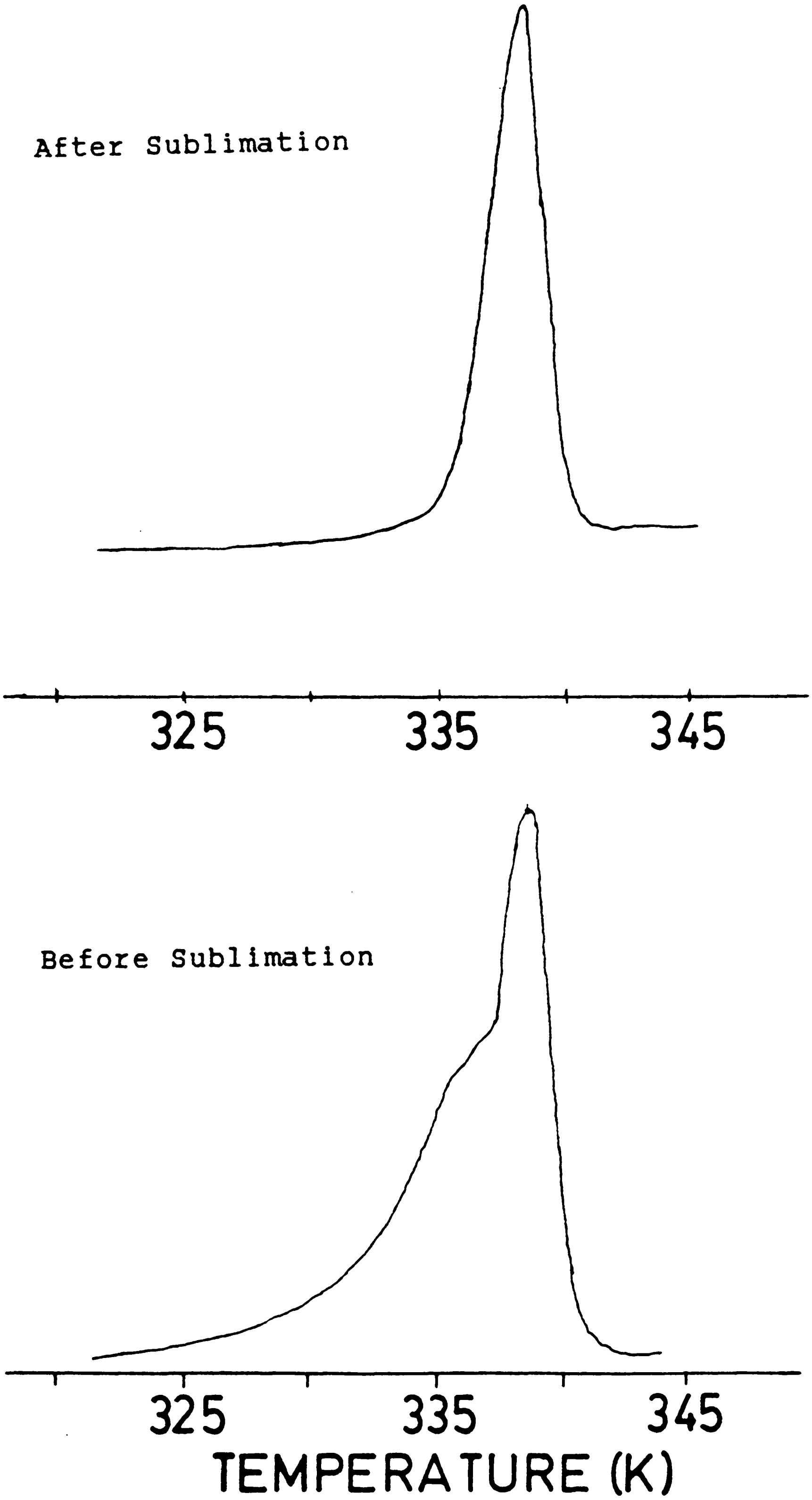


Figure 9. DSC Analysis of D_3 Purity

compatible for the subsequent copolymerizations. Also, cyclohexane is a good choice for long term storage due to its lack of side reactions and hydrophobic character. Finally, the choice of cyclohexane was also based on the fact that initiation was to be carried out in a hydrocarbon solvent and promoting solvents, which are often reactive with strong bases, could be added in a second step, which should help to avoid side reactions.

Various initiators were used such as n-butyl lithium, s-butyl lithium, oligomeric styryl lithium, and diphenyl hexyl lithium. One of the problems with n-BuLi as an anionic initiator in some systems is that its high degree of association results in a slow initiation. Initiation must be rapid relative to propagation to obtain narrow molecular weight distributions. The choice of cyclohexane as a solvent however allows the initiation to be completed before adding a promoting solvent, which is necessary for propagation. Thus, we can force initiation to be rapid relative to propagation even for slow initiations.

Initiators based on s-butyl lithium work well as do those based on styryl lithium oligomers. Diphenyl hexyl lithium however does not initiate D_3 either in pure cyclohexane or in the presence of even large amounts of THF. The steric hinderance of the anion can be assumed to be the reason for the effect. The same trend of initiation rates of D_3, by the polymeric series styryl lithium, p-methylstyryl lithium, and p-t-butyl styryl lithium was also observed and will be discussed.

Initiation with s-Butyl Lithium and termination with chlorotrimethyl silane produces a polymer which has a refractive index nearly identical to THF and has no UV absorbance. These features limit characterization by standard GPC techniques. Oligomeric styryl lithiums are useful as initiators since the polymer produced has a UV absorbance. These efforts demonstrated that narrow distribution homopolymers could be prepared.

Termination with chlorosilanes is another controversial matter in the literature. For many years termination with chlorosilanes was undertaken with simple mechanical stirring. Yamashita has however reported some inconsistent results with simple stirring, and has recommended that sonification be carried out to increase the yields of termination [183-188]. Very little consistent data has been presented however that show the advantage of sonification. The major disadvantage of sonification is the danger of chain scission that sonification can cause. Many reports have appeared in the literature on the chain scission ability of sonification. One possible explanation of some of the inconsistencies reported without sonifications lies in the induction period that seems to follow after addition of chlorosilane. Typically, after addition of terminating agent a slight exotherm occurs in the solution, especially when sufficiently concentrated. This would indicate that termination was, in fact occuring. However, there is often an induction period before precipitation of lithium chloride occurs, but once precipitation starts there is usually a rapid growth of particle size. Sonification could possibly be activating the particle growth, and without sonification the reaction probably proceeds but not always at the same rate. The results obtained in this work would indicate that sonification was not needed to obtain quantitative termination.

Kinetic studies were conducted in which samples of a living polymerization were taken with time and terminated with chlorodimethyl silane. Poly(dimethylsiloxanes) were then obtained with terminal Si-H functionality. The concentration of end groups is detectable by FTIR even up to very high molecular weights (~50,000 g/mole) due, to the high absorptivity of the Si-H functionality at about 2125 cm^{-1}. Figure 10 depicts a typical FTIR spectra with the Si-H peak labeled.

GPC's were also run on the polymers to evidence that molecular weight increased with time and that broadening of the molecular weight distribution did not occur after

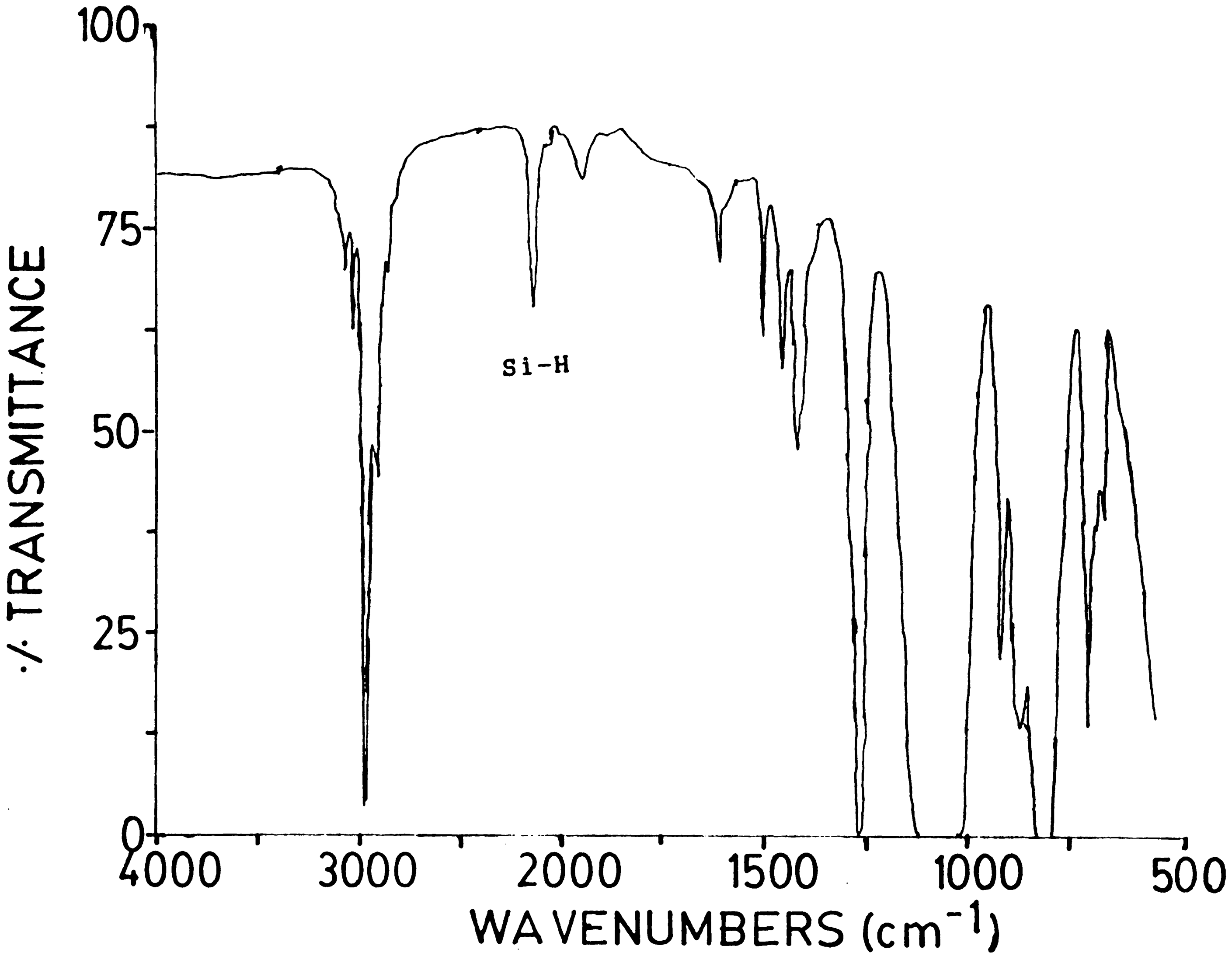


Figure 10. FTIR Spectrum of Si-H Functional PSX

the reaction went to completion.

Figure 11 shows a plot of the ratio of the absorbances of the Si-H endgroups to the Si-methyls along the polymer chain. Measurements at 2125 cm-1 and 1413 cm-1 were used for the respective functionalities. As can be seen the ratio intially changes linearly with time until complete conversion is achieved, as confirmed by GPC molecular weights and gravimetric analysis of the samples. Samples were taken for an additional 36 hours, and GPC indicated no change in molecular weight or molecular weight distribution.

Polymers were prepared with molecular weights from 1000 g/mole to 100,000g/mole and all had narrow molecular weight ditributions (<1.2) based on polystyrene standards. Characterization of these polymers by DSC, showed some interesting results of the molecular weight effect on thermal properties. Figures 12-14 show the DSC thermograms of a series of poly(dimethyl siloxanes) with molecular weights from 10,000 to 100,000 g/mole. It is evident that the Tc's and Tm's change dramatically as a function of molecular weight, and only at molecular weights above 20K is the typical bimodal melting point seen.

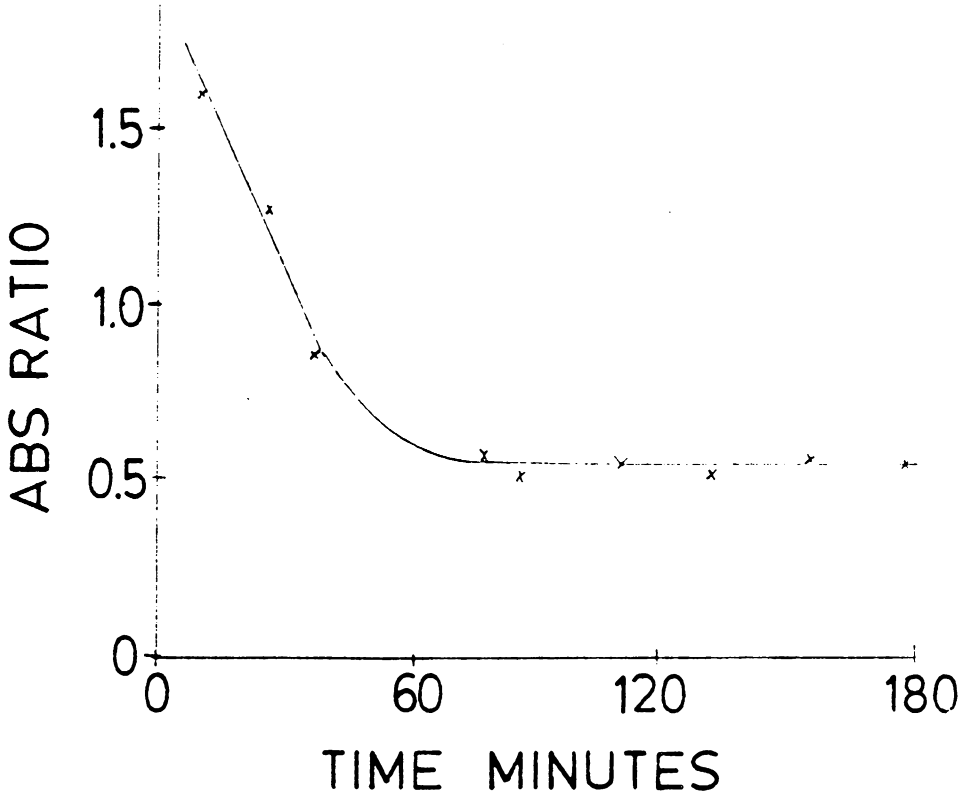


Figure 11. Ratios of Si-H/ Si-CH3 as a function of Reaction Conversion

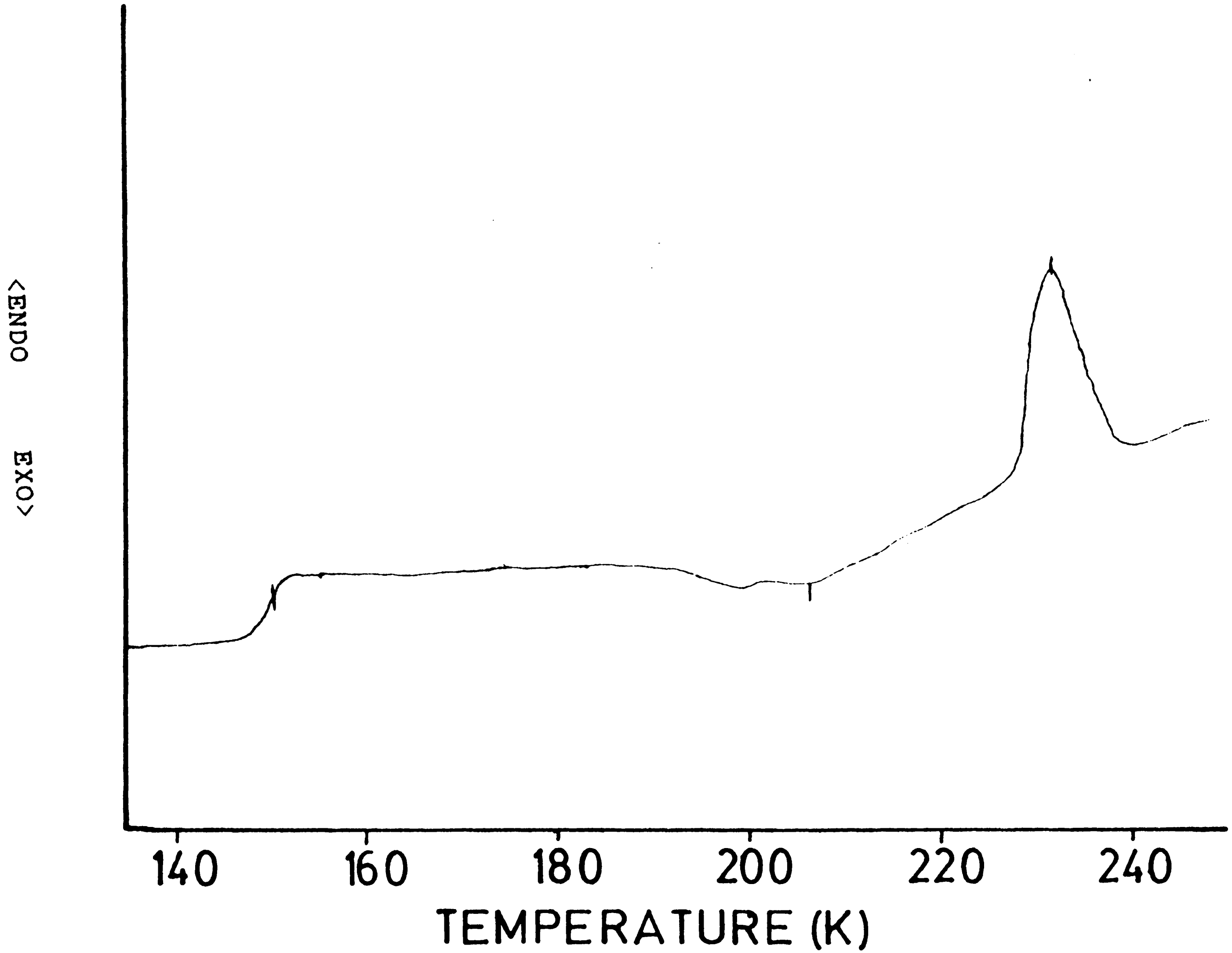


Figure 12. DSC of 10K Poly(dimethyl siloxane)

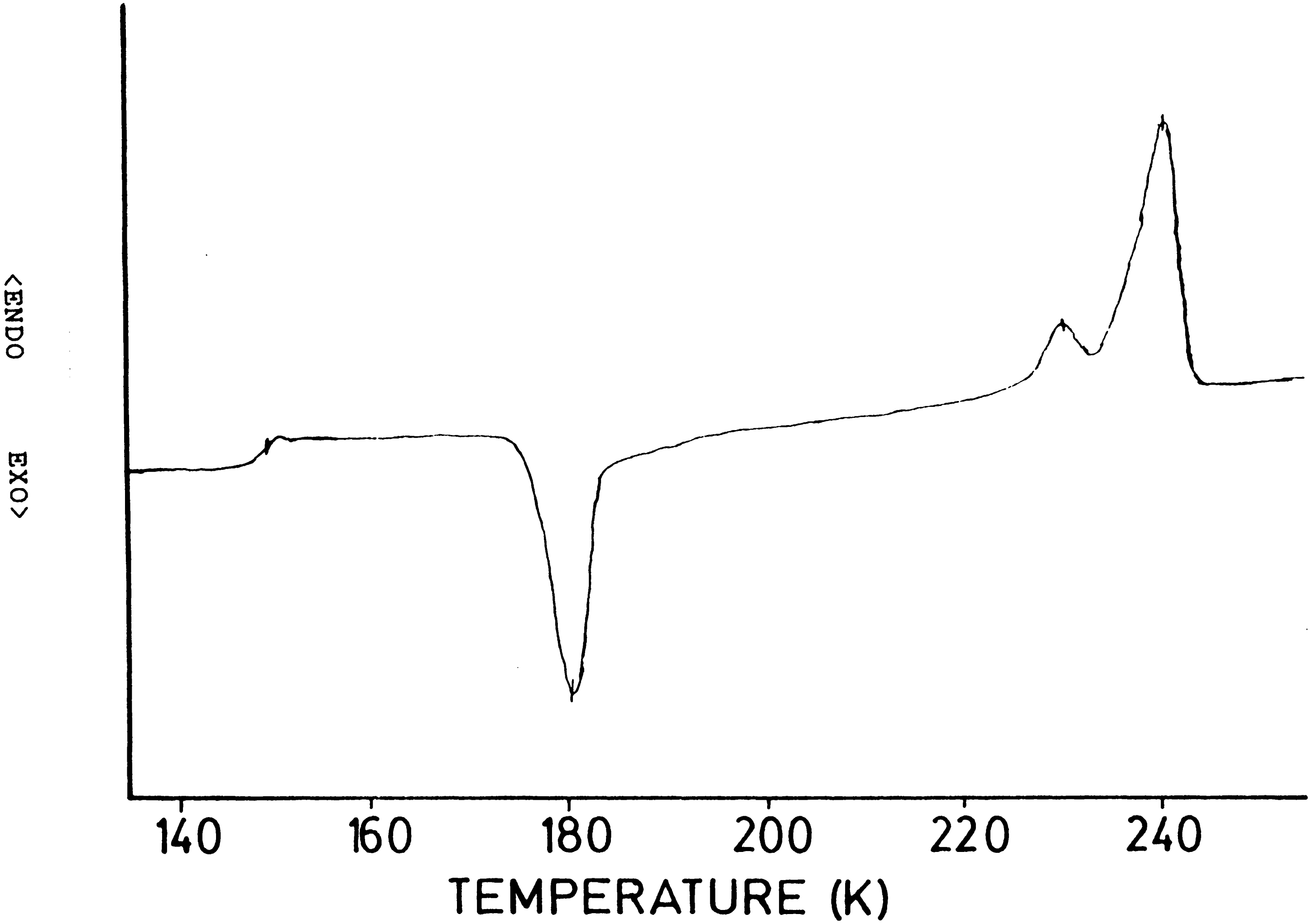


Figure 13. DSC of 20K Poly(dimethyl siloxane)

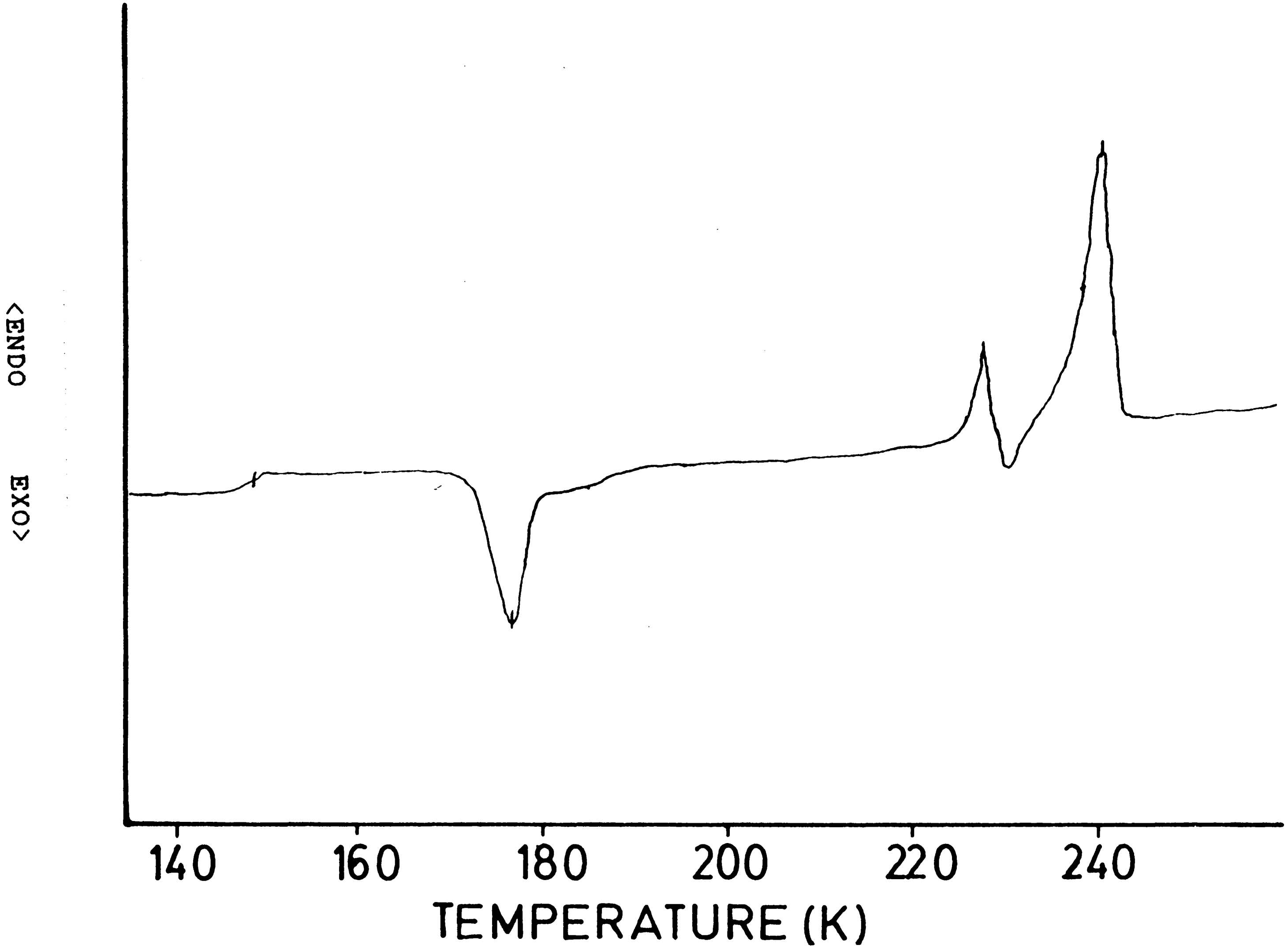
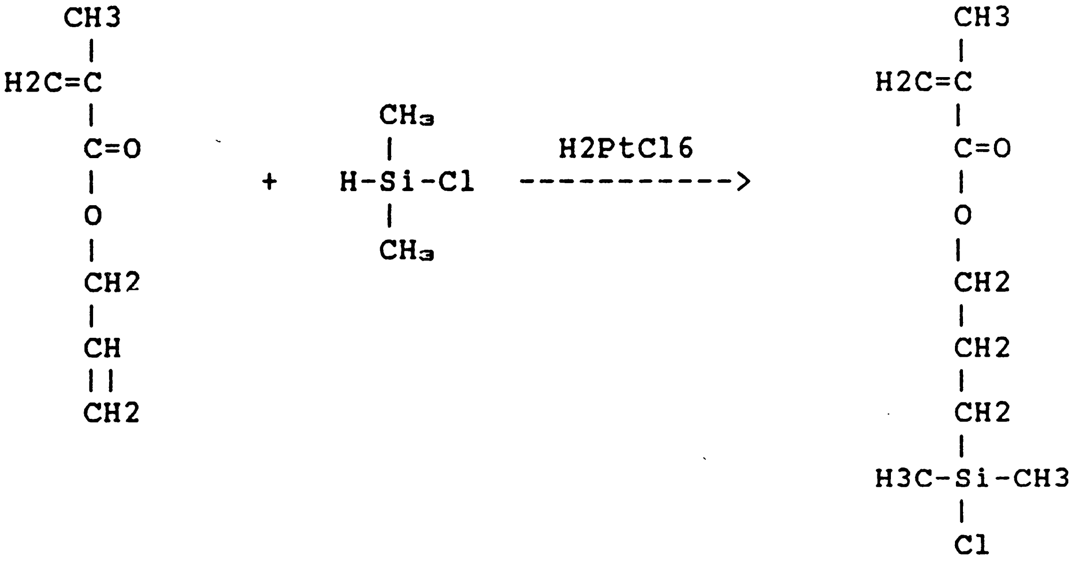


Figure 14. DSC of 100K Poly(dimethyl siloxane)

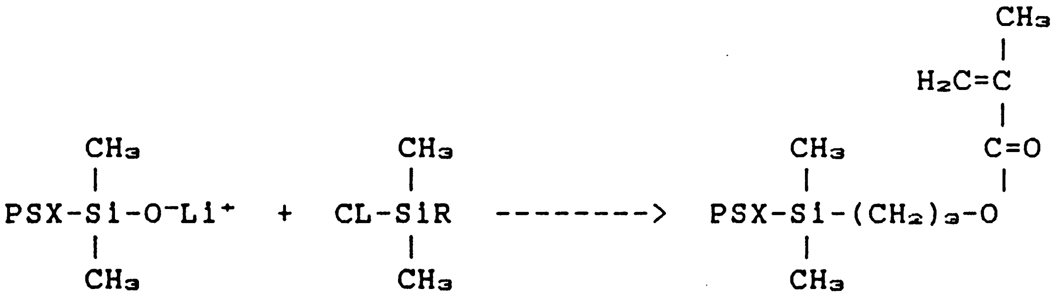
B. Synthesis of Siloxane Macromonomers

The preparation of siloxane macromonomers involved changing the termination agent from chloro dimethyl silane to 3-Methacryloxy-propyldimethylchlorosilane. This compound is an adduct prepared by the hydrosilylation of allyl methacrylate and chlorodimethyl silane, as depicted in Scheme VII. The living siloxanolate anion diplaces the chloride to eliminate lithium chloride, but the anion is too weak to attack the methacrylate functionality, as shown in Scheme VIII.



$$H_2C{=}C(CH_3)\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}CH{=}CH_2 + H\text{-}Si(CH_3)_2\text{-}Cl \xrightarrow{H_2PtCl_6} H_2C{=}C(CH_3)\text{-}C(=O)\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Si(CH_3)_2\text{-}Cl$$

Scheme VII. Hydrosilylation of Allyl Methacrylate To Form The Terminator

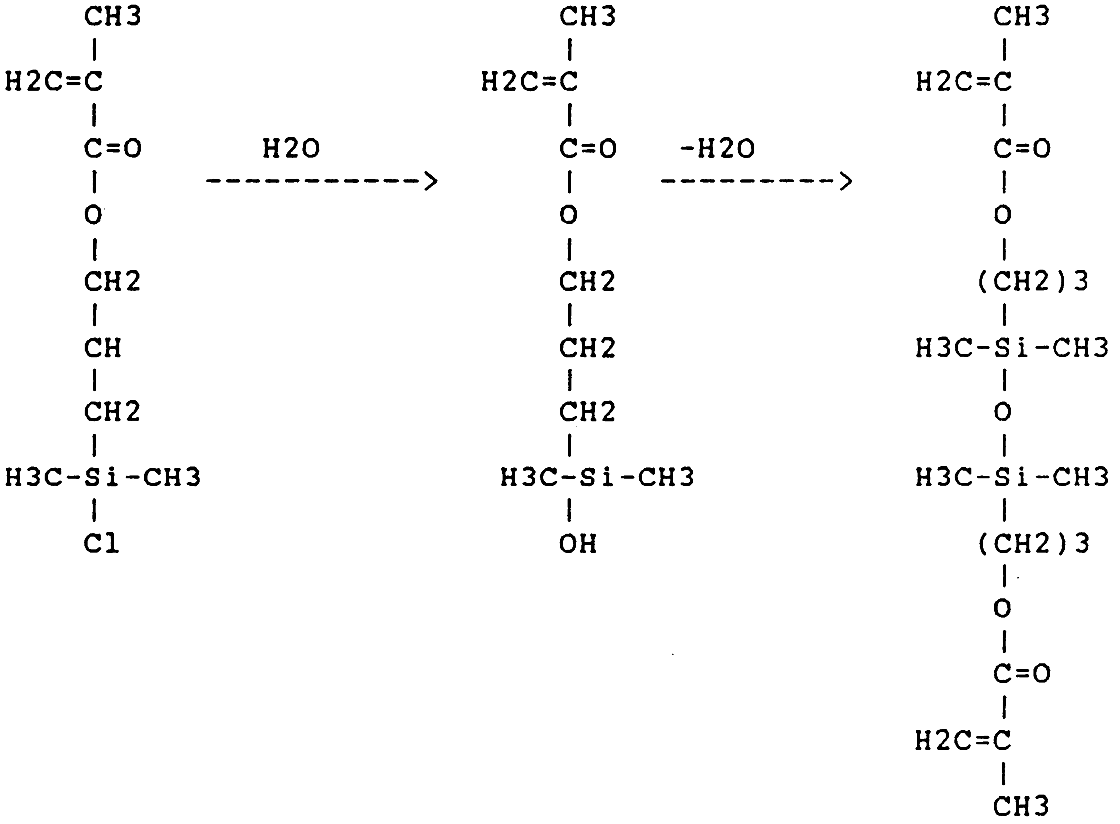


$$\mathrm{PSX{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O^{-}Li^{+}} + \mathrm{CL{-}\overset{CH_3}{\underset{CH_3}{Si}}R} \longrightarrow \mathrm{PSX{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}(CH_2)_3{-}O{-}C({=}O){-}C(CH_3){=}CH_2}$$

Scheme VIII. Reaction of A Siloxanolate With A Terminator To Form The Macromonomer

The macromonomers once terminated were then precipitated into methanol and neutralized with sodium bicarbonate. Excess terminating agent will react with water to form hydrochloric acid and silanols. Hydrochloric acid should be neutralized to prevent equilibration side reactions later on. Silanols will typically self condense to form difunctional methacrylate species, as shown in Scheme IX, and should also be removed to prevent gelation during the copolymerizations. The dimethacrylate species is readily soluble in methanol and precipitation seems to remove it well, in cases when macromonomer molecular weight is above 3000 g/mole. On very low molecular weight macromonomers however the partial solubilities becomes a problem. The dimethacrylate adduct has a molecular weight of 388, and the weight of the methacrylate end group in low molecular weight macromonomers plays a significant role in the solubility. Thus low molecular weight macromonomers are best precipitated twice to obtain pure monofunctional species.

The characterization of the macromonomers included GPC, VPO, UV spectroscopy, FTIR, and NMR. The methacrylate end capping agent provides a label which can be used to characterize the macromonomer. As mentioned, poly(dimethyl siloxane) is a UV transparent polymer, while the methacrylate functionality has a strong absorbance around 214nm, as can be seen in Figure 15. Thus GPC's can be run with a UV detector set at 214 nm. to detect macromonomer. More importantly, the UV absorbance of the end group can



Scheme IX. Reaction of Terminator To Form Silanols and Dimethacrylate

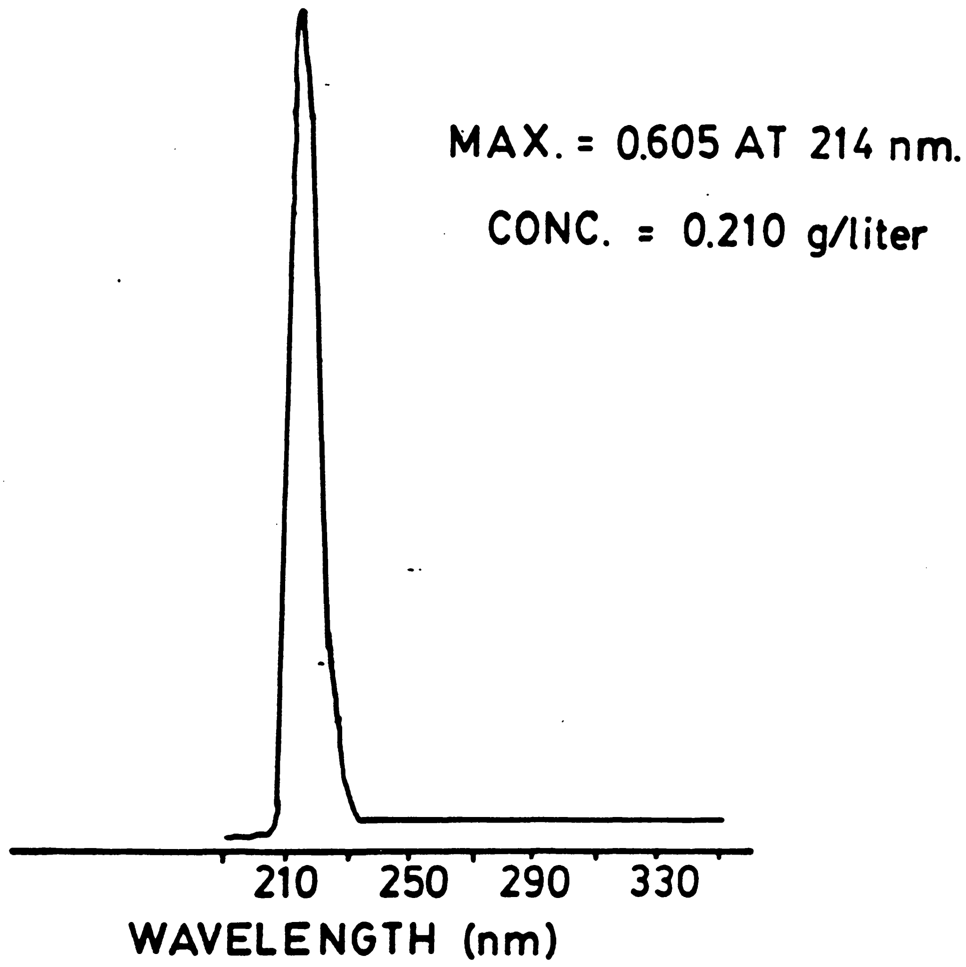


Figure 15. UV Spectrum of a Macromonomer with Mn of 1600

be used to establish an end group functional molecular weight and functionality. A series of solutions of methyl methacrylate in THF were analyzed by UV spectroscopy to prepare a Beer's Law plot of absorbance versus methacrylate concentration. Macromonomers were then analyzed to determine their effective methacrylate concentration. Thus, end group functional molecular weights were obtained. NMR analysis of low molecular weight PSX macromonomers also provides functional molecular weights, but above number average molecular weights of about 2-3000 g/mole, the concentration of methacrylate groups is so low that the ratioing is insensitive.

Absolute molecular weights were also determined by Vapor Phase Osmometry or VPO, and a comparison of some of the numbers obtained can be seen in Table 10. Generally, the functional molecular weights should be higher than the absolute number average molecular weight if functionality is less than one. As can be seen experimental error causes overlap in either direction, and thus we assume that high functionality was achieved. Another indirect check was the copolymerizability and incorporation into copolymers.

Macromonomers in the molecular weight range 1000-20,000 g/mole range were synthesized. In particular, macromonomers of molecular weight 1K, 5K, 10K, and 20K

Table 10

Determination of the Functionality of PSX Macromonomers by various Methods

Sample	H NMR[a]	VPO[b]	UV[c]
1	---	6500	6000
2	1600	1500	1700
3	900	1030	900

a) Comparison of Silicon Methyls with Methacrylate Methyl

b) Solvent: toluene

c) From Methacrylate Absorbance (214 nm) were used for the preparation of graft copolymers, in order to provide a good range of compositions and hence properties.

C. Alkyl Methacrylate- Siloxane Graft Copolymers

Initial investigations were run in benzene and toluene at varying solids concentrations with AIBN as initiator. It was found that macroscopic phase separation could occur at an early stage in the copolymerization under certain conditions. These were identified as high macromonomer molecular weights, poor cosolvents, and high solids reactions. The composition also plays a role, since either low or high macromonomer levels did not phase separate badly. In contrast, certain "mid range" amounts of macromonomer were very incompatible. Milkovich explained this effect in terms of phase volumes and phase diagrams.

Toluene was found to be a good cosolvent and did not show problems of chain transfer with the methacrylate monomers. Table 11 summarizes the rate constants of propogation and transfer for methyl methacrylate and styrene for cyclohexane and toluene. It was surprising that the chain transfer constants for both monomers were similar for toluene. The high molecular weights obtained in the methacrylate polymerizations in toluene can be explained by the fact that the rate of propogation is a

Table 11

Rate Constants for Methyl Methacrylate and Styrene Polymerizations at 60°C

Monomer	k_p	Cs(Toluene)	Cs(cyclohexane)
MMA	515	0.15	---
Styrene	165	0.125	0.031

k_p units liter/mole-sec.

$Cs = k_{t,s}/k_p$

factor of three to four times higher in the methacrylate case, than with styrene. Concentrations of 20-30% solids were adequate to afford high molecular weight film forming materials and minimal amounts of phase separation occured during the polymerization.

Copolymers with the 1K, 5K, 10K, and 20K macromonomers were synthesized under the above conditions over a composition range of 5-50 weight percent siloxane.

Characterizations by NMR, GPC, Super Critical Fluid Extractions, Membrane osmometry, Light scattering, DSC, DMTA, Thermal Gravimetric Analysis (TGA), contact angles, ESCA, SAXS, and TEM, were carried out to determine the effect of architecture on copolymer structure and physical properties.

Table 12 presents some typical data for the composition of copolymers in comparison to the charged composition. Generally incorporations in the 70-90% of theory, range were achieved; although the higher molecular weight macromonomers seem to incorporate to a lesser extent, possibly due to the higher degree of phase separation during copolymerization. The reasons for lack of incorporation can be attributed to several factors, including lack of functionality or incorporation into extremely short methacrylate chains which are then extracted with the pure siloxane. Also the

Table 12

Siloxane Macromonomer Incorporation Into PMMA Graft Copolymers

Macromonomer Mn	WT% Charged	WT% Via NMR
1000	5	4
	10	8
	20	15
	40	32
5000	5	>4
	10	7
	20	13
	40	32
10,000	5	5
	10	10
	20	16
	40	30
20,000	5	4
	10	7
	20	12
	40	25

copolymerizability is a function of the absolute reactivity of the two monomer structures, and of the steric problems involved in the copolymerization of the macromonomer. Importantly, in the styrenic-g-PSX section one notes that incorporation of the macromonomer is better due to the better copolymerizability of styrenic monomers with methacrylate end groups. It would therefore probably be beneficial to polymerize styrenic end group macromonomers with methacrylate monomers, and methacrylate end group macromonomers with styrenic monomers.

One ramification that occurs when the reactivity of the macromonommer is lower than that of the monomer is that as the reaction occurs, the unreacted mixture of monomer and macromonomer becomes rich in macromonomer. As the feed ratio changes we might expect a significant upturn in siloxane content in the copolymer formed later in the reaction. Investigations of the kinetic aspect of the copolymerization were undertaken to clarify this point and others. Polymerizations of methyl methacrylate and 5000 molecular weight poly(dimethylsiloxane) macromonomer were carried out under the standard conditions and samples were taken as a function of time. Analysis of these samples by proton NMR and GPC showed that no large amount of residual macromonomer remains after the reaction, if the copolymerization were kept homogeneous. Tables 13 and

14 show data for two typical polymerizations at different levels of siloxane. Figure 16 represents the series of GPC chromatograms of samples taken with time from a copolymerization with 20 weight percent siloxane. It can be seen that macromonomer content decreases as the amount of copolymer formed increases.

The composition of the copolymer remained constant within experimental error, throughout the reaction. Phase separation, the diluted state of the macromonomer chain ends near the end of the polymerization, and limited chain mobilities may restrict the copolymerization from forming materials extremely high in siloxane content. The final extraction with a solvent for siloxanes might also remove copolymers that are extremely high in siloxane content and therefore skew the data.

Before proceeding into a discussion on branched structure it would be helpful to characterize the architecture present in these systems as a function of graft molecular weight and composition. Therefore, calculations were performed to determine the number of grafts per chain, assuming a total number average molecular weight of 100K. Of course there will be a distribution present in a copolymer, but this calculation was performed to provide some idea of what the average chain might look like. In Table 15, we can see three

Table 13

NMR Analysis of PMMA-g-PSX Copolymers as a Function of Conversion (20 WT% PSX 5K Grafts)

Sample	Conversion	% PSX
B	11%	19.1%
C	20%	19.5%
D	27%	22.6%
E	31%	19.8%
G	60%	22.3%
J	83%	18.6%
K	90%	21.5%
L	95%	22.5%
M	97%	20.9%
N	99%	21.0%
O	100%	21.2%

Table 14

NMR Analysis of PMMA-g-PSX Copolymers as a Function of Conversion (40 WT % PSX 10K Grafts)

SAMPLE	Time	%PSX
C	3 hr.	36%
D	5 hr.	39%
E	6 hr.	37%
F	8 hr.	37%
G	24 hr.	43%

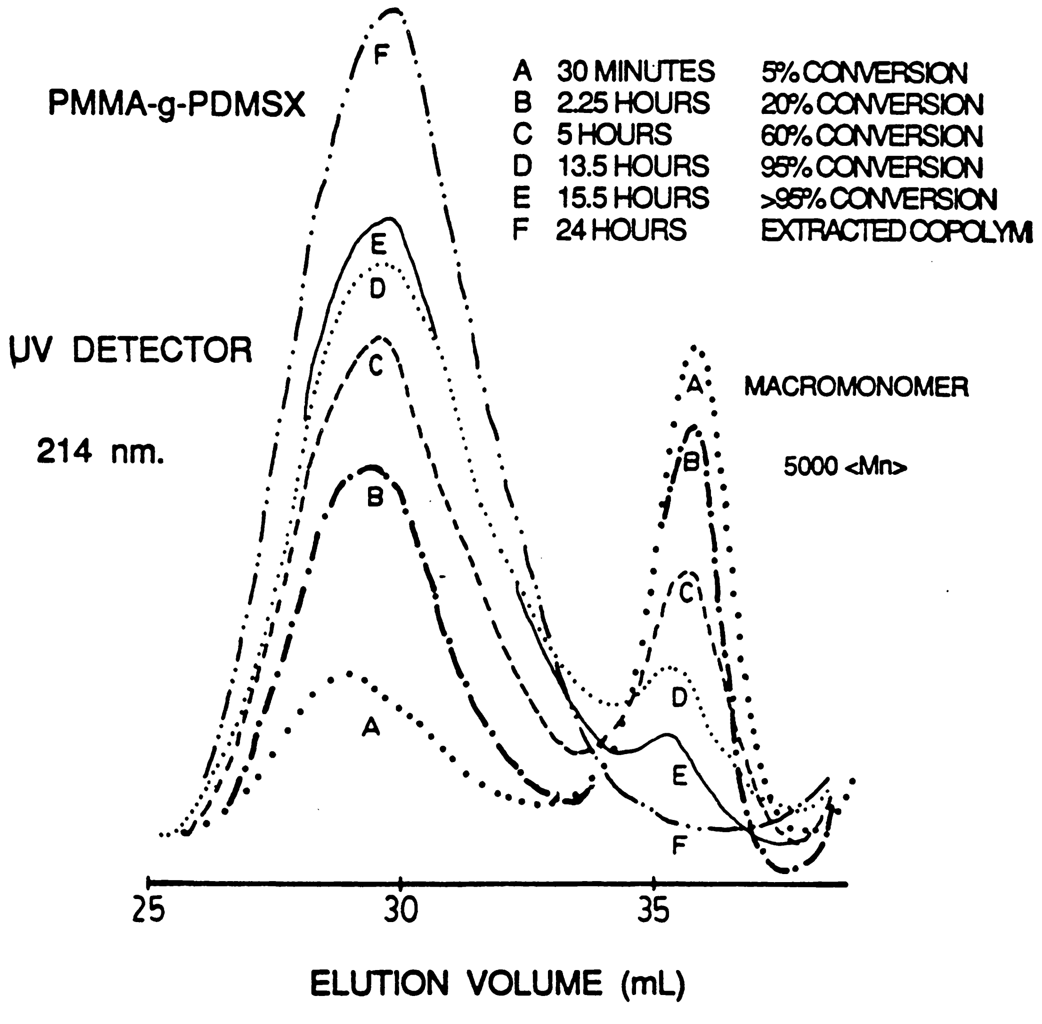


Figure 16. Size Exclusion Chromatograms of a Macromonomer Copolymerization as a Function of Conversion

Table 15

Calculated Number of Branches per Copolymer Molecule of Total <Mn> = 100,000 g/mole

	Weight Percent Graft				
Graft Mn	10%	20%	30%	40%	50%
1000	10	20	30	40	50
5000	2	4	6	8	10
10,000	1	2	3	4	5
20,000	0.5	1	1.5	2	2.5

important factors, that for any given composition there are a wide range of architectures available depending on the graft molecular weight. A few long chains or many short chains can yield a polymer with the same composition but markedly different structure and probably therefore different properties. Secondly, at low siloxane contents and high graft molecular weights the polymer prepared is actually a blend of homopolymer of the backbone with graft copolymer. Lastly, it can be seen that cases where the number of grafts per backbone is approximately two, which can be compared to a triblock copolymer.

GPC measurements allow the calculation of "equivalent" molecular weights, based on linear polystyrene or polymethyl methacrylate standards. However, the effect of branching on hydrodynamic volume is important here. GPC typically fractionates a linear polymer by hydrodynamic volume, which is directly relatable to molecular weight. Graft copolymers are also fractionated by hydrodynamic volume, which is a function of molecular weight, composition and architecture. Figure 17 presents a model depicting the three dimensionality of copolymer structure which has a distribution of molecular weight and composition superimposed. These two variables have a complex effect on the hydrodynamic volume of any chain. High molecular weight, highly branched chains might have much smaller hydrodynamic volumes than a linear chain of the same molecular weight. It can be assumed that under any given elution volume in a GPC run, there are a range of copolymer structures. The average composition of the copolymer is likely to be represented at any given elution volume, (which is itself an average), and conclusions in the literature on copolymer homogeneity based on dual detectors on a GPC may be inherently misleading.

Membrane osmometry was therefore employed to determine absolute number average molecular weights. Light scattering measurements were used to determine weight average molecular weights. This study in conjunction with Dr. J. Stejskal, and Prof. P. Kratochvil has led to some very interesting results, which are summarized in Table 16. Firstly, the molecular weight distributions increased dramatically with increasing siloxane content. The number average molecular weights remained fairly constant, which can also be interpreted as the backbone chain length having decreased with an increasing number of grafts. It was also determined by isorefractive solvent studies that the broadening of molecular weight distribution was caused by a broadening of PMMA backbone molecular weight distribution. A constant molecular weight distribution of siloxane chains per backbone was found.

This decrease of PMMA chain length could be caused by

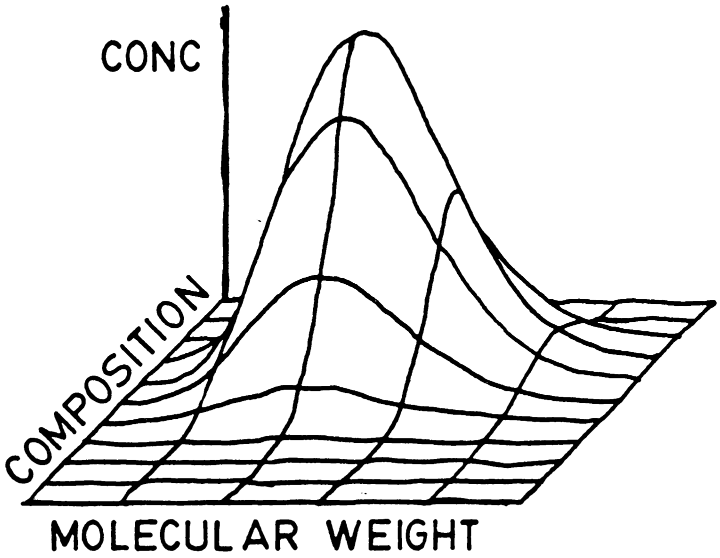


Figure 17. Simultaneous Variation of Composition and Molecular Weight for Graft Copolymers

Table 16

Molecular Weight Distributions of Free Radical PMMA-g-PSX
Total <Mn> ~ 100,000 g/mole (10K PSX Grafts)

%PSX	MWD	MWD(PMMA)	MWD(PSX)	#Grafts
20	2.1	2.7	~1	3.3
29	2.8	3.9	2.2	3.9
40	2.9	3.5	2.6	5.1
48	3.5	5.2	2.4	4.2

MWD = <Mw>/<Mn>
<Mw> Determined by Light Scattering
<Mn> Determined by Membrane Osmometry
PMMA and PSX MWD's Determined by
Isorefractive Solvent Analysis

concentration effects in the copolymerization since the MMA concentration is lower in high macromonomer composition copolymerizations, but it could also be a function of chain transfer reactions. It has been reported that the sterically hindered macromonomer active growing radical has a longer lifetime than a small monomer radical [218]. The probability of side reactions such as chain transfer are therefore increased when the end group is a macromonomer. If this were a severe side reaction then diblock copolymers would be prepared since termination would always occur when the macromonomer added. However, this is not the case here since chains can be prepared with more than one graft per backbone. But it is statistically possible that the end groups are macromonomer terminated, due to chain transfer reactions. This could be especially true if the transfer occurs to siloxane. Further evidence supporting this view will be presented later, which is based on thermal stability data.

A GPC both with a differential viscosity detector and refractive index detector can be used for absolute molecular weight determination [375], as have LALLS dectectors [376]. This works by the universal calibration method, in which the log of intrinsic viscosity times molecular weight is plotted versus elution volume. Thus, standards for each type of polymer are not necessary because this method is universal for all polymers. The intrinsic viscosity factor takes care of the differences in hydrodynamic volume between different types of polymers.

The viscosity and the concentration of each fraction eluting from the GPC are measured by the two detectors simultaneously. Then, by using the appropriate Mark-Houwink relationship, absolute molecular weights are calculated for each fraction and subsequently number average, weight average and higher orders of molecular weight may be calculated. Mark-Houwink K and α values, as well as the intrinsic viscosity are also calculated. This is valid for linear polymers, and for those with low degrees of branching. The validity of the absolute numbers here is therefore debatable. The trends however are very interesting and agree with the absolute numbers obtained by membrane osmometry and light scattering measurements. One may speculate that the graft copolymers are in a composition, molecular weight and architectural range where the degree of branching is low enough to accomodate the theory. Table 17, summarizes some of the data obtained for these graft copolymers. It is evident that the molecular weight distributions increase with increasing siloxane content. Also, the values of α decrease, as the chains become more flexible and assume random

Table 17

Molecular Weight Data for PMMA-g-PSX Free Radical Copolymers

Graft Mn	%PSX	<Mn>	MWD	Int.Vis.	Alpha	#Grafts
5K	5%	102K	2.5	0.66	0.59	1
5K	15%	108K	3.4	0.72	0.52	3
5K	50%	126K	4.6	0.62	0.49	10
10K	5%	90K	2.8	0.68	0.60	0.5
10K	15%	80K	3.6	0.64	0.53	1.5
10K	50%	100K	4.3	0.53	0.42	5

conformations. Figures 18 and 19 show the molecular weight distributions that were calculated for 5K and 10K PMMA-g-PSX copolymers with 16 and 45 weight percent siloxane. These calculations were based on the GPC data and the Mark-Houwink relationship. These plots clearly show the high molecular weight tail present in these systems, while the low molecular weight region is similar.

Conventional GPC's of these materials were all very similar and no high molecular weight tails were evident to explain the high weight average molecular weights that had been found. However, the viscosity detector showed that materials eluting at the same elution volume in two samples often had much different viscosities. Thus the high molecular weight species present in the high siloxane materials were eluting at an elution volume equivalent to a much lower molecular weight and only weight or viscosity sensitive detectors could indicate this. Figure 20 compares the dual chromatograms obtained on samples of PMMA-g-PSX with 16 and 45 weight percent siloxane. It can be seen that the sample with 45 weight percent siloxane at similar elution volumes has much higher viscosity response due to this higher molecular weight fraction, at the same elution volume. Even though the absolute validity of numbers generated by the Mark-Houwink relationship is debatable, this qualitative trend is very real and

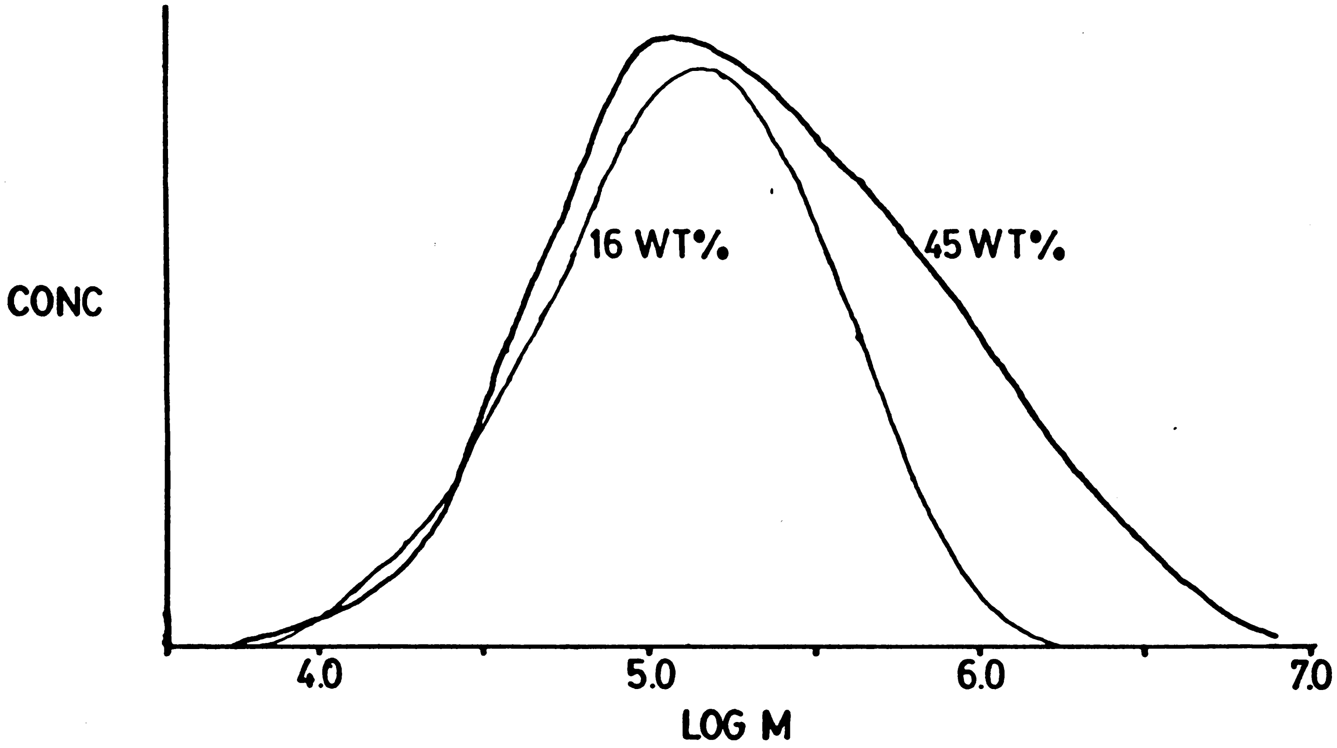


Figure 18. Calculated Molecular Weight Distributions for PMMA-g-PSX (5K Grafts) 16 and 45 Weight Percent PSX

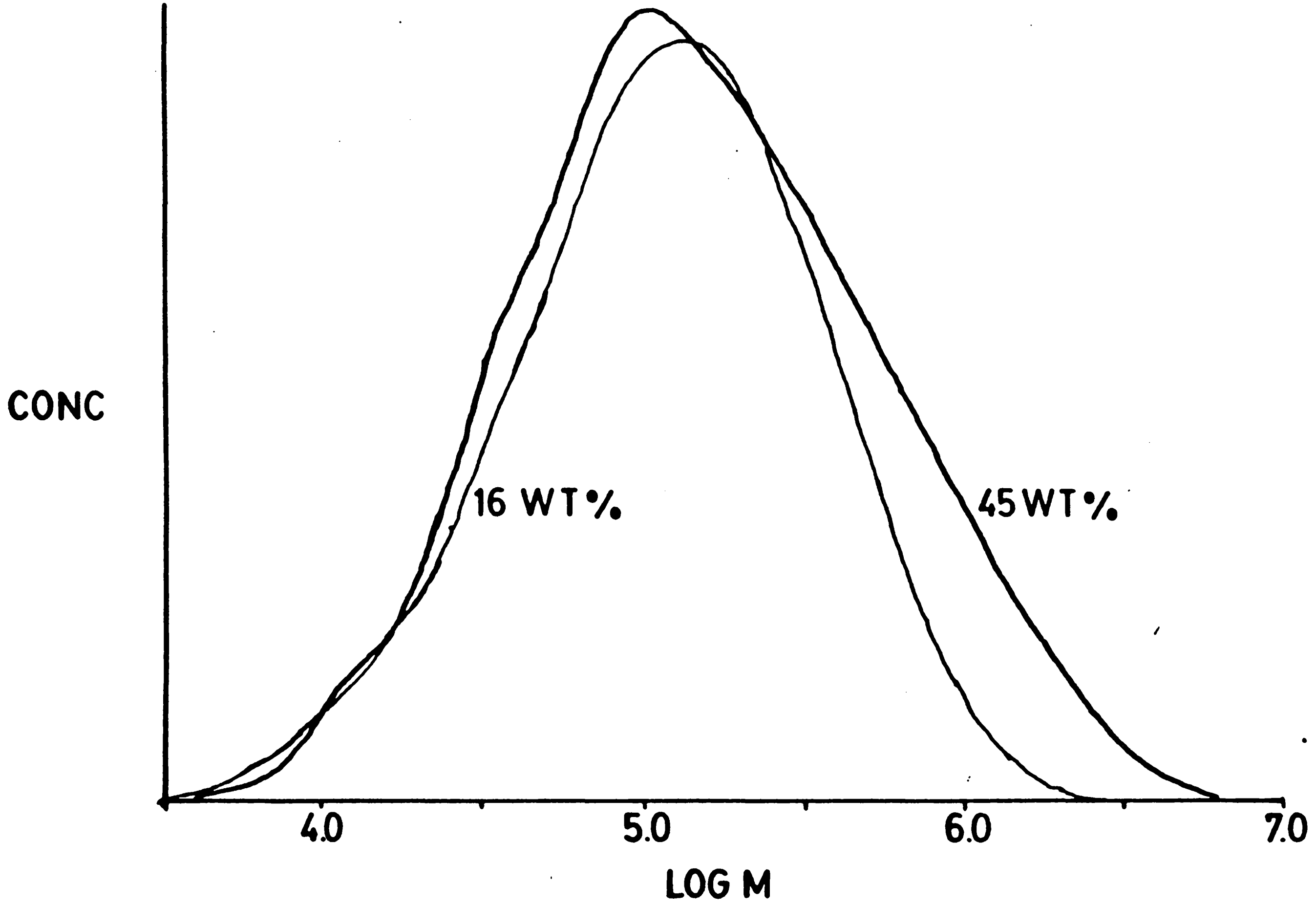


Figure 19. Calculated Molecular Weight Distributions for PMMA-g-PSX (10K Grafts) 16 and 45 Weight Percent PSX

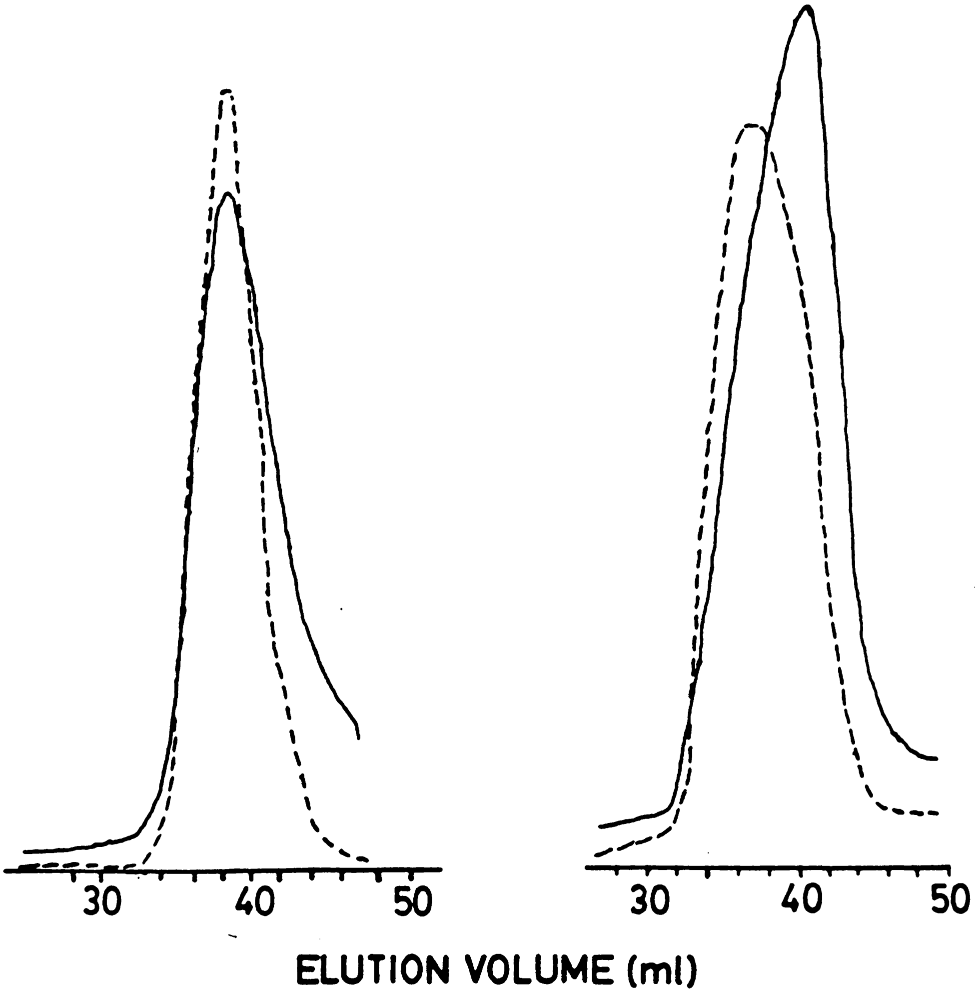


Figure 20. Dual Detector Size Exclusion Chromatograms of PMMA-g-PSX (5K) 16 and 45 WT% PSX. R.I.(———) and Differential Viscosity Detectors (- - -)

evident.

The trend in viscosity as calculated by the GPC measurements follows the theory as it should, although it is contrary to what one would expect at first. In Table 17, we can see that number average molecular weight remains fairly constant while the weight average molecular weight is increasing dramatically. One might expect that the intrinsic viscosity should increase therefore. However the degree of branching is increasing as well and thus viscosity should and does drop.

Intrinsic viscosities were determined separately to check on the accuracy of the GPC calculations and therefore their validity. In Table 18, we can see that fairly good agreement is achieved.

A recent article by Stejskal and Kratochvil [112] detailed the theory of composition distributions in a graft copolymer prepared under free radical conditions from a monomer and macromonomer. Very little homopolymer of the backbone is predicted to form, but rather there is actually a trend towards copolymers high in graft content. The distribution of chemical compositions is also a function of the number of branches per backbone with the limiting case being a random copolymer of two small monomers having a poisson distribution of composition. As the number of branches decreases, the breadth of the

Table 18

Comparison of Measured and Calculated Intrinsic Viscosities for PMMA-g-PSX Copolymers

Sample	Measured [ ]	Calculated [ ]
7M 1K 5 WT% PSX	0.56	0.55
7C 5K 5 WT% PSX	0.57	0.66
7J 10K 16 WT% PSX	0.69	0.64
11K 20K 5 WT% PSX	0.59	0.59
11N 20K 16 WT% PSX	0.46	0.56

distribution increases. Figures 21 and 22 are plots of the calculated chemical composition distributions for copolymers of 20 and 50 weight percent graft respectively, as a function of the number of grafts per 100K backbone. These are representative of typical graft copolymers with side chains of 1K to 20K, and the copolymers prepared in this study.

Super Critical Fluid Extraction studies were also conducted separately, to determine the ability of this technique to separate copolymers based on composition and/or molecular weight. Fractionation has been shown to be based on molecular weight for siloxane homopolymers in previous reports. Since fractionations are based on solubility it would also be expected to be a function of composition and molecular weight. Figure 23 depicts a SCFE set up as described previously [377].

PMMA is somewhat polar and as such is less soluble, in non-polar super critical gases such as butane than is PSX. Therefore, materials high in siloxane are expected to be more soluble than pure PMMA. Data obtained from this work indicated that the theory was valid. Table 19 presents some of the data based on NMR analysis of composition of the fractions obtained by SCFE. Copolymers 81A and 81C were of similar composition, with 81A having about twenty 1K grafts per backbone. By contrast, sample

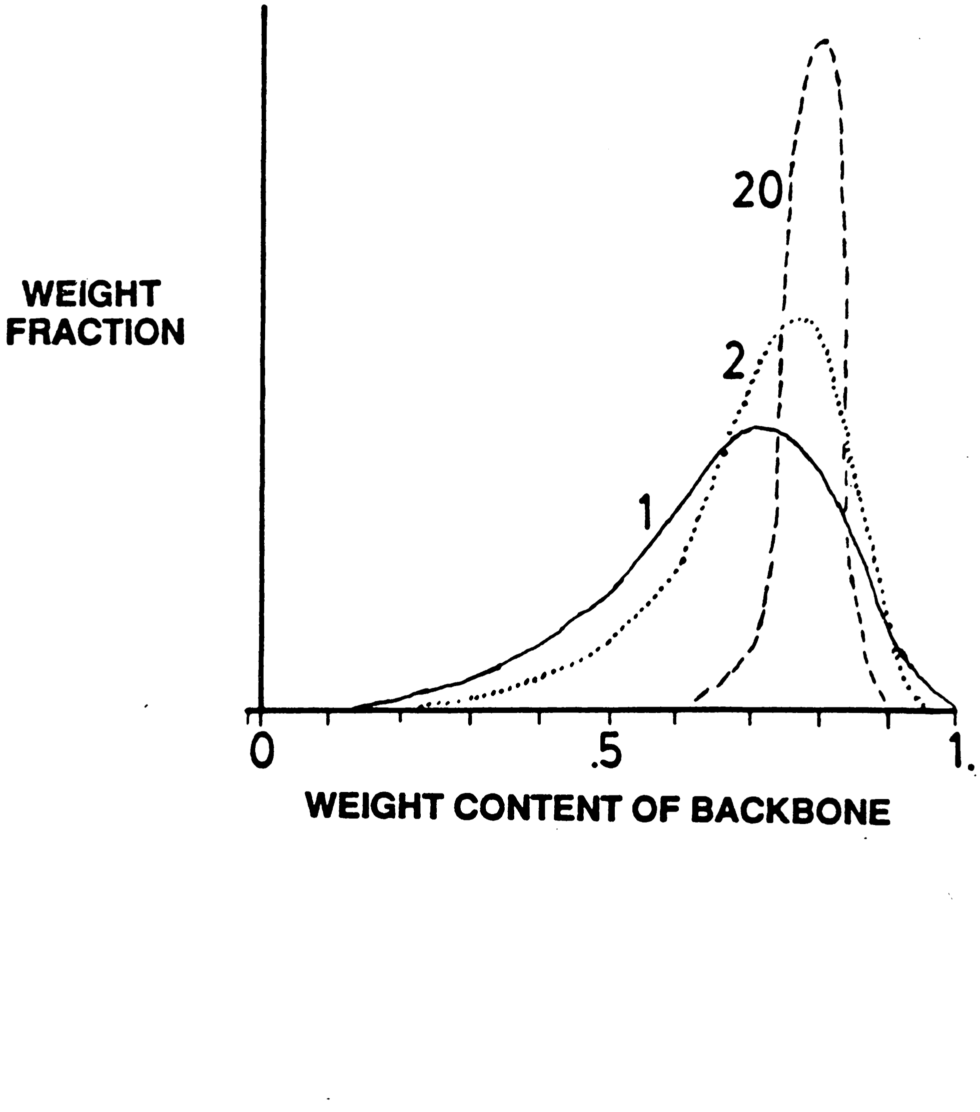


Figure 21. Calculated Chemical Composition Distribution for Graft Copolymer with 20 WT% Grafts

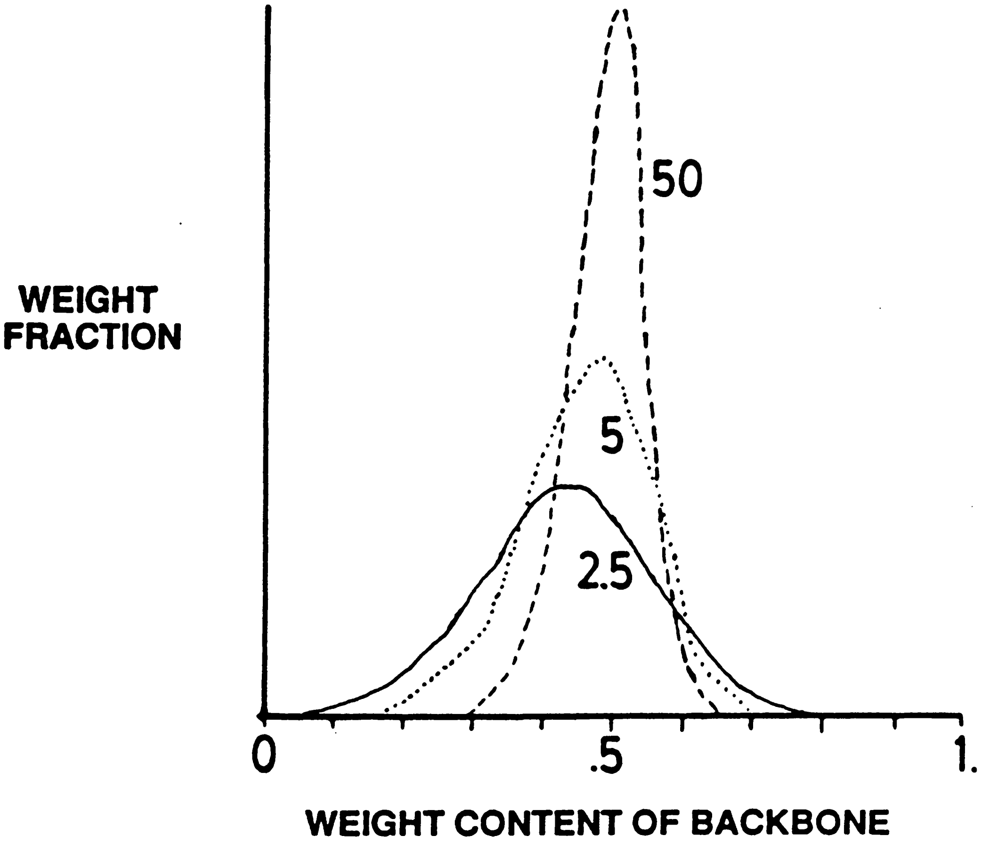


Figure 22. Calculated Chemical Composition Distribution for Graft Copolymer with 50 WT% Grafts

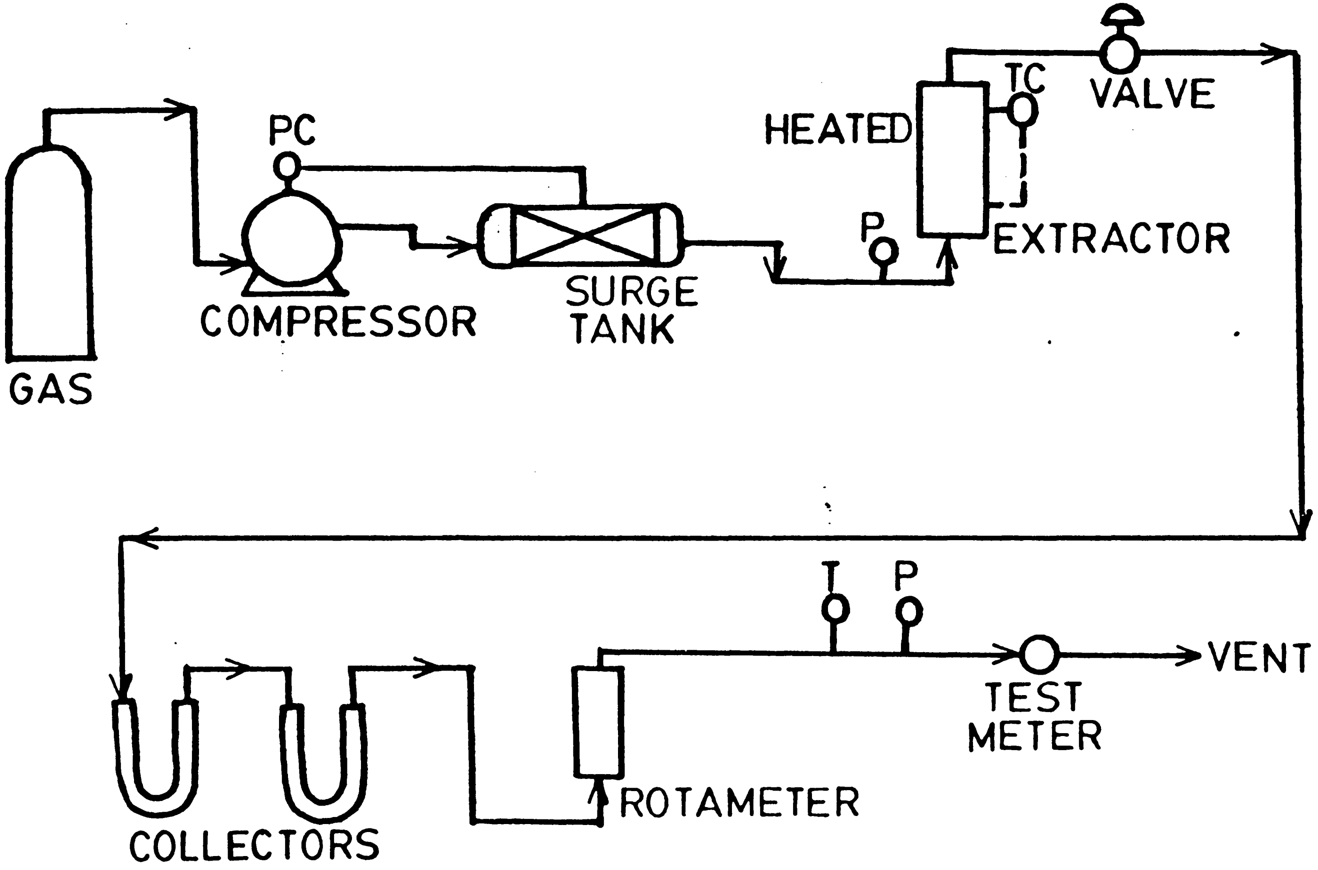


Figure 23. Super Critical Fluid Extraction (SCFE) Diagram

Table 19

Super Critical Fluid Extraction Separation of PMMA-g-PSX Copolymers With Butane

	Fractions						
Sample	1	2	3	4	5	6	7
81A	0.14g	0.26g	1.1g	2.4g	1.5g	2.7g	
22 WT% PSX							
1K Grafts	23%	23%	21%	21%	20%	19%	
20 Grafts/Backbone							
81B	0.3g	1.1g	0.8g	1.0g	0.9g	1.3g	0.3g
12.5 WT% PSX							
10K Grafts	35%	25%	11%	11%	9%	11%	11%
1 Graft/ Backbone							
81C	0.3g	0.7g	3.5g	0.9g	0.5g		
27.5 WT% PSX							
10K Grafts	47%	42%	22%	22%	24%		
3 Grafts/ Backbone							
81D	0.38g	0.87g	4.1g	0.5g	0.22g		
45 WT% PSX							
10K Grafts	54%	46%	44%	45%	44%		
4.5 Grafts/Backbone							

81C had about three 10K grafts per backbone. SCFE yielded a narrow range of compositions for 81A, with a total variation of only 4%, while sample 81C had copolymer with compositions over a range of 25%. This would fit the trend expected from Figure 21, where the sample with more grafts having a narrower range of compositions.

Fractionation of sample 81B also confirms that a material with even fewer grafts per backbone shows a broad range of compositions. With an average composition of only 13 Wt% PSX there is a range of 25 Wt% PSX in the fractions, which is very considerable.

Investigation of the molecular weights found in the fractions showed that sample 81C was not fractionated significantly by molecular weight. Figure 24 reveals that the peaks of the first and last fractions vary by less than one mililiter. It would thus seem that siloxane composition played the key role in fractionation. It is interesting that materials with a wide range of compositions have similar molecular weight distributions. Sample 81A was however separated by molecular weight to a greater extent, as can be seen in Figure 25. The peaks of the varying fractions varied by almost 3 milliliters in elution volume. This might indicate that with fairly homogeneous siloxane content, separation can occur by molecular weight.

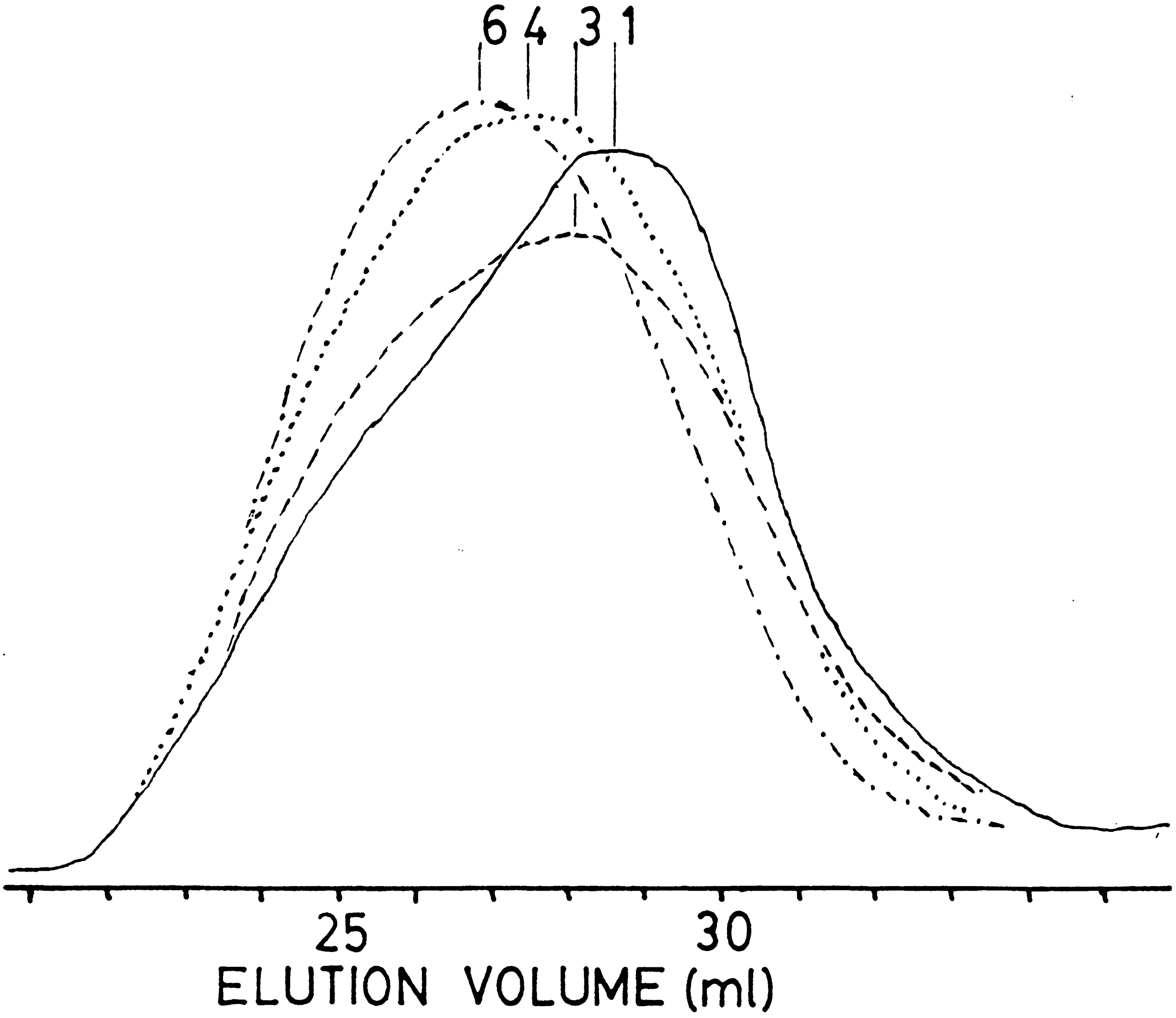


Figure 24. GPC of SCFE Fractions of PMMA-g-PSX

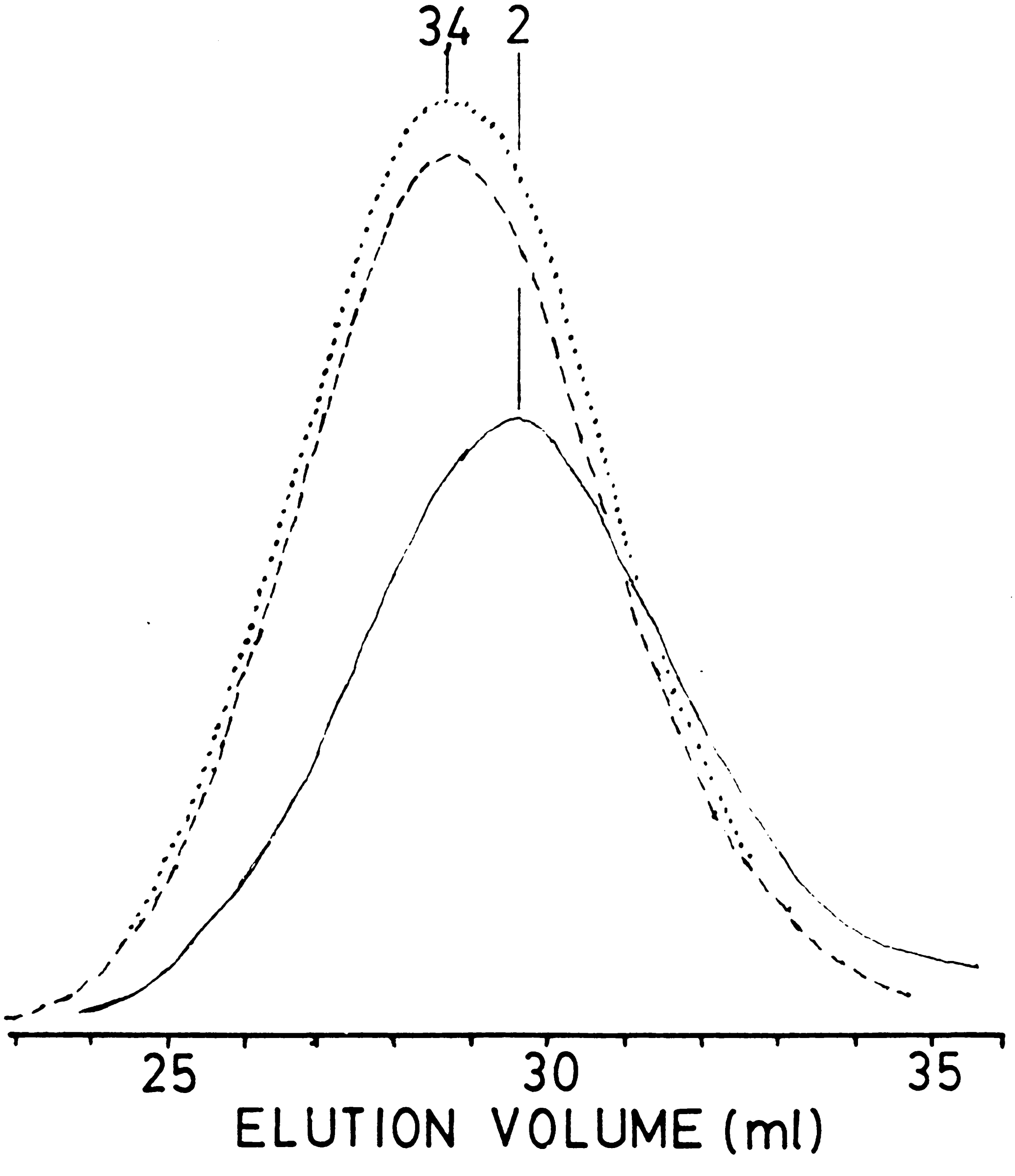


Figure 25. GPC of SCFE Fractions of PMMA-g-PSX

It becomes clear that this separation technique based on partial solubilization of a sample is being affected by both molecular weight and composition. Thus, even the samples fractionated are polydisperse in both composition and molecular weight. It is likely that samples of high siloxane content and lower molecular weight are most easily extracted. Low siloxane content and high molecular weight fractions are eluted last.

Sample 81D had approximately 4.5 grafts per backbone and was separated out into fractions having high siloxane content. No fractions with low siloxane content were observed. The spread of siloxane compositions fractionated was lower than expected, even though the number of grafts per backbone was increased and one might have expected a somewhat narrower range of compositions.

Another important factor is a determination of the effect of polymerization conversion on the composition distribution. A copolymerization with approxiamtely 25 wt% PSX was conducted and samples were worked up at 40, 60 and 80% conversion. SCFE was then carried out on these samples as summarized in Table 20. Even at lower conversions there exists a broad range of compositions, as the theory would predict. This rules out the possibility of changing feed ratios causing these high siloxane content materials to be formed late in the conversion. This would not be expected

Table 20

Super Critical Fluid Extraction Separation of PMMA-g-PSX Copolymers as a Function of Conversion

	Fractions					
Sample	1	2	3	4	5	6
95A 40% Conv.	0.02g	0.2g	2.0g	2.5g	0.3g	
21 WT% PSX						
10K Grafts	---	35%	23%	17%	13%	
2.0 Grafts/Backbone						
95B 60% Conv.	0.4g	2.0g	0.3g	1.3g	0.7g	0.5g
22 WT% PSX						
10K Grafts	41%	28%	21%	19%	19%	14%
2.0 Grafts/ Backbone						
95C 80% Conv.	0.1g	0.5g	0.7g	0.9g	1.8g	0.2g
23 WT% PSX						
10K Grafts	---	28%	24%	23%	18%	14%
2.0 Grafts/Backbone						

since sample 81A shows little heterogeneity and would be expected to if high conversion feed ratios were a problem. In contrast, in the lower conversion sample, 95A, a low siloxane content fraction was observed as predicted, while low siloxane content fractions were not observed at high conversions. Reactions taken to high conversion appear to be of a narrower distribution rather than a broader distribution which might not have been expected. The drift in monomer feed ratio produces copolymer with a slightly higher average composition but well within the overall distribution formed early on. These later formed chains do however not have the low siloxane compositions that are formed initially. Thus, as a function of conversion the siloxane content may drift slightly higher, at the expense of low siloxane composition materials. However, materials extremely high in siloxane are not formed.

DSC and DMTA analysis yielded interesting results on the phase mixing of the copolymers. In Figure 26, glass transition temperatures of poly(methyl methacrylate-g-PSX) copolymers are plotted as a function of weight percent siloxane for the four macromonomer molecular weights. The 1K systems would seem to be fairly miscible, while the 10K, and 20K systems show limited miscibility at low siloxane compositions and only at high siloxane contents is there a clear difference between the 10K and 20K

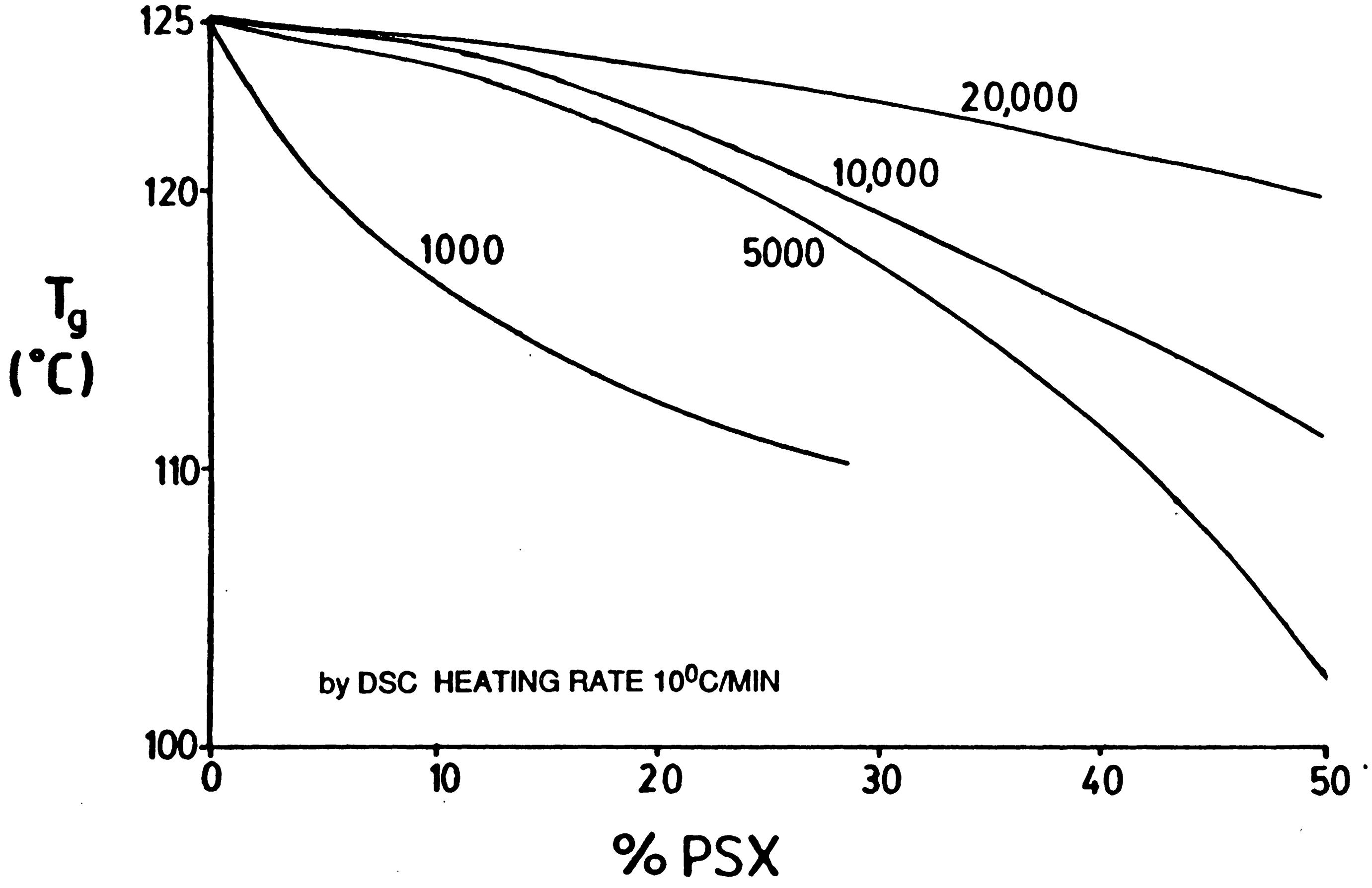


Figure 26. Glass Transition Temperatures of PMMA-g-PSX as a Function of Graft Mn and Percent PSX

properties. The 5K system shows properties intermediate, with some small amount of miscibility even at low siloxane contents. DSC traces for some copolymers are shown in Figures 27 and 28.

DMTA analysis on copolymers with 20 weight percent siloxane composition are shown in Figures 29 through 32. A copolymer with pendant oligomeric species of molecular weight 300 (about 4 units of siloxane) was also analyzed. The high temperature transition is a function of graft molecular weight up to about 10,000 g/ mole. The low temperature transition is not evident until 10,000 g/mole as well, although weak transitions are evident by DSC measurements.

Low temperature transitions are unusually weak by DSC measurements and Tm's are only evident in very high siloxane content materials, even for the high graft molecular weights. The later should be well phase separated and crystalizable at lower siloxane contents. Table 21 provides a summary of the results obtained. It is also evident that materials with melting points show different Tc's due to the ease of crystaliztion. For example sample 11Q has a lower Tc than sample 11J because the 10K graft sample requires more energy for crystalilzation to occur.

Degrees of mixing can be determined by measuring the

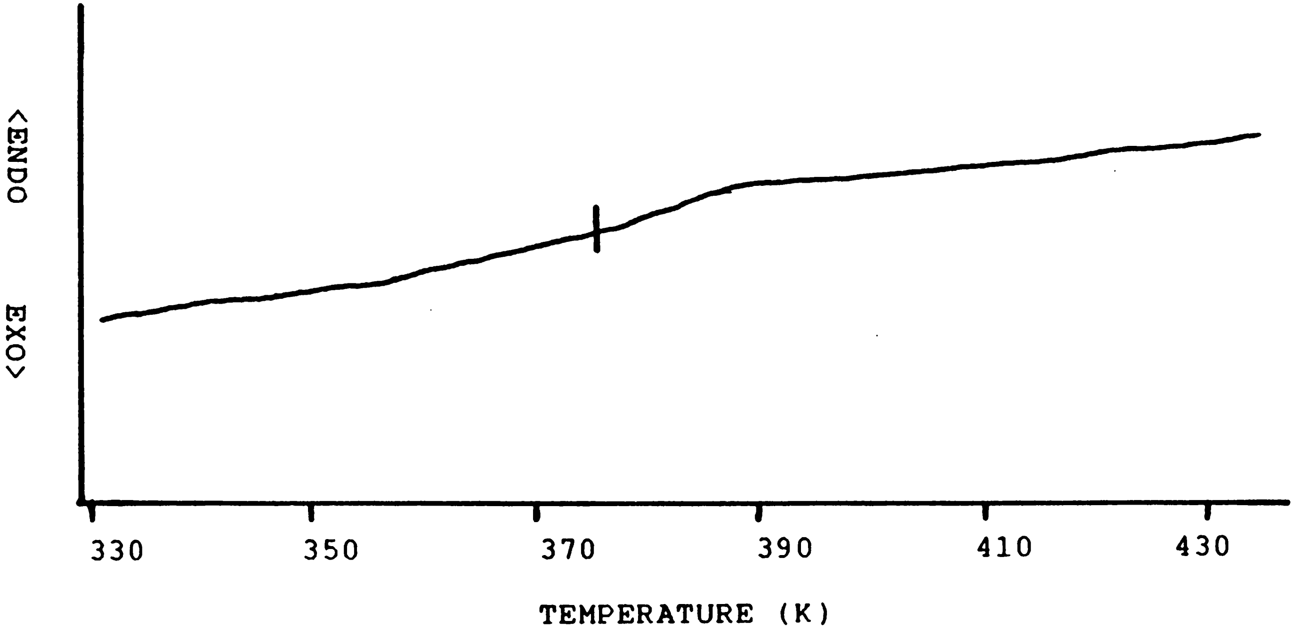


Figure 27. DSC of a PMMA-g-PSX Copolymer

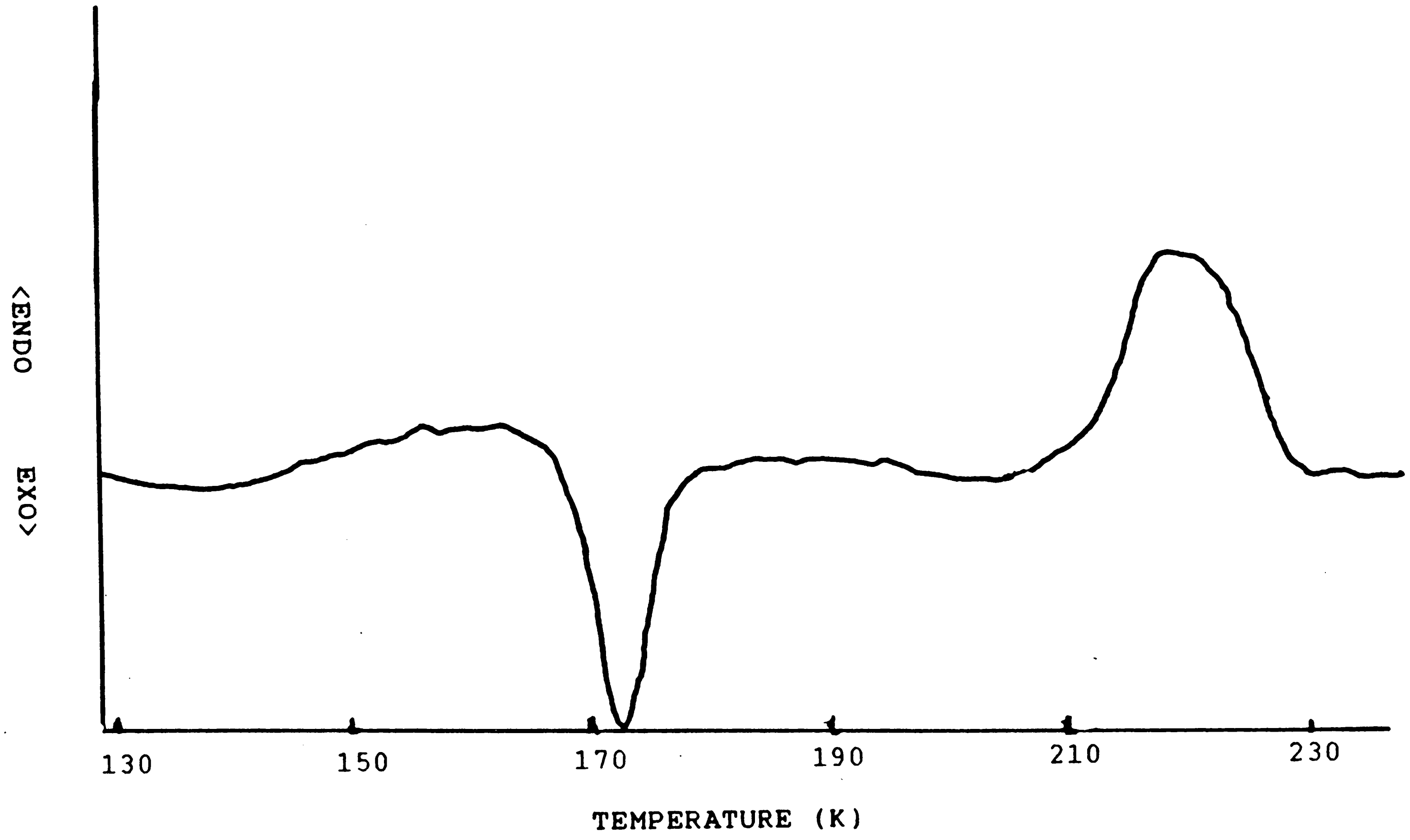


Figure 28. DSC of a PMMA-g-PSX Copolymer

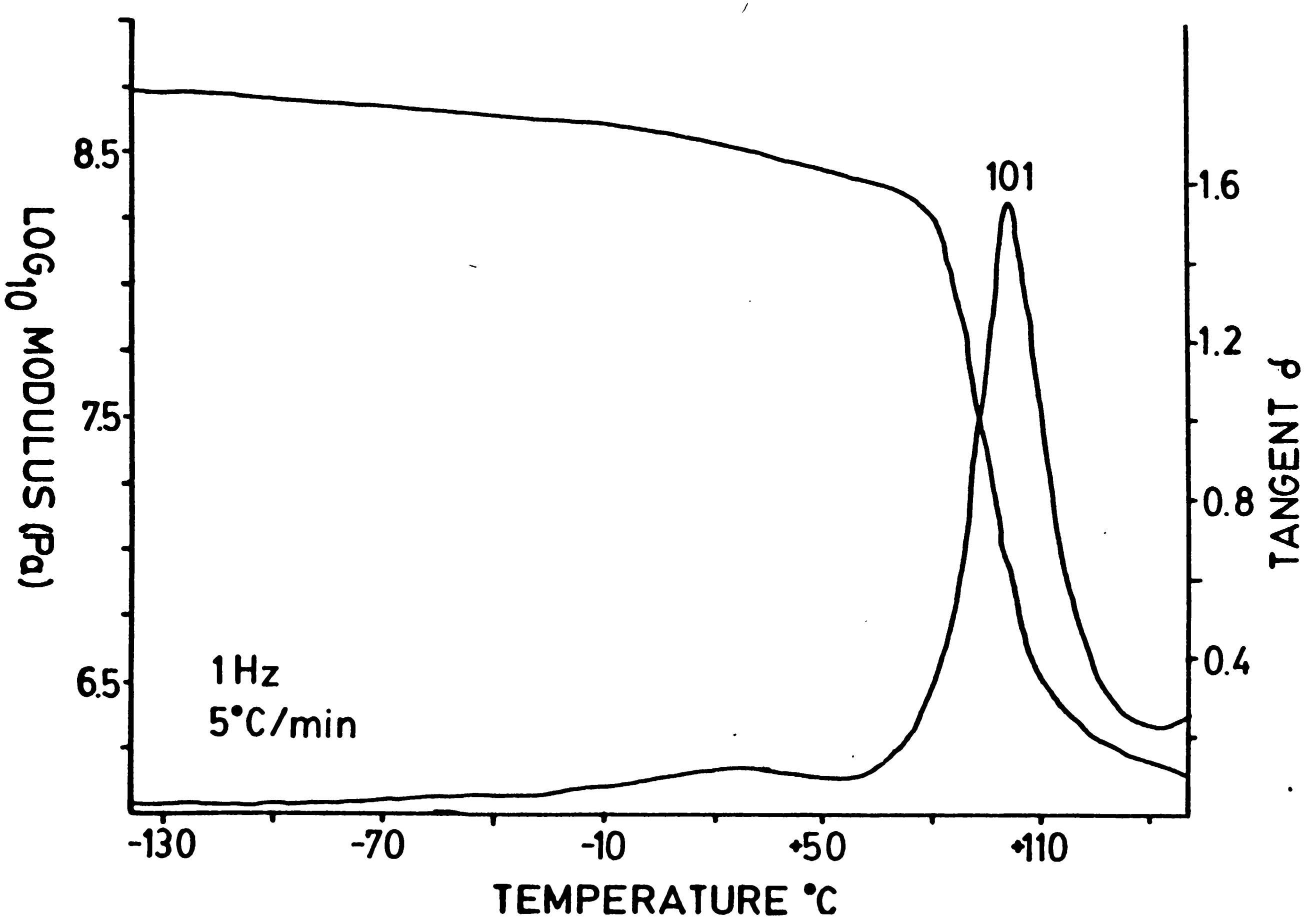


Figure 29. Dynamic Mechanical Behavior of PMMA-g-PSX Copolymer: 15 Weight PSX of Mn 300

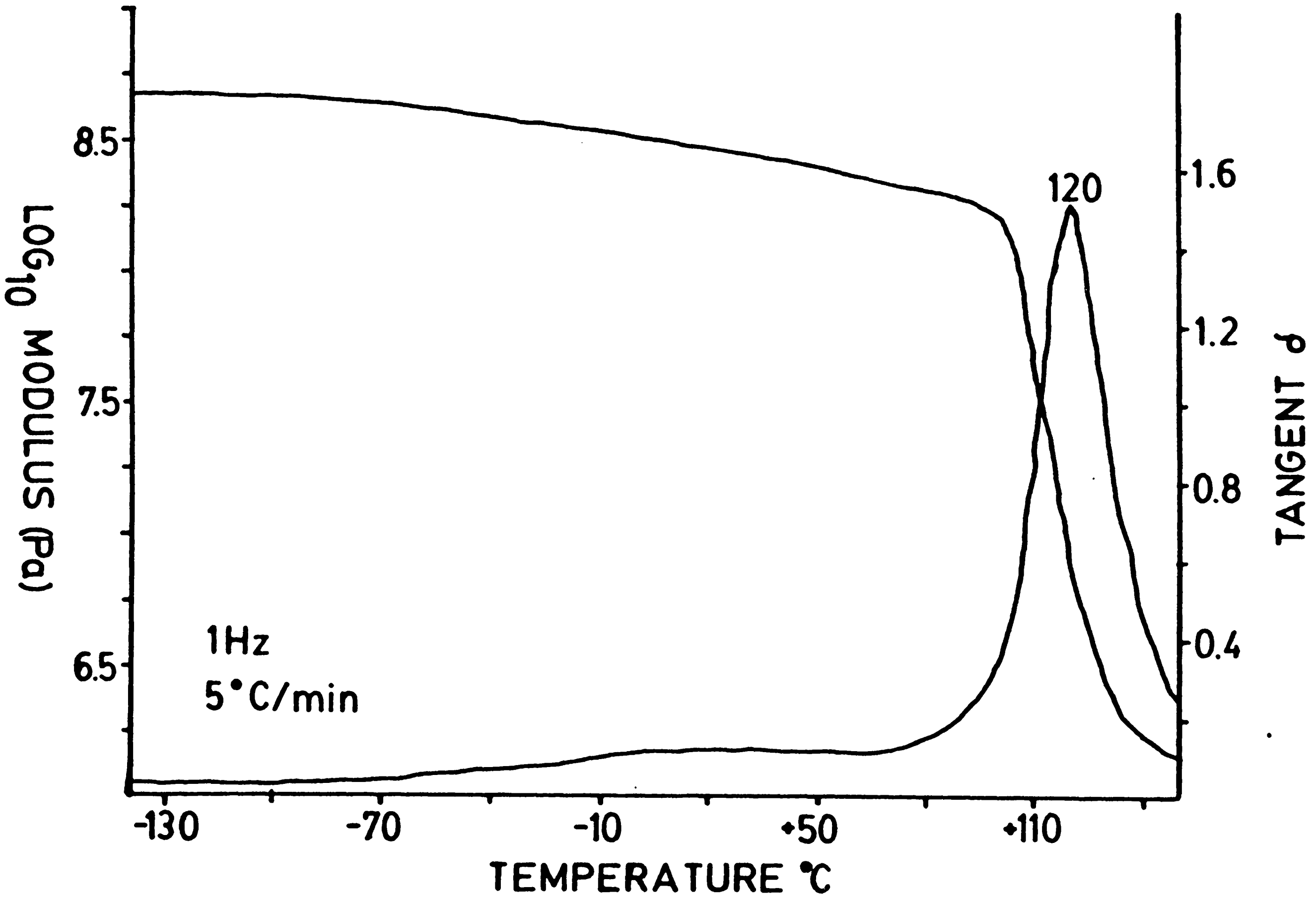


Figure 30. Dynamic Mechanical Behavior of PMMA-g-PSX Copolymer: 15 Weight PSX of Mn 1000

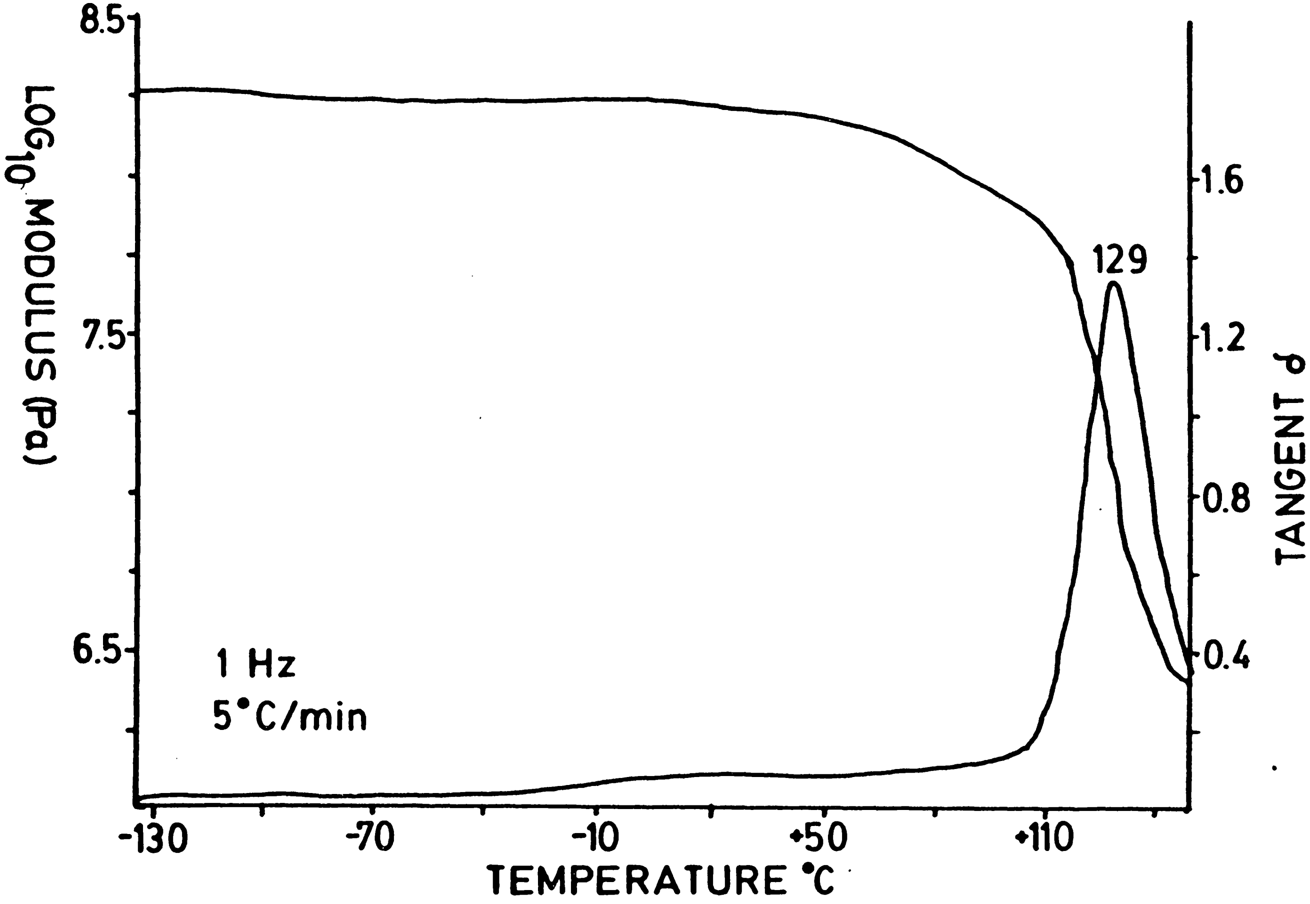


Figure 31. Dynamic Mechanical Behavior of PMMA-g-PSX Copolymer: 15 Weight PSX of Mn 5000

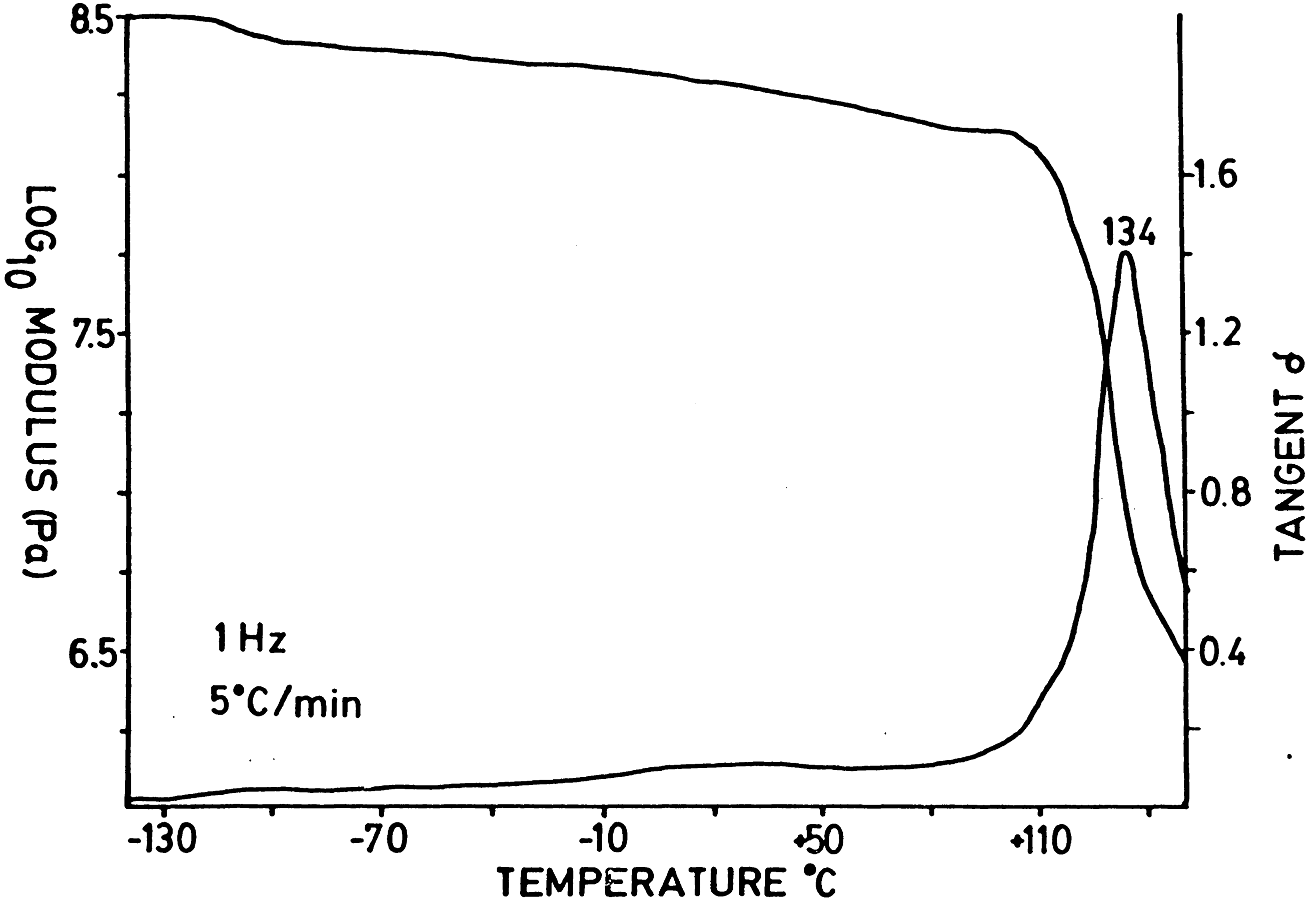


Figure 32. Dynamic Mechanical Behavior of PMMA-g-PSX Copolymer: 15 Weight PSX of Mn 10,000

Table 21

Glass Transition Temperatures of Some PMMA-g-PSX Copolymers

Sample	Description	Tg°C	Tc°C	Tm°C
7P	1K 20 WT% PSX	-112	-	-
7F	5K 20 WT%	-110	-	-
7K	10K 20 WT%	-113	-	-
11N	20K 20 WT%	-126		
11H	5K 45 WT%	-126	-	-
11J	10K 45 WT%	-127	-101	-55
11Q	20K 45 WT%	-123	-111	-45

Cp, normalized for sample weight, for the copolymers. [378] Phase mixing tends to decrease the enthalpy of transition by plasticizing the phase and lowers not only the temperature of the transition, but also the energy required for the transition. It should also be noted here that measurements determined by mid-point are insensitive to the onset of mixing, whereas onset and Tg interval measurements are very sensitive to small amounts of mixing.

It has been reported that mixing of small amounts of the hard phase into the soft phase can occur without mixing of soft phase into the hard phase. Thus a significant change in the low temperature thermal transition occurs without depression of the high temperature transition. This has little effect on the high temperature transition since on a weight basis most of the hard phase is unmixed. This could very well explain what we are seeing here since there is some mixing, as evidenced by lowering of the high temperature transition, and even when no high Tg depression is evident, the low temperature transitions are weak.

TGA analysis provided an unexpected indication of the polymer structure. The typical thermal stability of free radical poly(methyl methacrylate) is a problem for many thermoplastic processed of PMMA. Temperatures of 170-200°C that would be used to even compression mold pieces are high enough to cause degradation of PMMA, due to the head to head linkages and unsaturated end groups [330-332]. In contrast poly(methyl methacrylate) produced with saturated end groups is thermally stable past 300°C. However, until recently the only synthetic technique was the use of the living anionic polymerization of MMA in THF at -78°C. The cost of this cryogenic synthesis is prohibitive for general commercial uses of PMMA. The introduction of the Group Transfer Polymerization or GTP technique has provided a second technique for the preparation of well defined PMMA, however only relatively low molecular weight synthesis have been demonstrated. The purity requirements of the reagents for GTP are the same as for anionic polymerizations, which are also expensive, but the advantage is that low temperatures are not required.

The initial TGA's are presented in Figure 33, for samples of PMMA-g-PSX run in a nitrogen atmosphere, along with a free radical PMMA control. It was quite surprising that the copolymers exhibited significant thermal stability improvements in relation to free radical PMMA. Thermal stabilities over 300°C by TGA were found. The other surprising result was that there was an apparent influence of graft molecular weight as well. An explanation for this could be based on an antioxidant

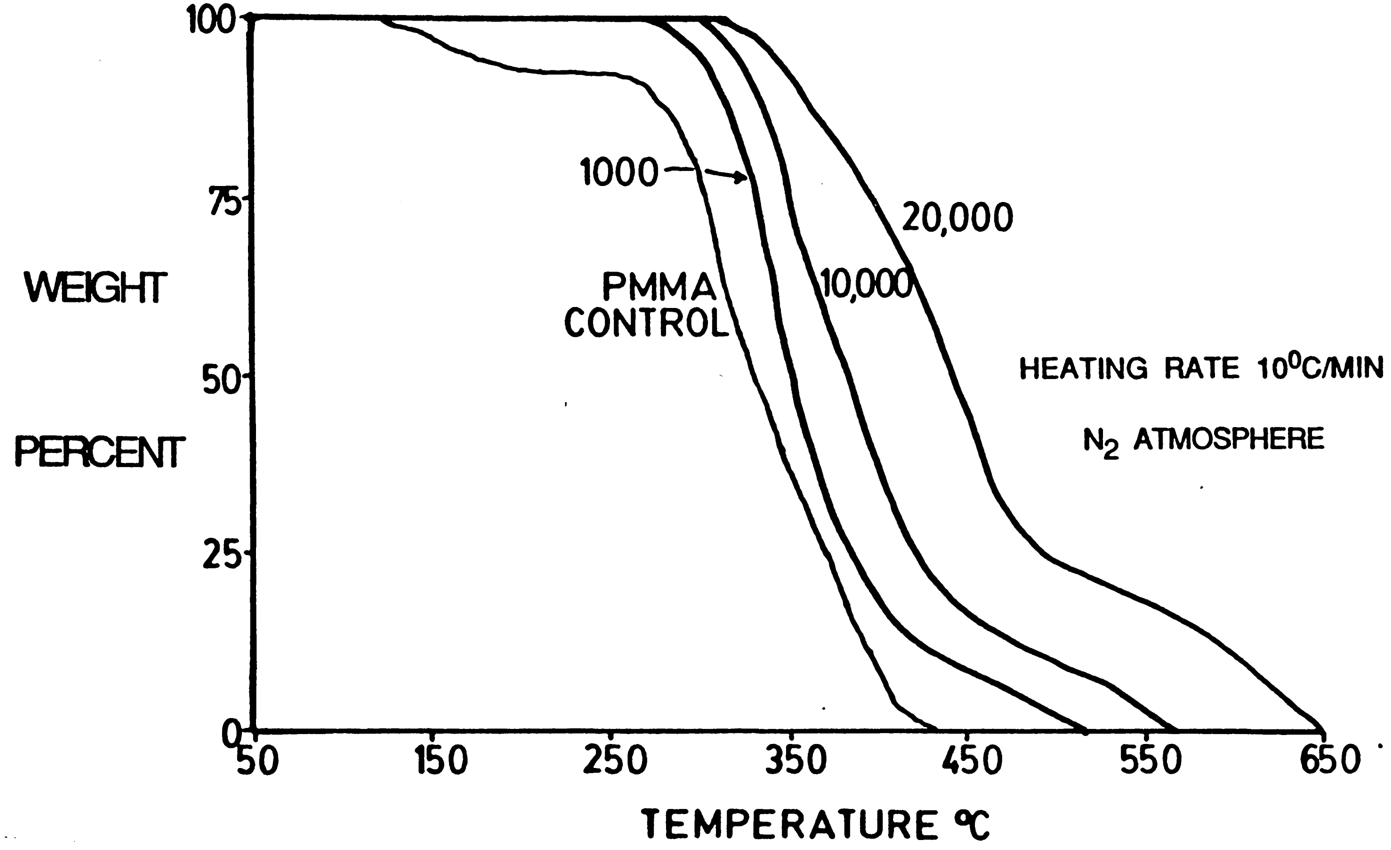


Figure 33. Thermal Gravimetric Analysis of PMMA-g-PSX as a Function of PSX Molecular Weights (20 WT % PSX)

effect of the poly(dimethyl siloxane) towards the radical degradation of PMMA. It would be expected that a better distribution of the antioxidant through the matrix would improve stability. However, in this case, the lower graft molecular weights which are more phase mixed show less of a stabilization effect. Therefore the trend is that the more phase separated materials have greater stability.

effect of the poly(dimethyl siloxane) towards the radical degradation of PMMA. It would be expected that a better distribution of the antioxidant through the matrix would improve stability. However, in this case, the lower graft molecular weights which are more phase mixed show less of a stabilization effect. Therefore the trend is that the more phase separated materials have greater stability.

This could be a surface effect since these high graft molecular weight materials also dominate the surface to a larger extent, as was already shown. A second possibility is that the quenching reaction takes place inside the PSX domains, possibly by a hydrogen abstraction and siloxane crosslinking reaction.

The fact that the materials are thermally stable past 300°C is indicative that saturated end groups are present. The exclusive presence of saturated end groups can only be explained by a chain transfer reaction since combination or disproportionation reactions lead to thermally unstable groups. As mentioned in the section on molecular weights, a chain transfer reaction that occurs while the macromonomer is the end group is likely.

Further investigations were continued to support these initial findings. Figure 34 compares the thermal stabilities of PMMA-g-PSX as a function of graft molecular weight for some materials at 5 weight percent siloxane. It is important to consider here that the number of grafts per backbone spans the range of 5 grafts/backbone for the 1K system to 1 graft/backbone for the 5K system to 0.5 grafts/ backbone for the 10K system, and 0.25 grafts/ backbone for the 20K graft system. It is evident that with more than one graft per backbone, thermal stabilities are increased dramatically and that when the number of grafts per backbone is less than one, an important effect on the amount of weight lost at relatively low temperatures is observed. There seems to be a direct trend starting with free radical PMMA and increasing stability with fractional numbers of grafts.

Another trend that was investigated further was that increased graft length increased thermal stability, even when more than one graft per backbone was present. In Figure 35, we can see the effect of siloxane content on thermal stability at a constant siloxane graft molecular weight of 20,000 g/mole. Thermal stabilities above 315°C

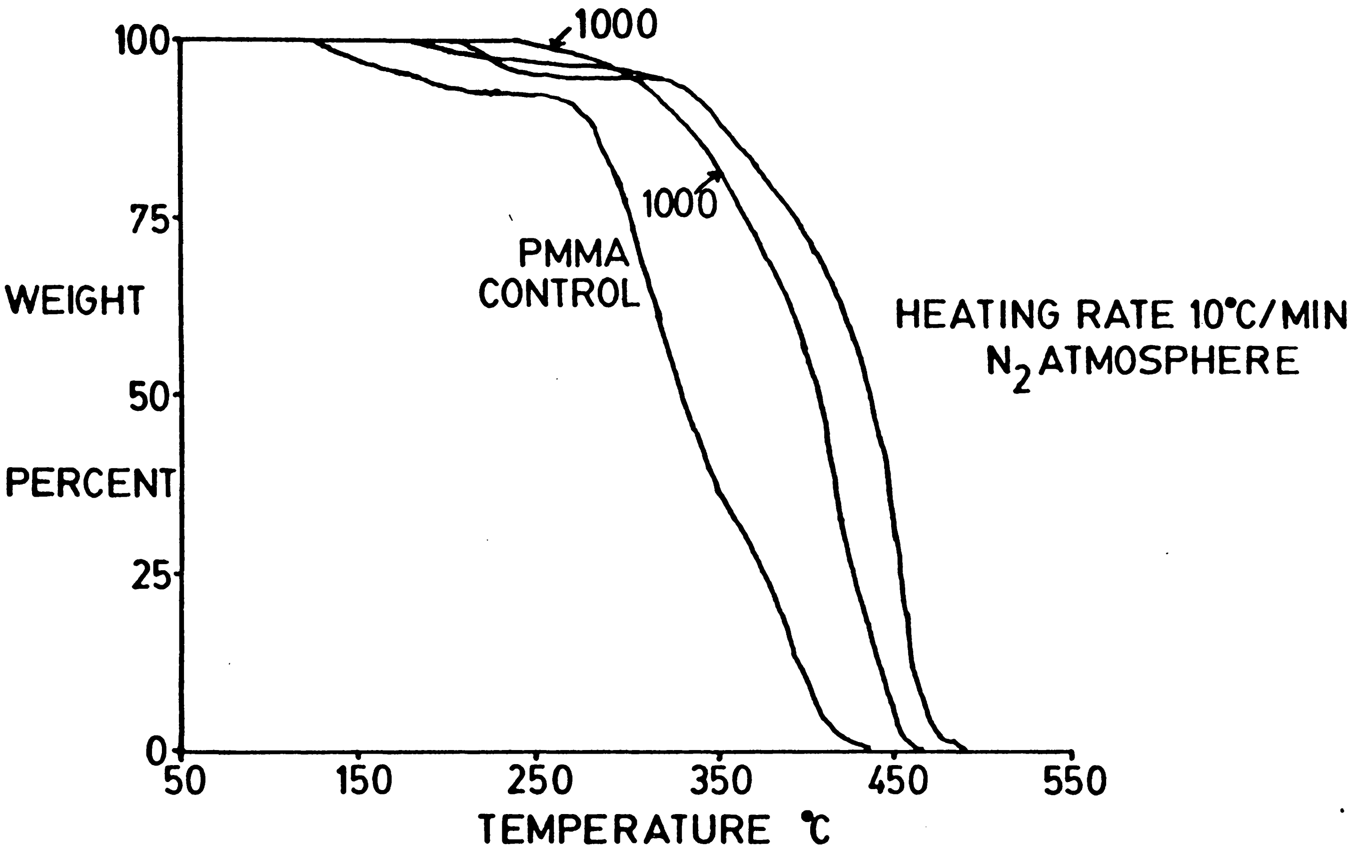


Figure 34. Thermal Gravimetric Analysis of PMMA-g-PSX as a Function of Graft Mn (5 WT % PSX)

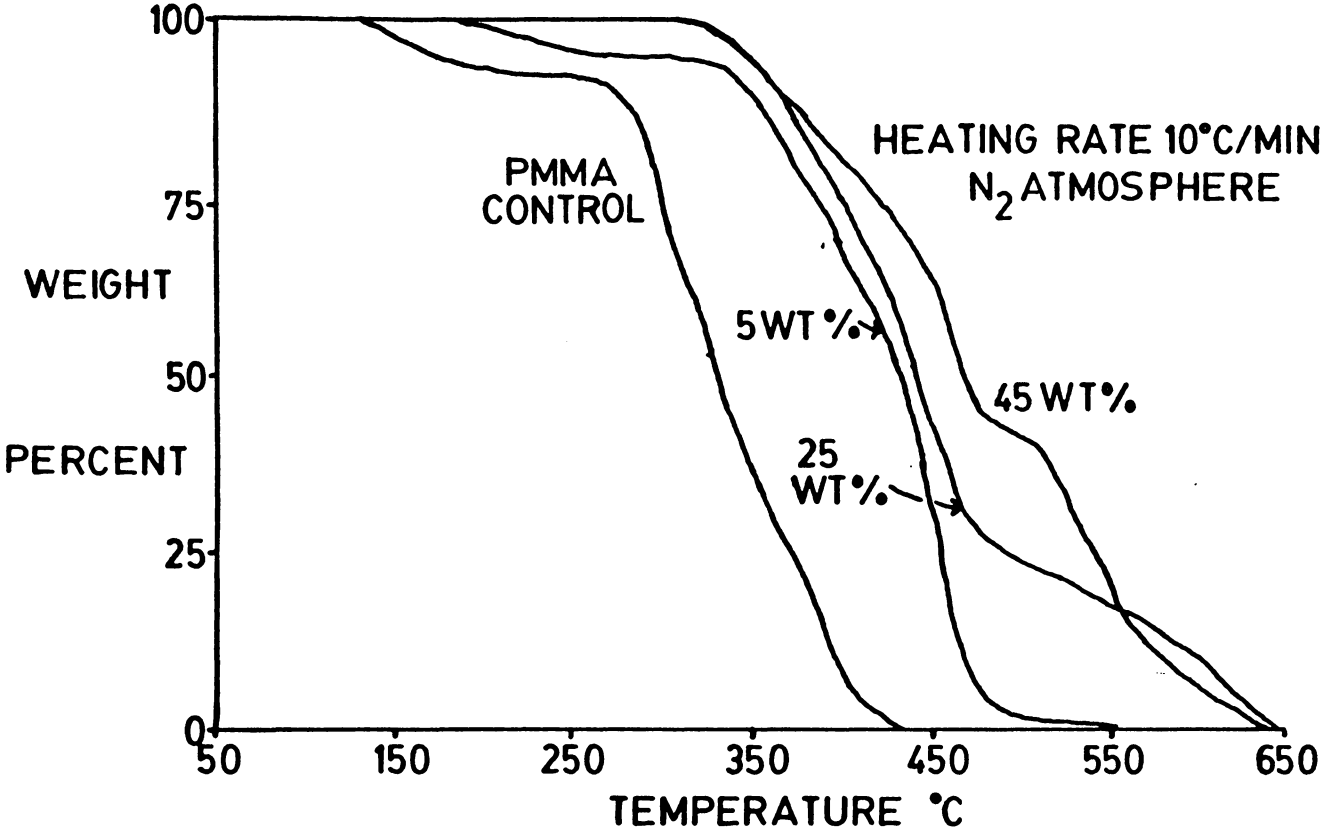


Figure 35. Thermal Gravimetric Analysis of PMMA-g-PSX as a Function of % PSX (20K Graft Mn)

are noted while the 1K systems showed thermal stability to only 280°C. Increased levels of graft content beyond the 1 graft/ backbone do not increase the temperature of weight loss onset, but only raise the char yield which is assumed to be SiO2.

TGA analysis in an air atmosphere reveals the same trends in onset of weight loss, although the differences in stability are not as marked and the lines of weight loss tend to cross each other.

TGA analysis of blends with pure PMMA were also undertaken as can be found in that section. The conclusion was that the siloxane segments present in the graft copolymer did not stabilize the unsaturated end groups present in the homo-PMMA used to blend.

Thin films of free radical, anionic, and PSX graft copolymers were irradiated with a UV mineral lamp for 30 minutes, to induce degradation of the PMMA chains. The radicals generated will be trapped in the glassy matrix or coupled by oxygen to form peroxide groups. Heating in the TGA experiment then, should lead to increased mobility of radicals which can then depolymerize. Degradation of peroxide linkages will also lead to depolymerization processes. In all cases, degradation starts at approximately 180°C, and as can be seen in Figure 36, no increased stability is imparted by the siloxane chains

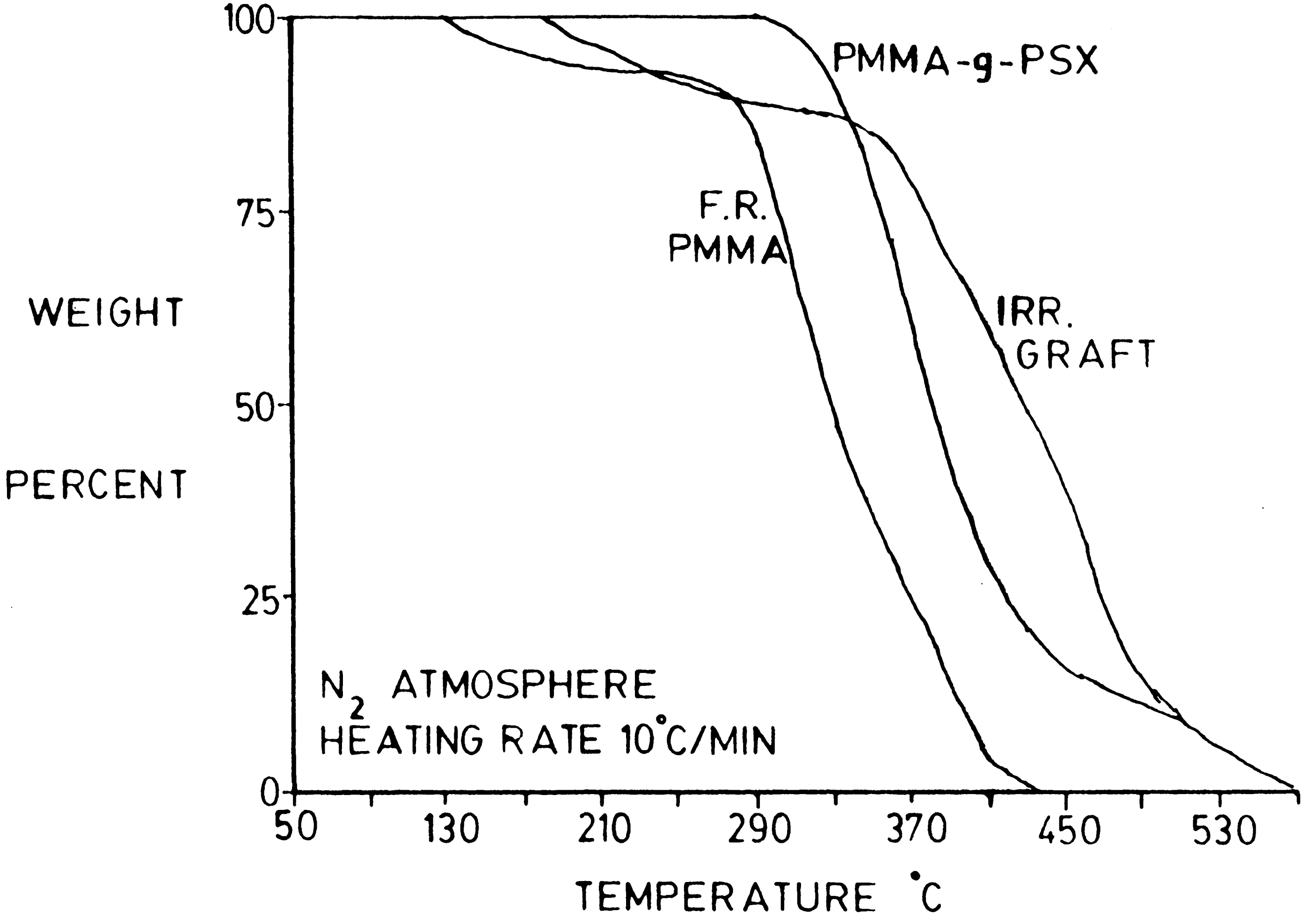


Figure 36. TGA of A UV Exposed PMMA-g-PSX Copolymer

when degradable linkages are present in the system. This would tend to strengthen the arguement that the end groups must be thermally stable in the graft copolymers.

Contact angle analysis of films of these copolymers with water droplets showed another interesting trend, as seen in Table 22. Increasing macromonomer molecular weight increases the contact angle and therefore the siloxane content of the surface. Increasing siloxane composition also increases the contact angle for any given graft molecular weight as might be expected. ESCA analysis allows us to quantify the composition of the surface as a function of depth into the surface. In Table 23, we can see that not only do the higher graft molecular weight copolymers contain more siloxane at the surface but also show less of a drop in composition with increasing depth.

Refractive Index measurements on films of the copolymers indicated that an averaging of the refractive indices of the two homopolymers occurred. Table 24 summarizes the refractive indices measured for PMMA-g-PSX copolymers. With increasing siloxane content the materials are increasingly difficult to get a repeatable measurement on and a loss of linearity occurs in the plot.

Transmission Electron Microscopy or TEM were run on films of these copolymers prepared by several techniques [379]. One method was to add a drop of a dilute solution

Table 22

Contact Angle Analysis of PMMA-g-PSX Copolymers

Sample	Contact Angle
PMMA Control	74°
1K 5 WT% PSX	97°
1K 16 WT% PSX	105°
5K 5 WT% PSX	99°
5K 16 WT% PSX	107°
10K 5 WT% PSX	108°
10K 16 WT% PSX	109°
20K 5 WT% PSX	109°
20K 16 WT% PSX	109°

Table 23

Dependence of Siloxane Molecular Weight and Composition on Surface Composition of PMMA-g-PSX Copolymers by Variable Angle XPS (ESCA) (Copolymers ~ 5 WT% PSX)

	%PSX		
ANGLE	10°	30°	90°
Macromonomer Mn			
1000	79	52	41
5000	86	86	69
10,000	100	97	72
20,000	100	100	90

Table 24

Summary of Apparent Refractive Indices of PMMA-g-PSX Copolymers

Sample	Description	R.I.(25°C)
7I	10K 7 WT%	1.485
7J	10K 14 WT%	1.476
7K	10K 20 WT%	1.466
7L	10K 29 WT%	1.452

of polymer in chloroform onto a water surface. After spreading, films of less than 1000 angstroms can be obtained for TEM measurements. A second method was the slow evaporation of solutions to form "thick" films, which are then cryogenically ultra-microtomed at low temperature. The second method is more representative of "equilibrium" type morphologies, since the film forms under slow evaporation conditions, while the first method has very fast evaporation rates and may thus trap morphologies in a non-equilibrium state.

Figures 37 through 39 depict the typical TEM's of PMMA-g-PSX over a range of compositions and siloxane graft molecular weights. These samples were prepared via the slow evaporation and microtome technique. No domains were evident for any samples with 1K grafts. TEM's were taken with no staining agent since the difference in electron density is sufficient to allow direct visualization of the contrast between phases. However, when phase mixing occurs the absolute difference in electron density between phases decreases. This is taken as the reason that no domains were visible for the 1K samples.

Table 25 summarizes the domain sizes measured from the PMMA-g-PSX samples with 16 weight percent siloxane, Figure 37. Several techniques were used to measure the domain sizes, including hand measuring of domains in

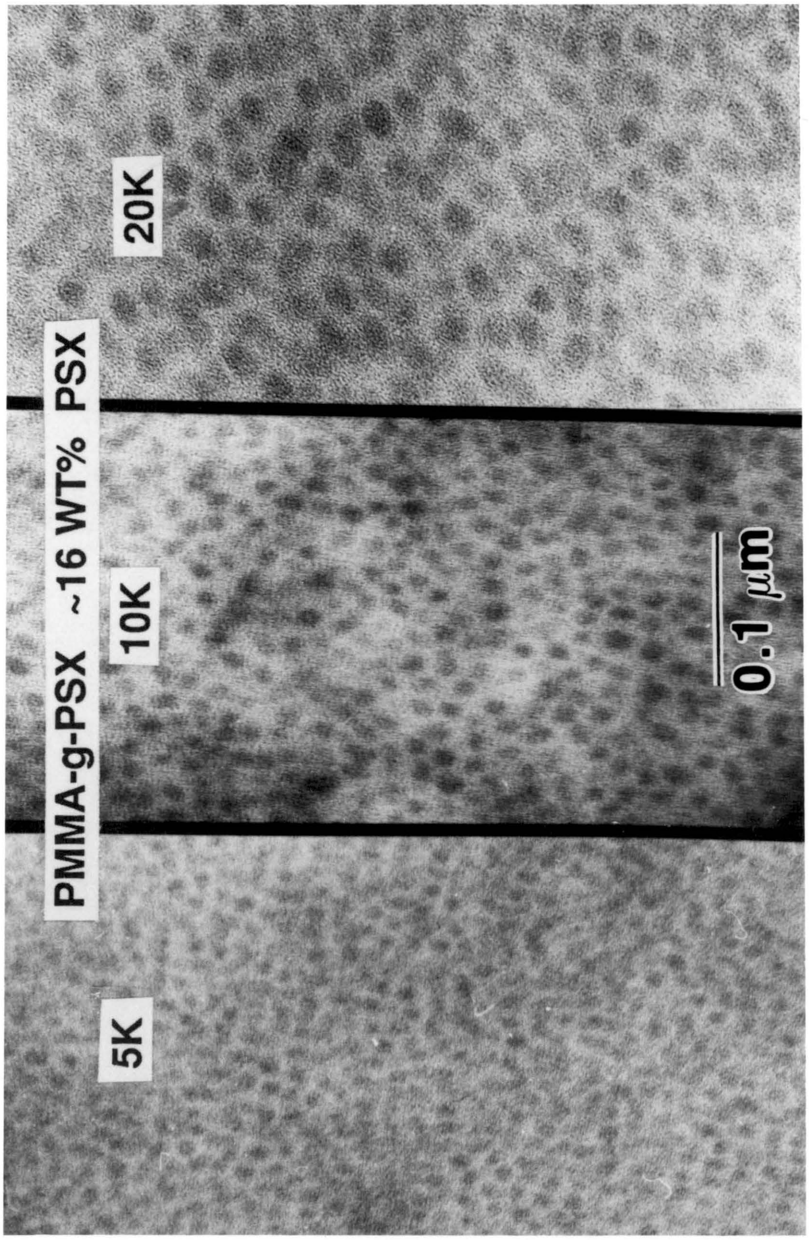


Figure 37. TEM's of PMMA-g-PSX 16 WT% PSX

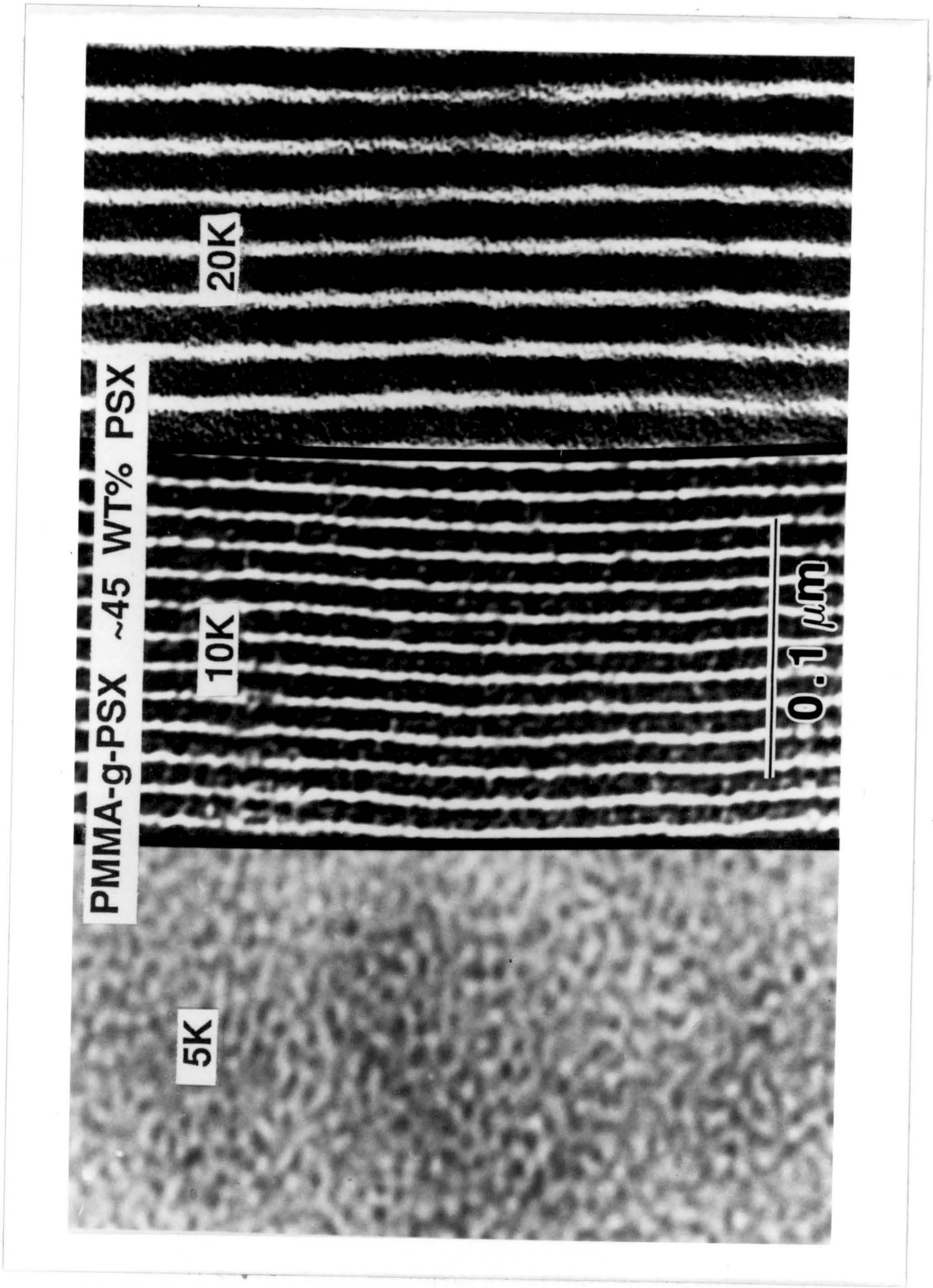


Figure 38. TEM's of PMMA-g-PSX 45 WT% PSX

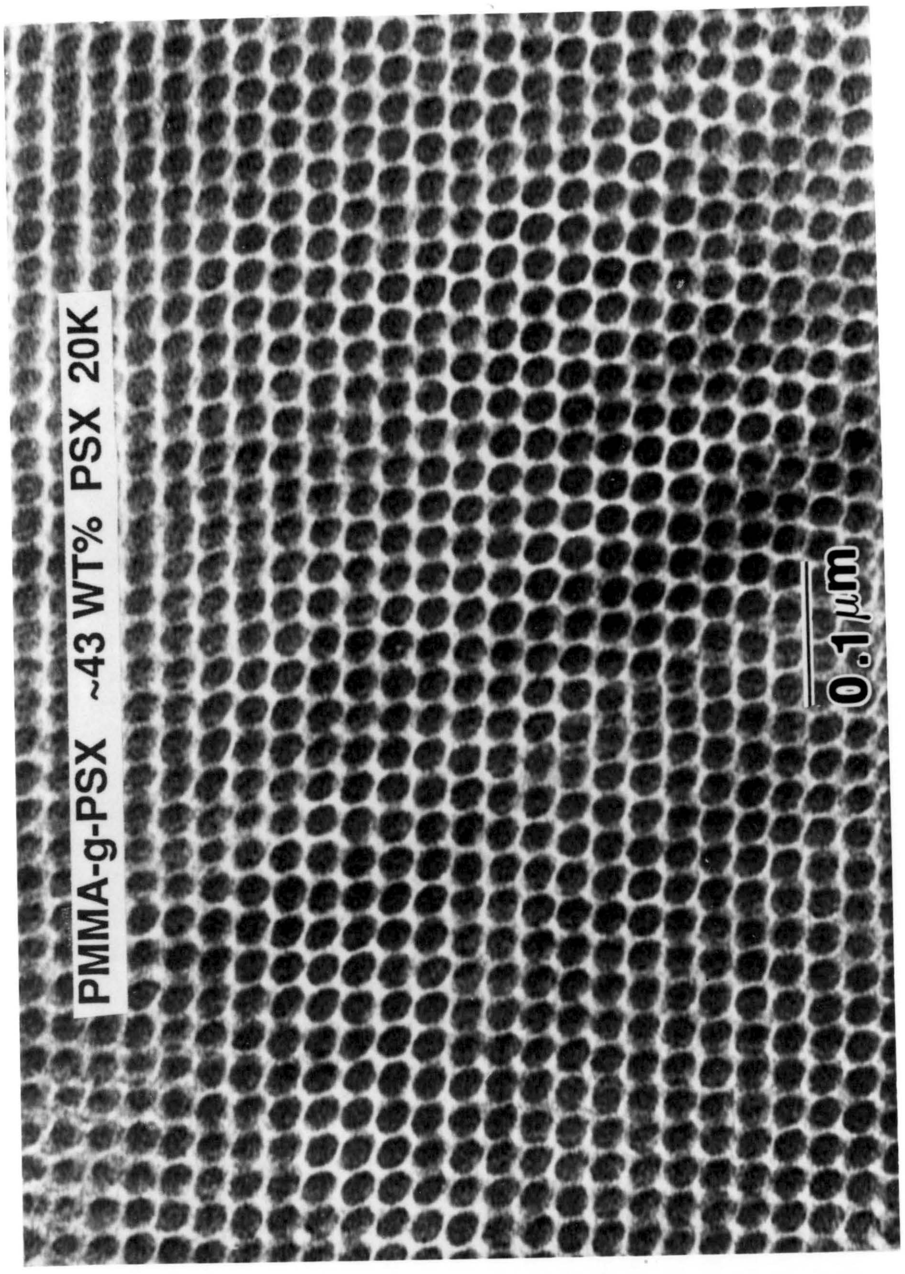


Figure 39. TEM of PMMA-g-PSX 20K PSX 43 WT% PSX

Table 25

Small Angle X-Ray Scattering and TEM Analysis of PMMA-g-PSX Copolymers (~16 WT% PSX)

Macromonomer Mn	Domain Size	Interdomain Spacing	Max. Scattering Intensity
1000	---	13.6 nm	30
5000	8 nm	20.7 nm	110
10,000	12 nm	32.5 nm	260
20,000	20 nm	42.0 nm	540
30,000	24 nm		
40,000	30 nm		

prints developed. Also computer imaging analysis were used which provides size distributions.

Figure 38 depcits a side by side series of TEM's of PMMA-g-PSX samples with approximately 45 weight percent siloxane (for 5K, 10K and 20K grafts). Sample 11Q with 20K grafts and 43 weight percent siloxane can be shown to have about 2 grafts per backbone (Table 15) and thus could be compared to a "triblock" structure. Indeed, the hexagonally packed rod structure, Figure 39, has never been presented before in a graft copolymer, but has only been seen in anionically prepared triblock copolymers. It is noteworthy that as siloxane content increases to 45-50 weight percent and the morpholgy switches to a hexagonally packed rod structure the domain size does not increase, but rather the ordering of the system increases.

Sample 11J with 10K grafts and 47 weight percent siloxane shows a lamellae morpholgy, Figure 38, while sample 11H with 5K grafts has a muddled bicontinuous morpholgy. Thus, TEM shows several differences that phase mixing has on morpholgy. In Figure 40, a TEM of sample 88G shows that samples with 10K grafts and a siloxane content of 42 weight percent forms a lamellae morpholgy. The tendency for samples to form spherical domains converting to rod like structures and then switching over to lamellae structure with increasing graft content is not followed as for block copolymers.

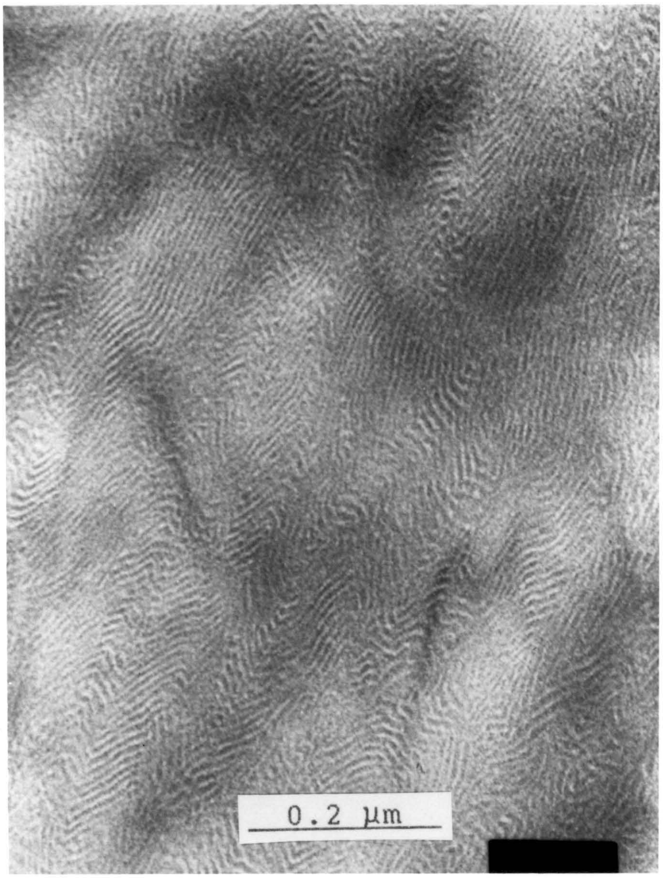


Figure 40. TEM of PMMA-g-PSX 10K PSX 42 WT% PSX

The last casting technique is representative of the method used for formation of lithographic films. It involves the spin casting of films less than 1000 angstroms, from chlorobenzene at 1000-3000 rpm. These films are spun onto salt plates, baked at 160°C for 1 hour and the salt plate dissolved in water to yield a free standing film which can then be analyzed by TEM.

The initial spinning involves fairly fast evaporation rates, but the baking above Tg has been shown to change the surface composition by allowing polymer mobility. The ability of the polymer to form oriented structures such as that of 11Q or 11J were of interest.

Small Angle X-ray scattering (in cooperation with Prof. Garth L. Wilkes, and Hao Hsim Huang) complimented the TEM method. The results obtained from SAXS are represented typically as an interdomain spacing. The ratio of SAXS values of interdomain sizes to domain sizes determined by TEM can be compared from sample to sample. Table 25 summarizes the data from SAXS measurements of interdomain sizes as well as the domain sizes as measured from TEM. Another piece of information determined from the SAXS experiments is the value of the maximum in scattering intensity. This can be related to the degree of phase separation, since as mentioned, mixing will decrease the difference in electron density between phases and thus the amount of scattering will decrease. It can be seen in Table 25 that as the graft molecular weight increases the scattering intensity increases. Scattering intensity will thus be a function of interdomain spacing and degree of mixing and the large differences between samples is due to differences in phase mixing. It is important to note that an interdomain spacing was determined for materials with 1K grafts, and therefore domains must exist but the maximum in scattering intensity was a factor of 20 less than for the 20K grafts. This would provide an adequate reason for lack of domain visibility by the TEM method. Also, the use of the invariant calculation leads to information on the degree of mixing of the two phases. Figures 42 through 45 reproduce the SAXS traces of the series of samples of PMMA-g-PSX of 16 weight percent PSX. As can be seen, not only are the scattering intensities increasing with increasing graft molecular weight, but also the breadth of the peaks are decreasing. This narrower narrower peak is indicative of better phase separation.

The use of SAXS is also important to investigate the ordered structures such as those found in samples 11J and 11Q. With proper analysis of SAXS information on a film such as 11Q the packing orders should be discernable from the higher orders of scattering. Figure 45 reproduces the

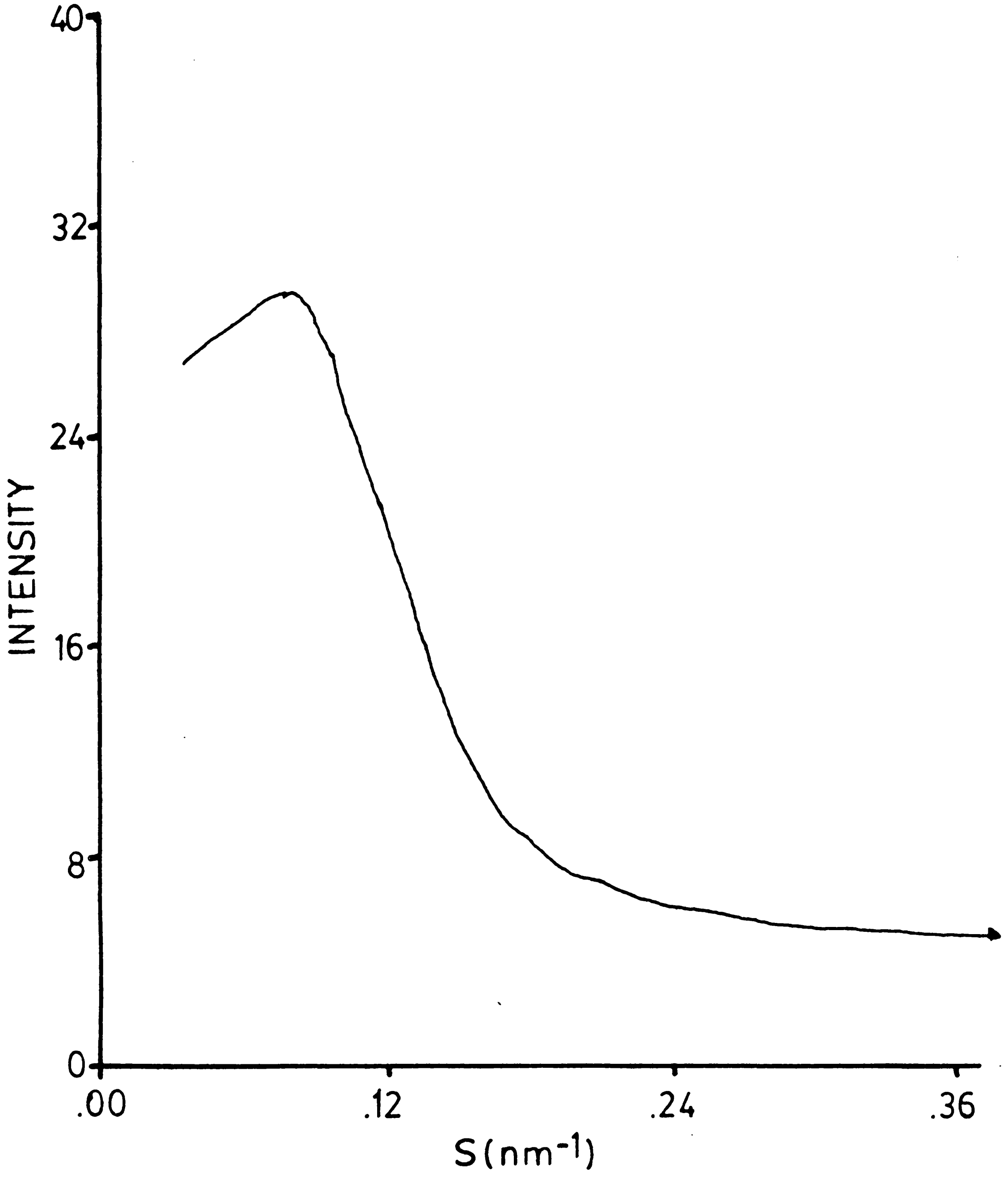


Figure 41. Small Angle X-ray Scattering (SAXS) of PMMA-g-PSX 1K 16 WT% PSX

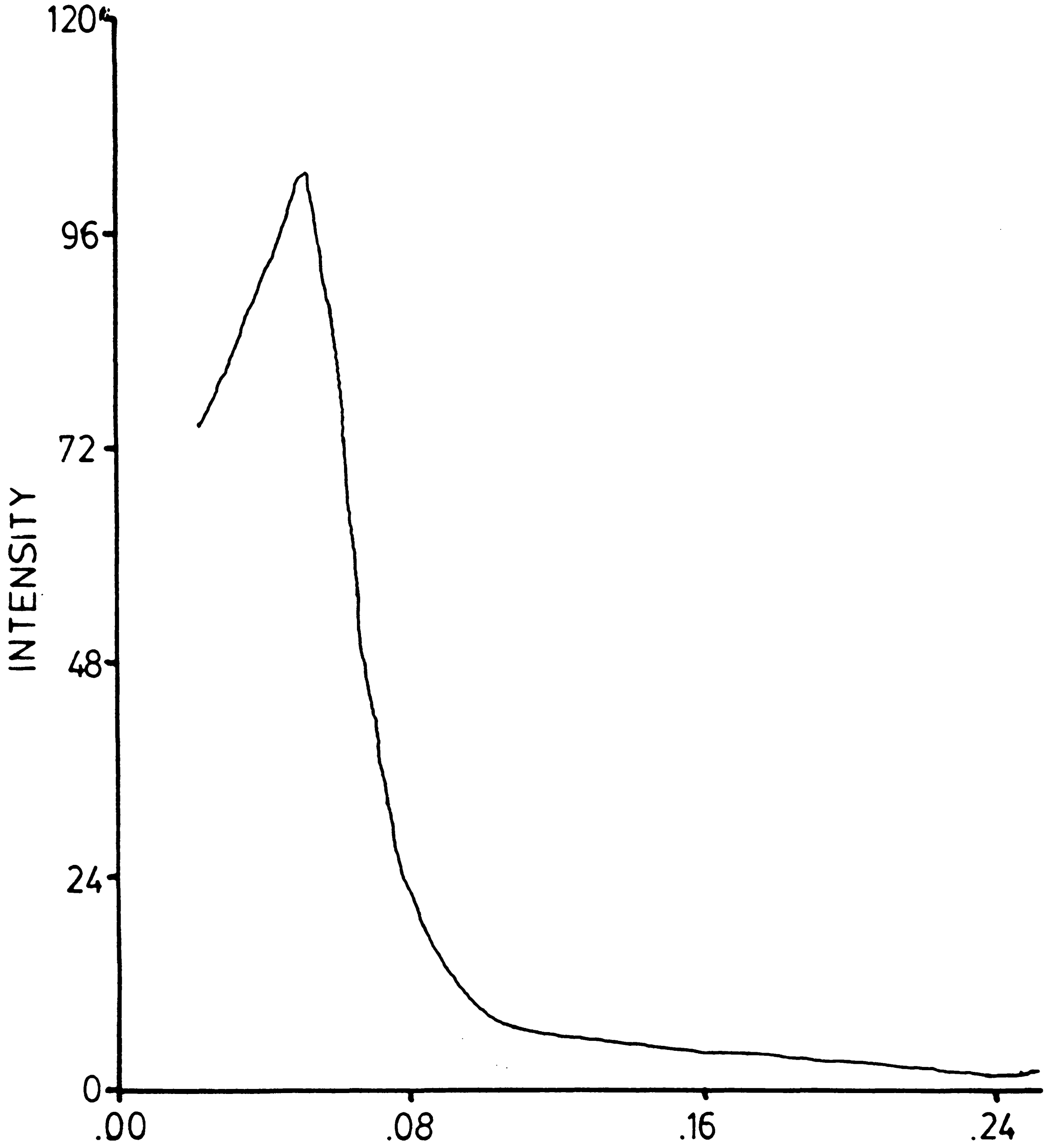


Figure 42. Small Angle X-ray Scattering (SAXS) of PMMA-g-PSX 5K 16 WT% PSX

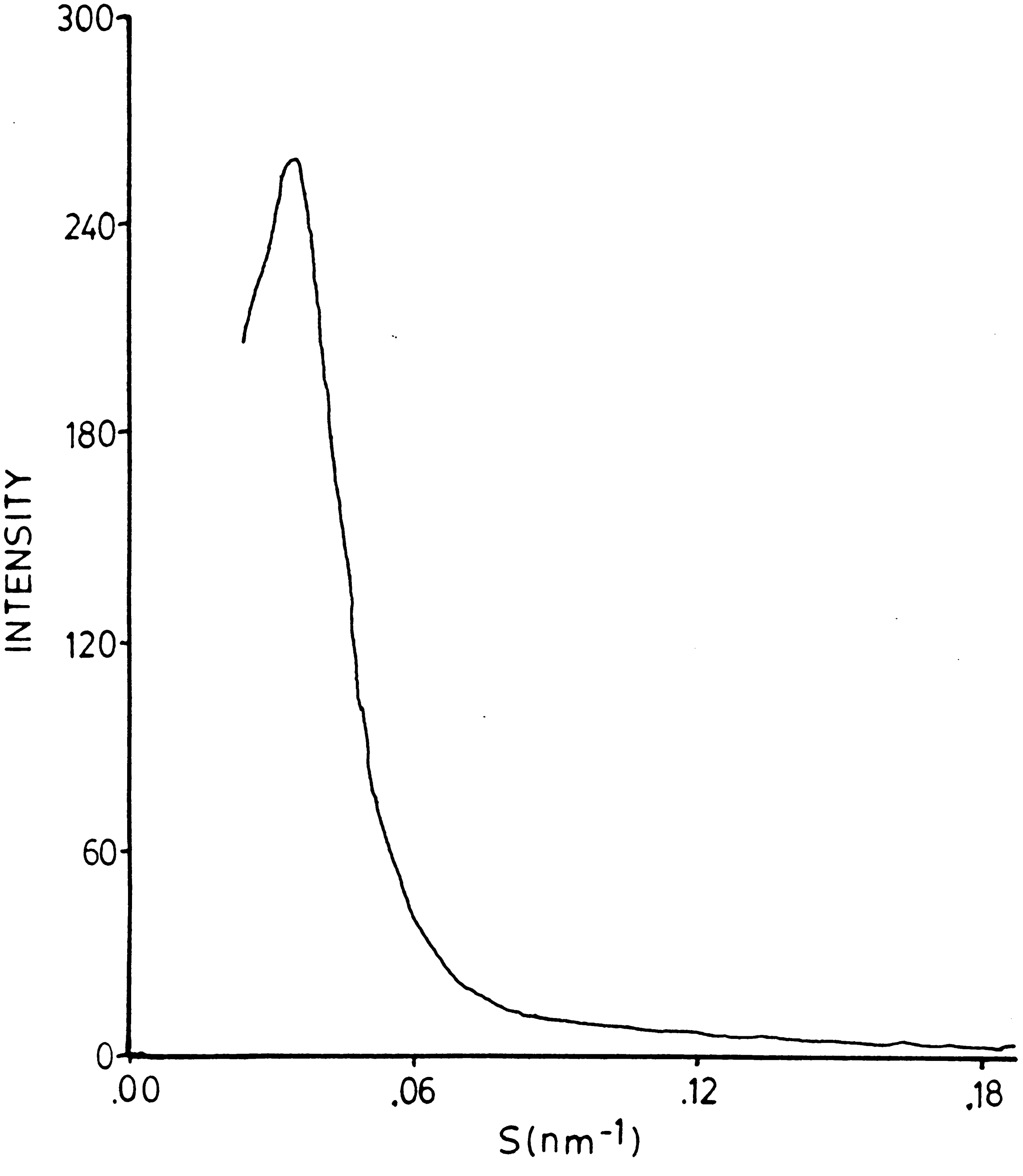


Figure 43. Small Angle X-ray Scattering (SAXS) of PMMA-g-PSX 10K 16 WT% PSX

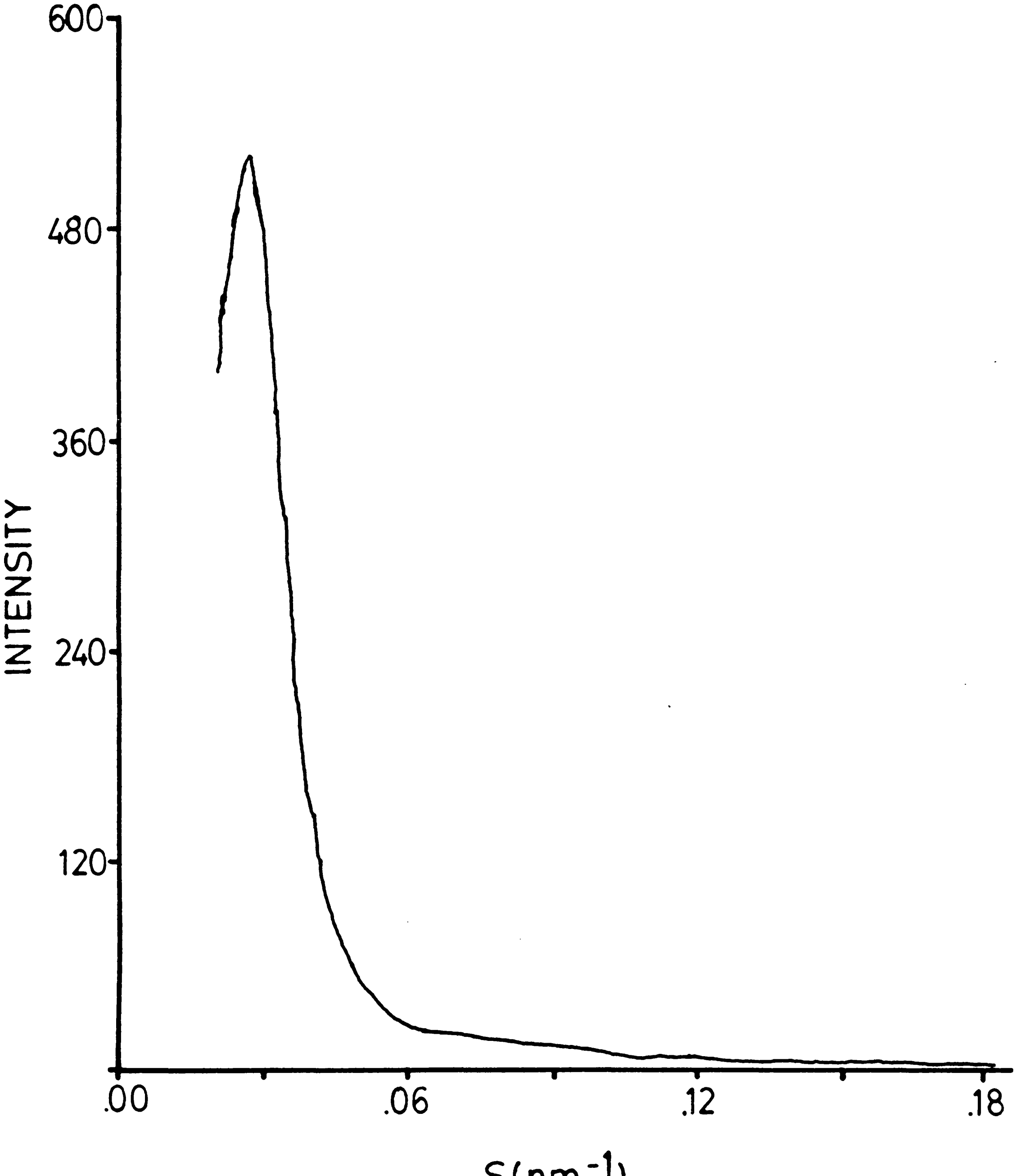


Figure 44. Small Angle X-ray Scattering (SAXS) of PMMA-g-PSX 20K 16 WT% PSX

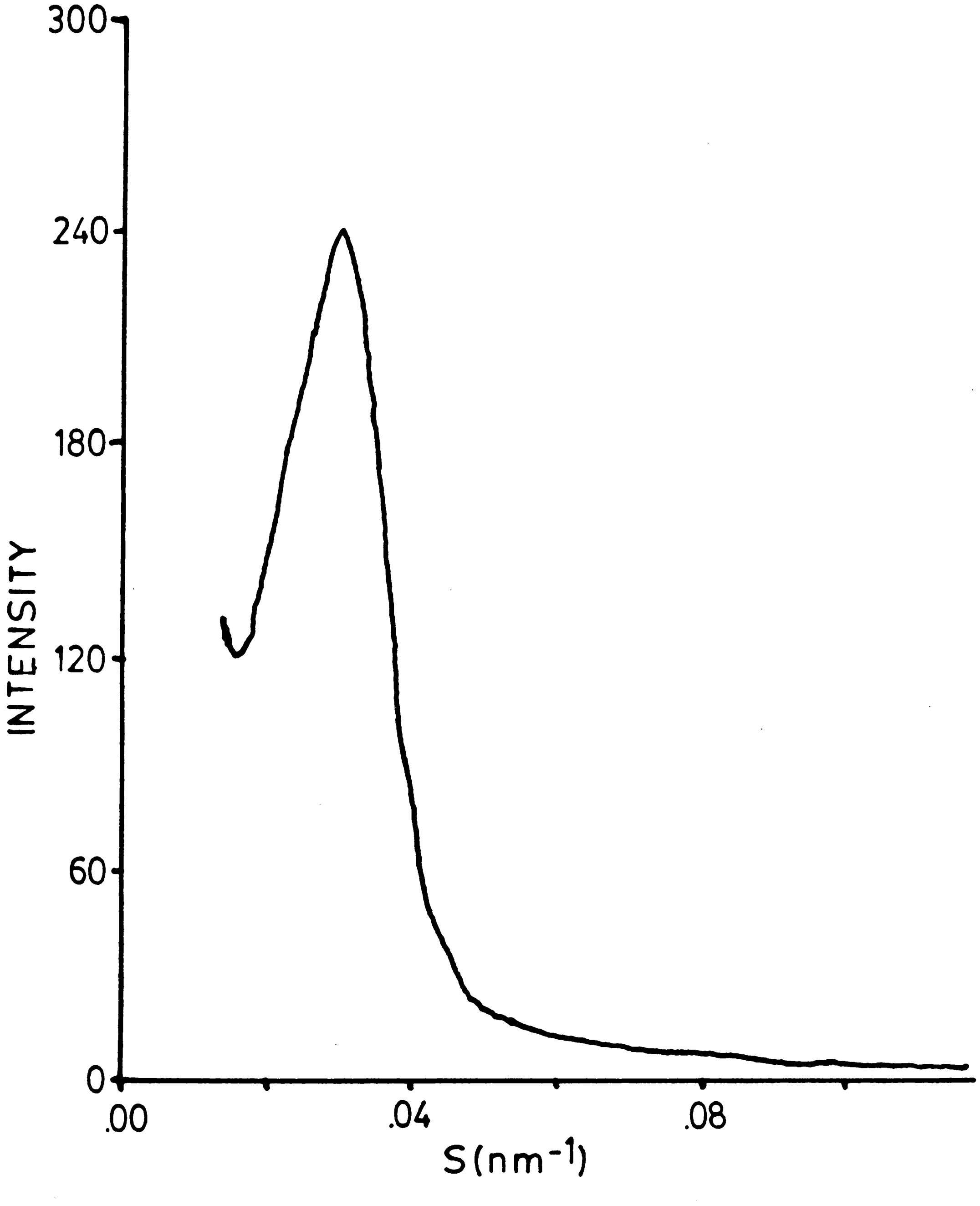


Figure 45. Small Angle X-ray Scattering (SAXS) of PMMA-g-PSX 20K 43 WT% PSX

SAXS analysis of sample SSII-11Q which showed a packed rod structure in the TEM method.

Lithographic evaluation of these materials as UV and e-beam resists was carried out at Bell Communications Research by Dr. Murrae Bowden and coworkers [380]. It was found that the copolymers exhibited the sensitivity of PMMA towards UV degradation, however e-beam irradiation of the copolymers causes two mechanisms of reaction to occur. PMMA classically degrades while siloxanes crosslink, and the crosslinking reaction of siloxanes is much more sensitive than the chain scission reaction of PMMA. While the materials act as positive photoresists under UV irradiation, they act as negative resists under e-beam irradiation. Figures 46 through 53, show some patterns developed by oxygen reactive ion etching into a 1.5 micron planarizing layer.

One micron lines could easily be developed in a positive manner with UV irradiation as shown in Figures 46 thorugh 49, while with only 27 weight percent siloxane in the system, the materials were poor negative resists. Figures 50 through 53 are patterns developed via e-beam exposure and show poor control of line width.

The surface of these copolymers were investigated by ESCA and SEM before and after reactive ion etching. Table 26 summarizes the ESCA results as a function of

Figure 46. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists UV Exposure

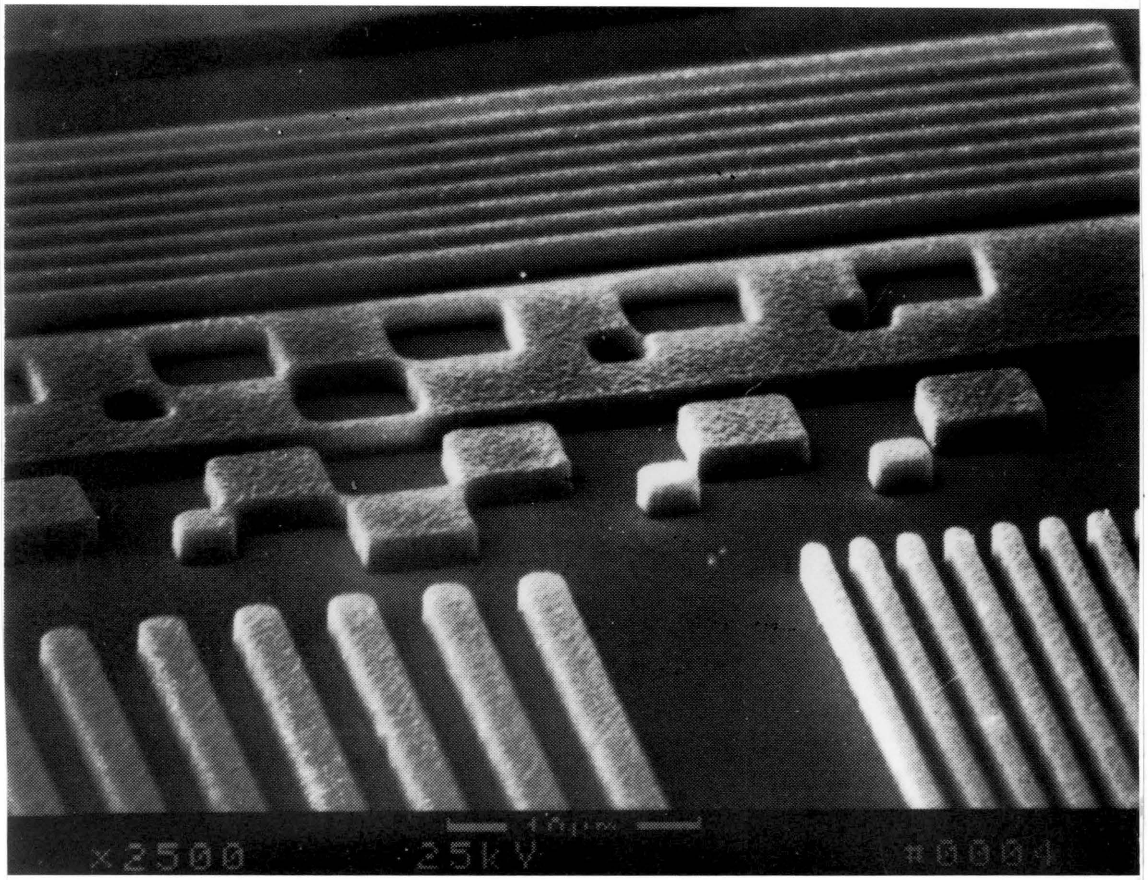


Figure 47. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists UV Exposure

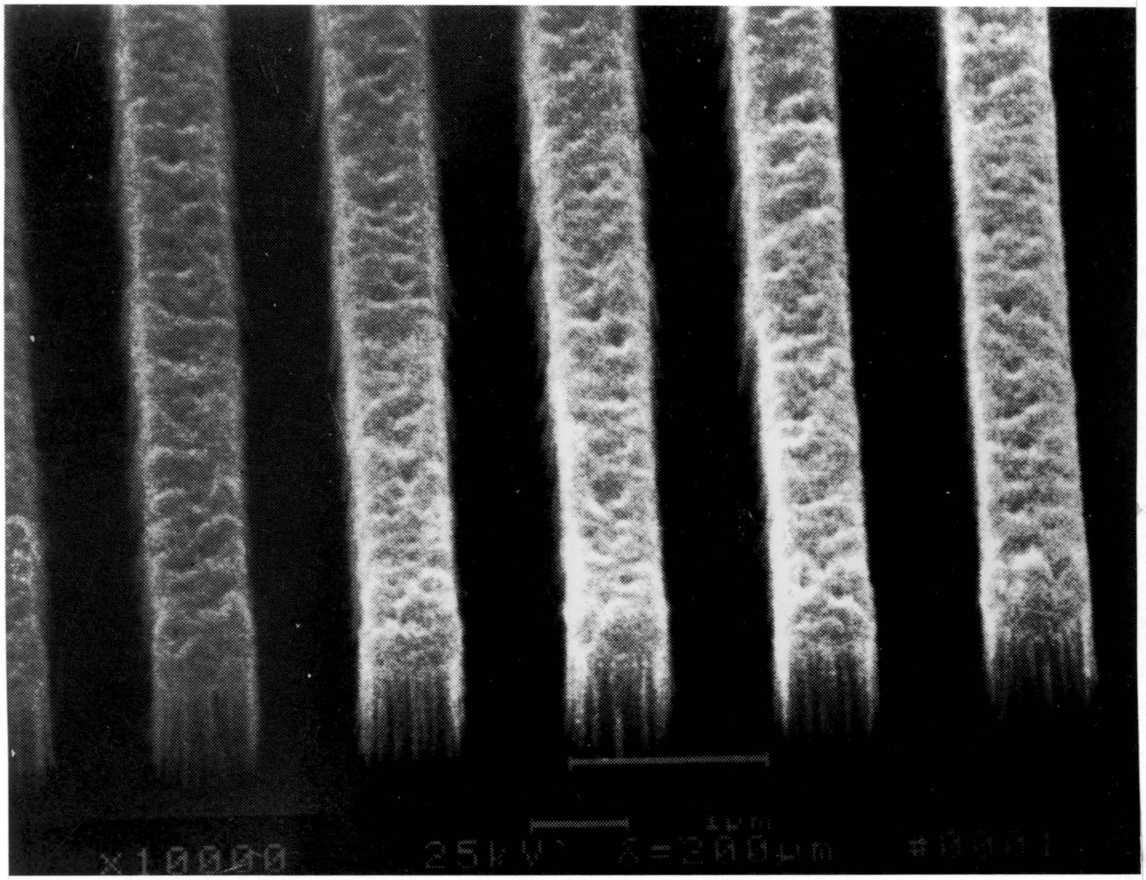


Figure 48. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists UV Exposure

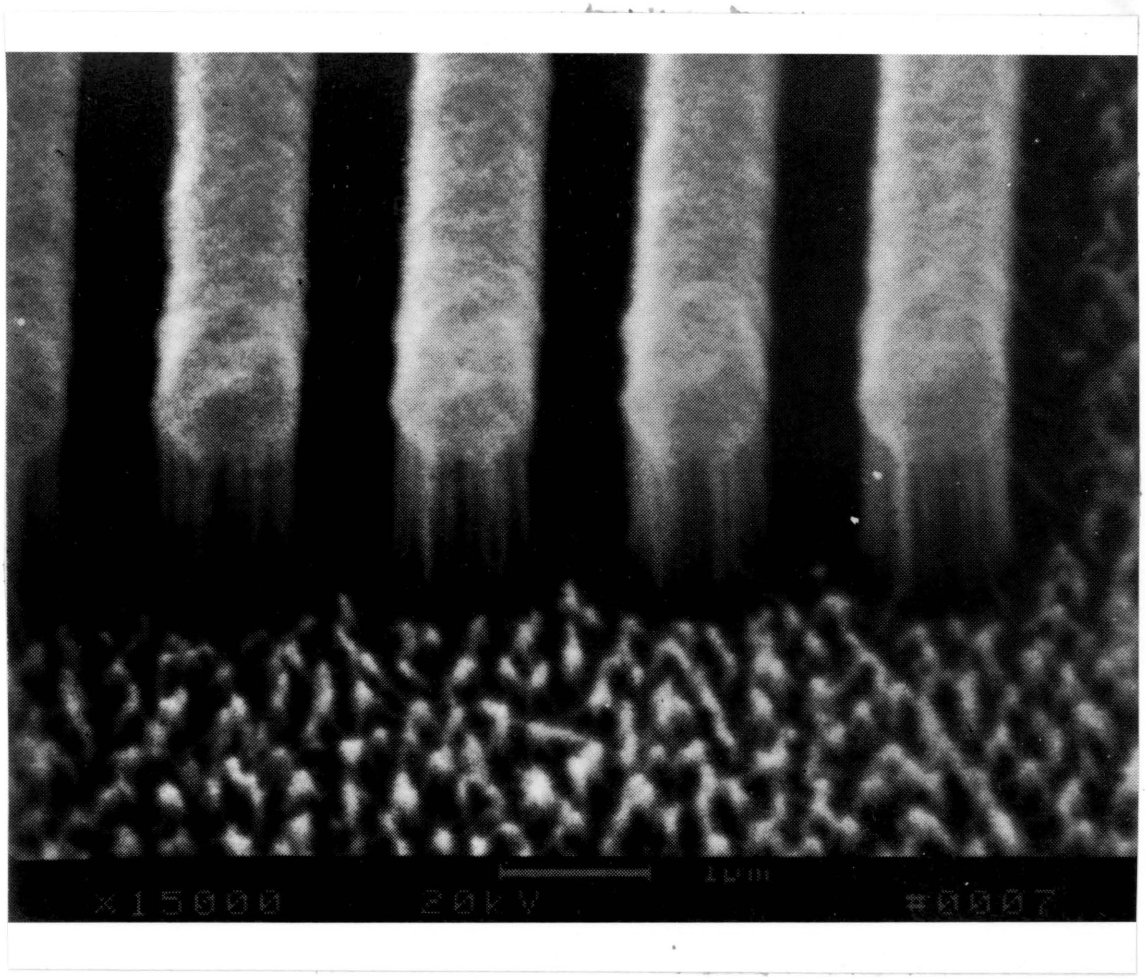


Figure 49. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists UV Exposure

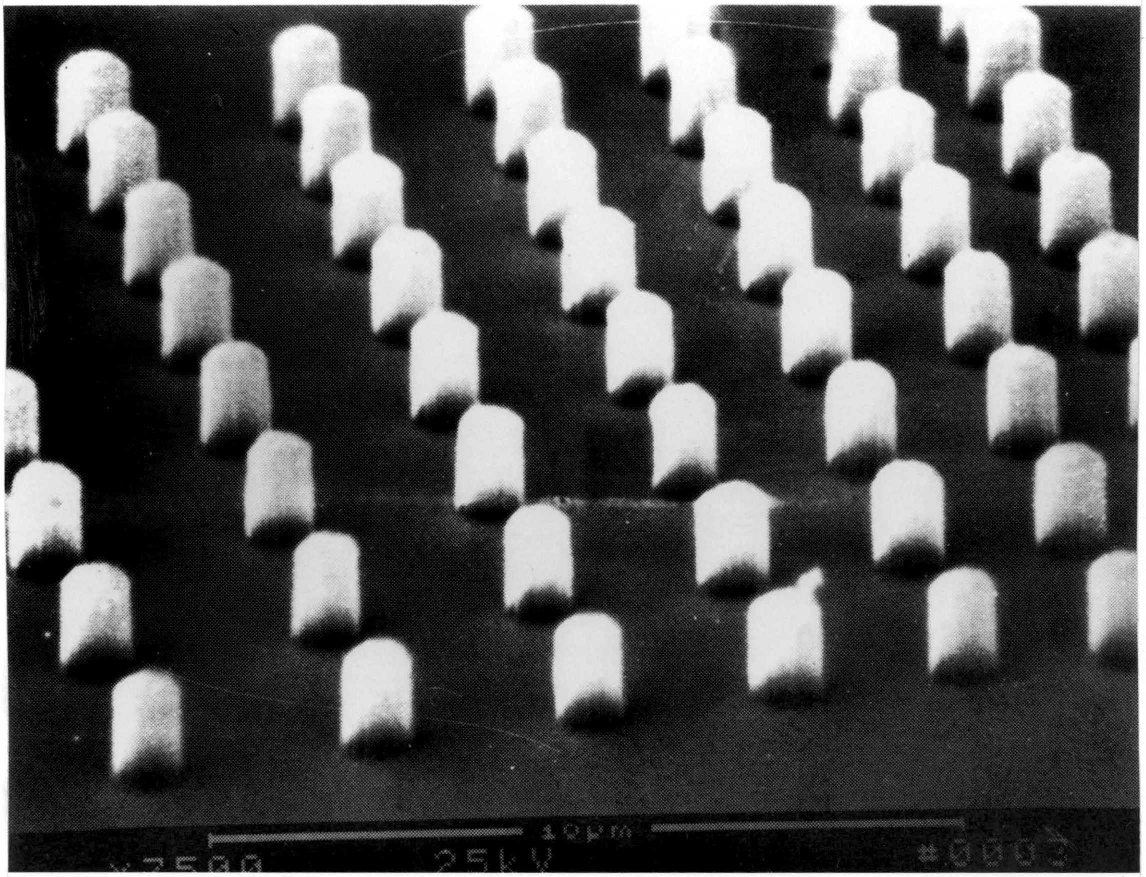


Figure 50. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists E-Beam Exposure

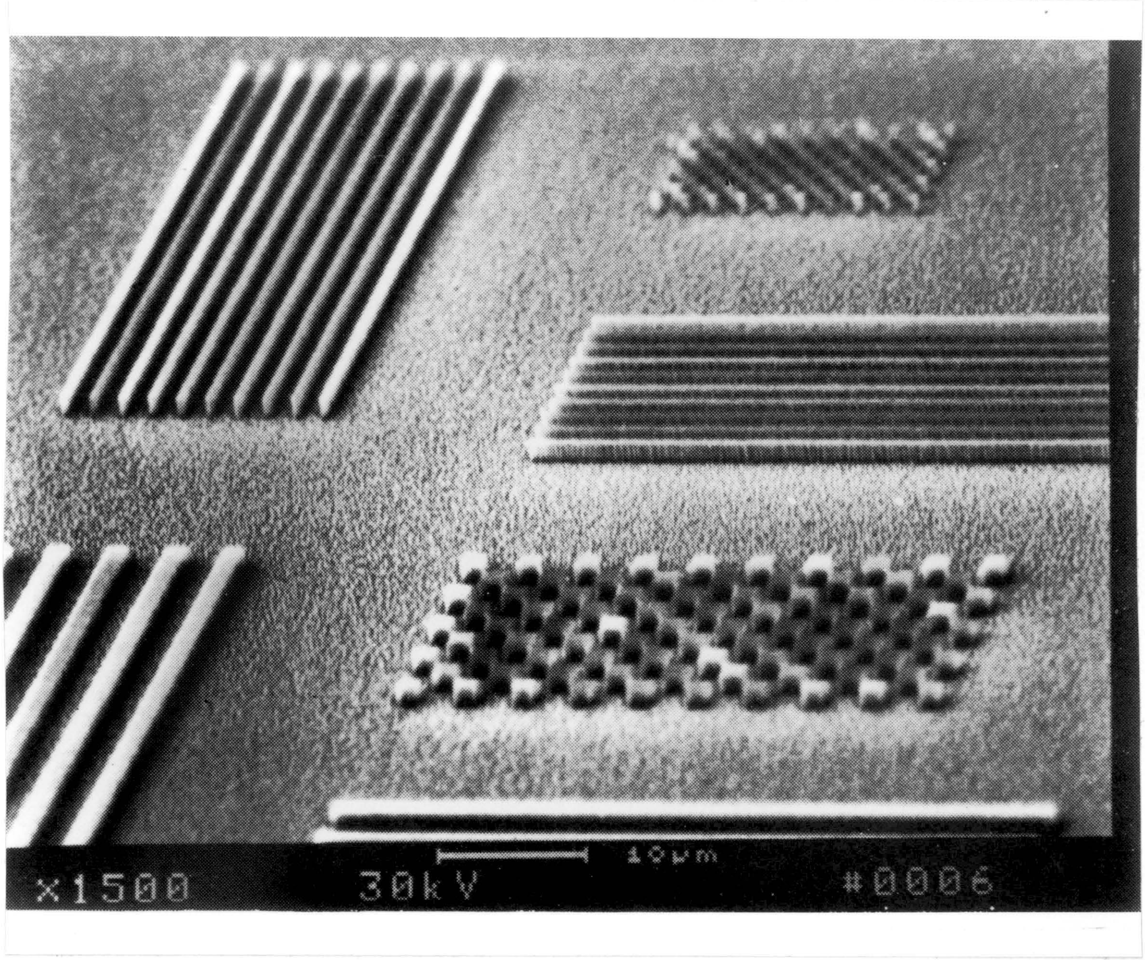


Figure 51. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists E-Beam Exposure

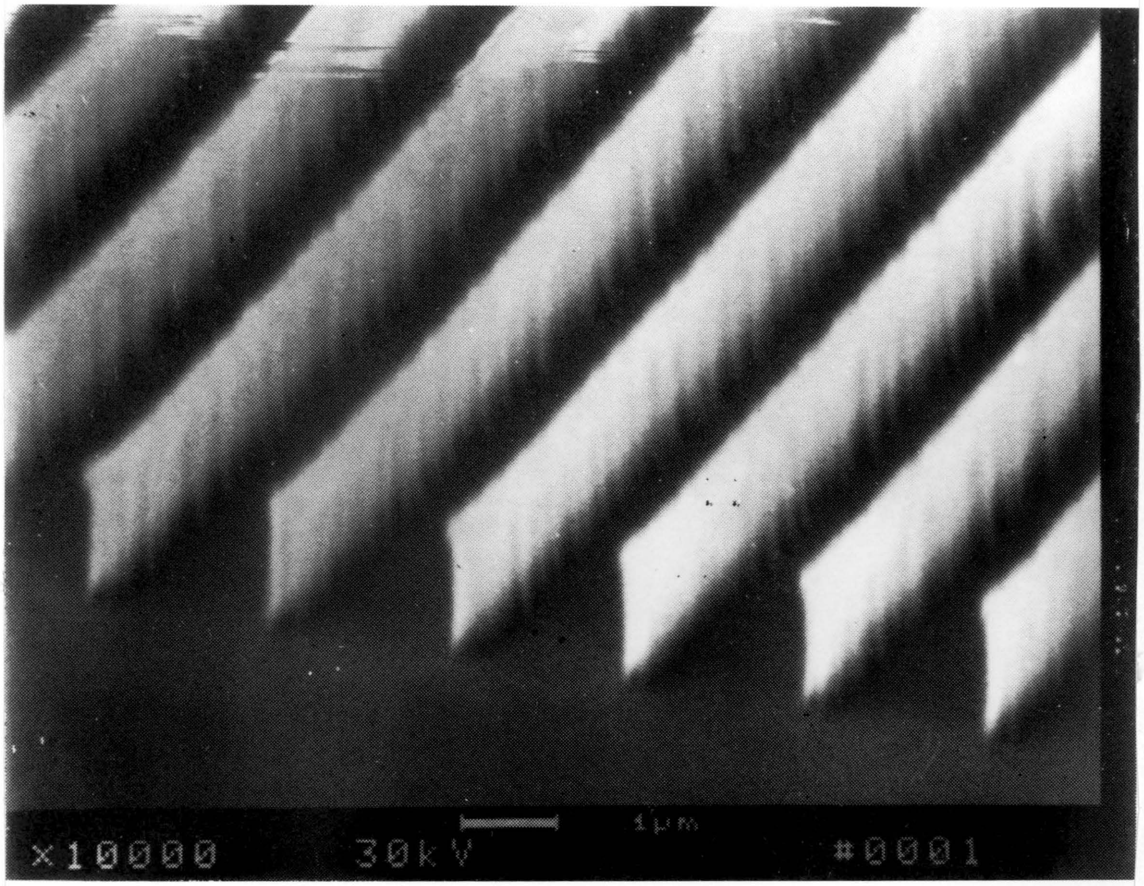


Figure 52. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists E-Beam Exposure

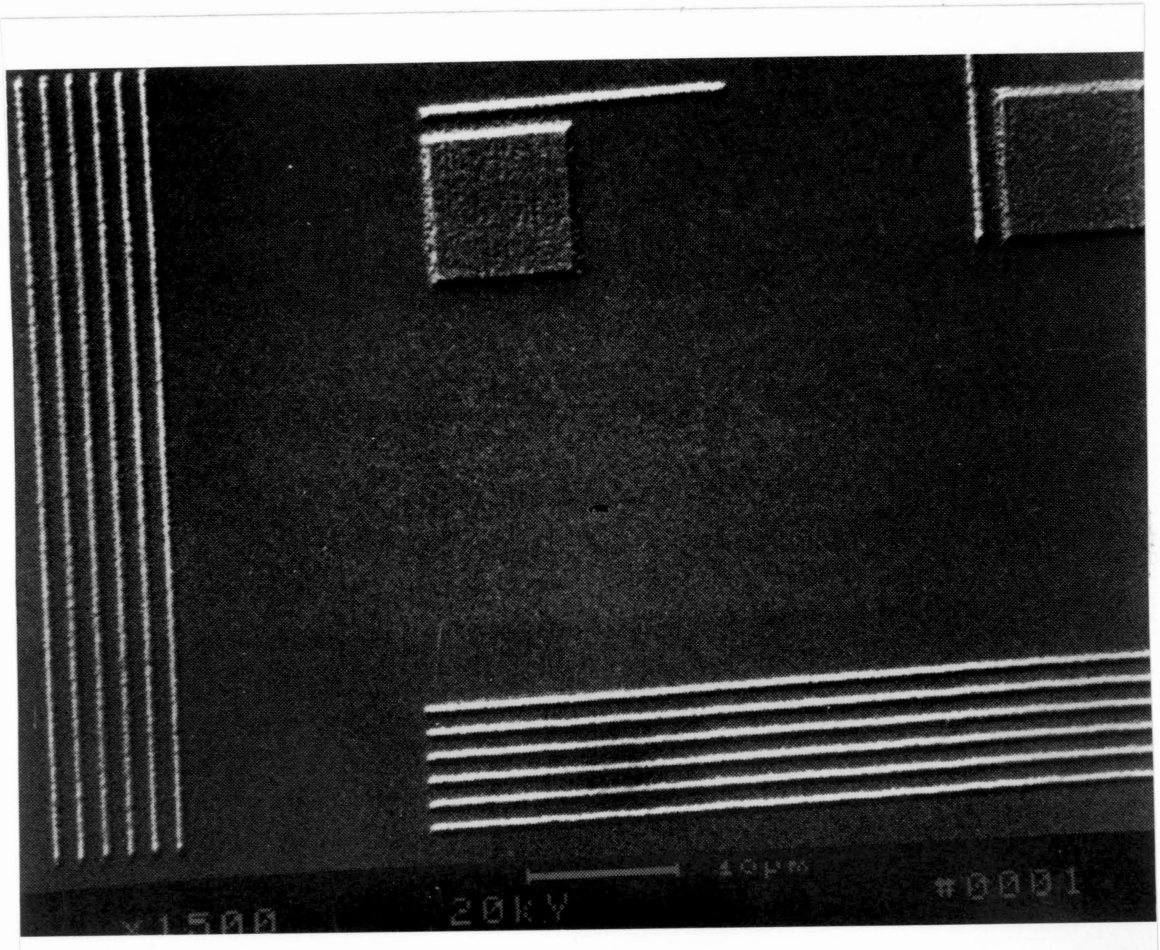


Figure 53. Lithographic Patterns Developed by RIE with PMMA-g-PSX Resists E-Beam Exposure

Table 26

ESCA Analysis of Lithographic Samples

Sample	%PSX		
	10°	30°	90°
26A Spun	100	85	69
26B Spun and Baked	94	92	80
26C Spun, Baked, and Washed	94	89	69

ALL ANGLES

	C	O	Si
26D Spun, Baked, and RIE	25	50	25
26E Spun, Dried, Washed, and RIE	25	50	25

Samples Spun from Chlorobenzene

Baked at 160°C for One Hour

Wash: Typical PMMA Developer

3:1 Mixture (Methyl Ethyl Ketone: Isopropanol) sample treatment in a typical procedure for lithographic production. The initially spun wafer can be compared to the post baked sample to evidence part of the effect of the baking. It can be imagined that a non-equilibrium film is formed by spinning which is then allowed to come to thermodynamic equilibrium by baking above the Tg of the copolymer. Siloxane migration to the surface would be expected due to the low surface energy of siloxanes. Surface washes with siloxane solvents such as hexanes produce no loss of siloxane content and also no effect on the reactive ion etch resistance of the materials. Washes with solvents for PMMA and siloxanes such as isopropanol do produce a lessening of the ion etch resistance but no surface composition change is noted. The presence of low molecular weight high siloxane graft materials, which were discovered by SCFE, might explain this phenomenon. These highly surface active materials are also much more soluble and could be removed much faster. They might also provide much greater ion etch resistance than higher molecular weight lower siloxane content materials.

SEM analysis of the polymers, as shown in Figures 53 and 54 before ion etching reveals a featureless surface. After ion etching a domain like remnant is present with features of approximately 50nm. These features would be 3-10 times the size of the domains in the starting materials, and are more likely a function of the etching conditions. Also evident is the difference between samples D (Figure 55) and E (Figure 54) which differ only in their pre-RIE treatment by the wash of MEK/IPA. Note that sample E which loses some RIE etch resistance, shows condiderable holes in the surface, probably resulting where siloxane has been removed, and RIE now proceeds into the surface.

These first copolymers were all prepared under free radical conditions so that the grafts have a narrow molecular weight distribution. However the backbone has a free radical distribution. Therefore, the overall molecular weight distribution and composition distribution are likely to be somewhat broad. It was of interest to prepare the copolymer by a mechanism which would provide a narrow molecular weight distribution backbone. The compositional heterogeneity of this type of copolymer might still be broad or narrow but, will not be complicated by the broad molecular weight distribution of the backbone. This system is thus an interesting study unto itself.

The anionic polymerization of alkyl methacrylate monomers to narrow molecular distribution polymers involves the use of highly pure monomers. In these laboratories a method was developed for the trialkyl aluminum titration of impurities from alkyl methacrylates

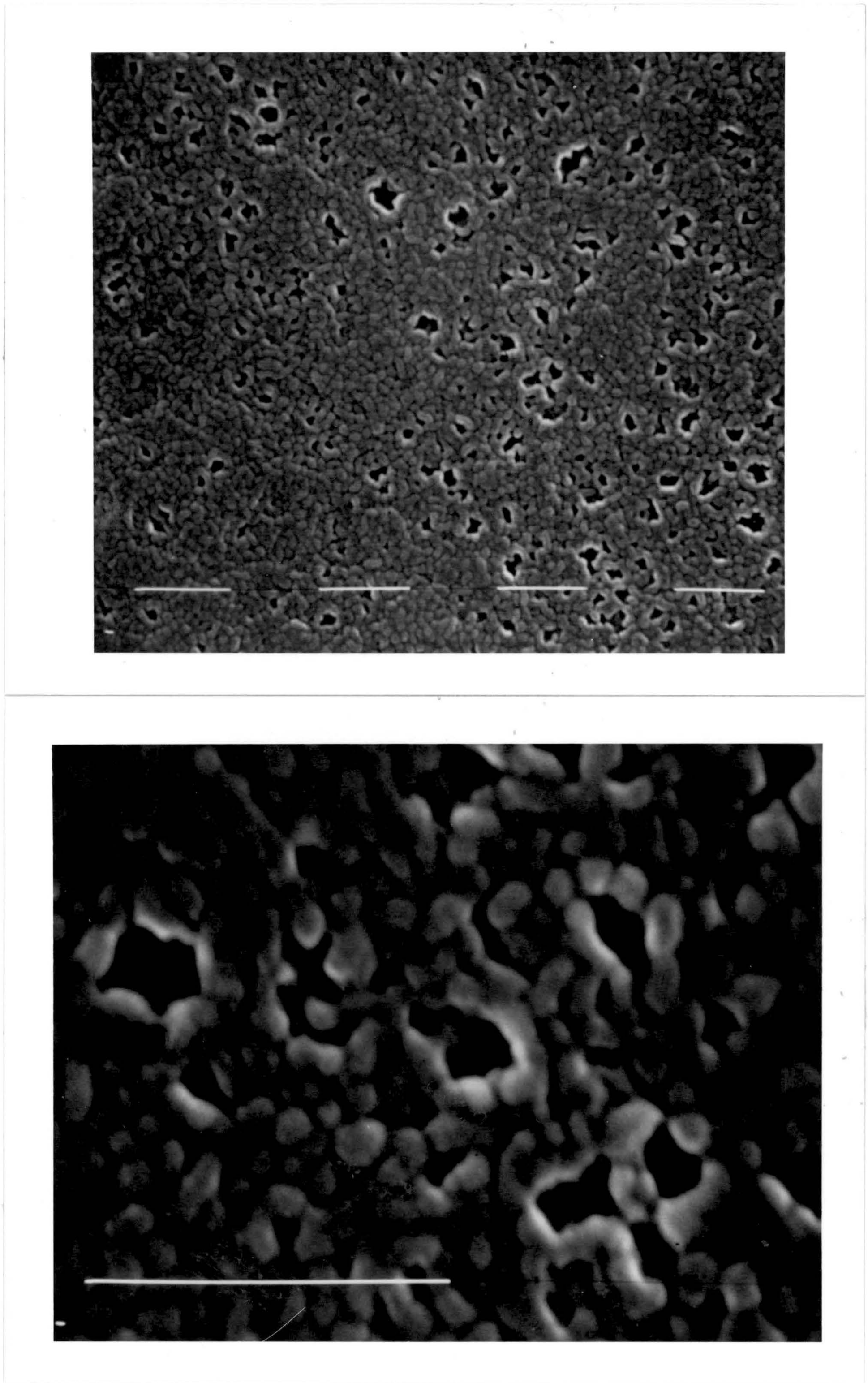


Figure 54. Surface Features of RIE Developed PMMA-g-PSX

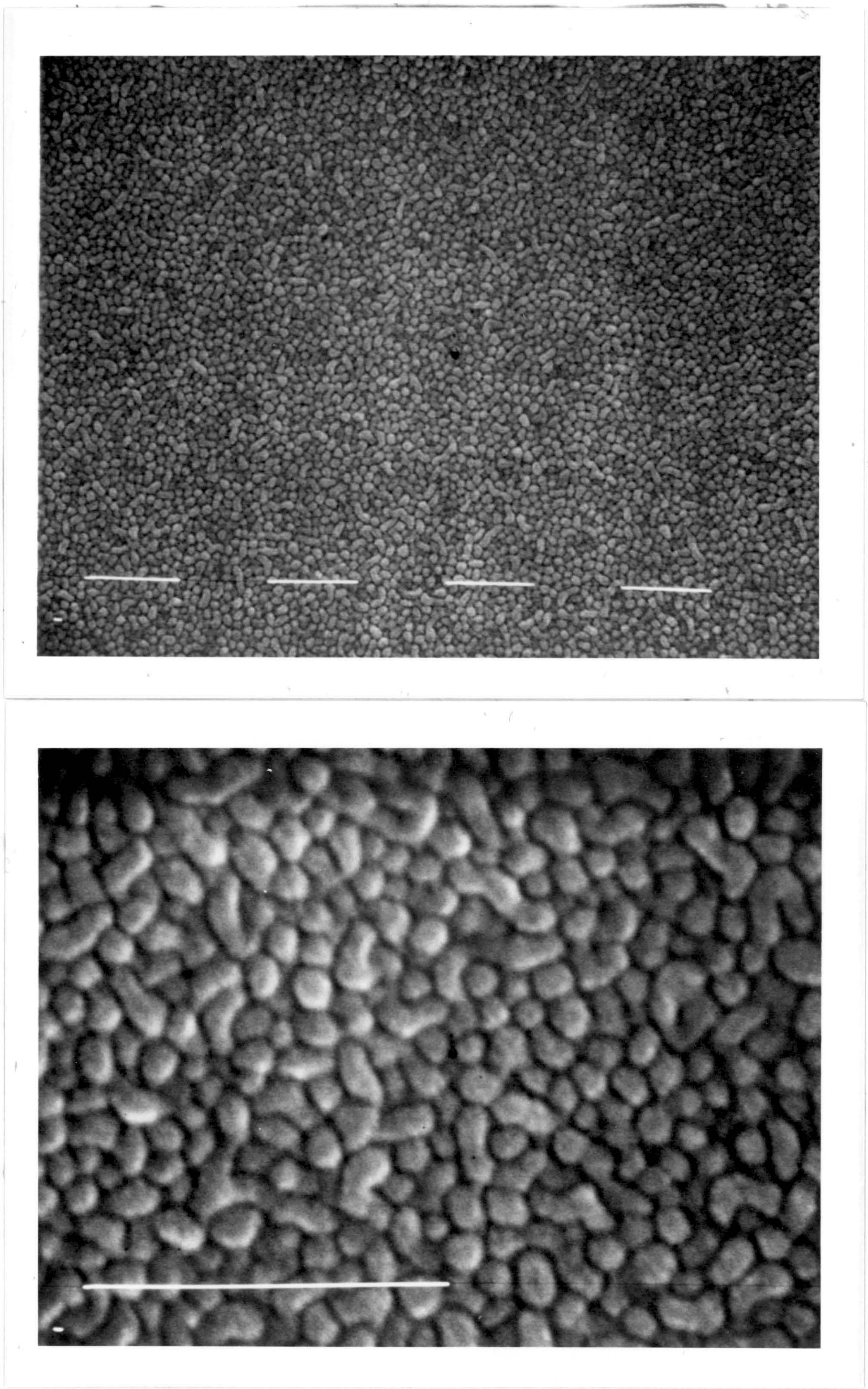


Figure 55. Surface Features of RIE Developed PMMA-g-PSX

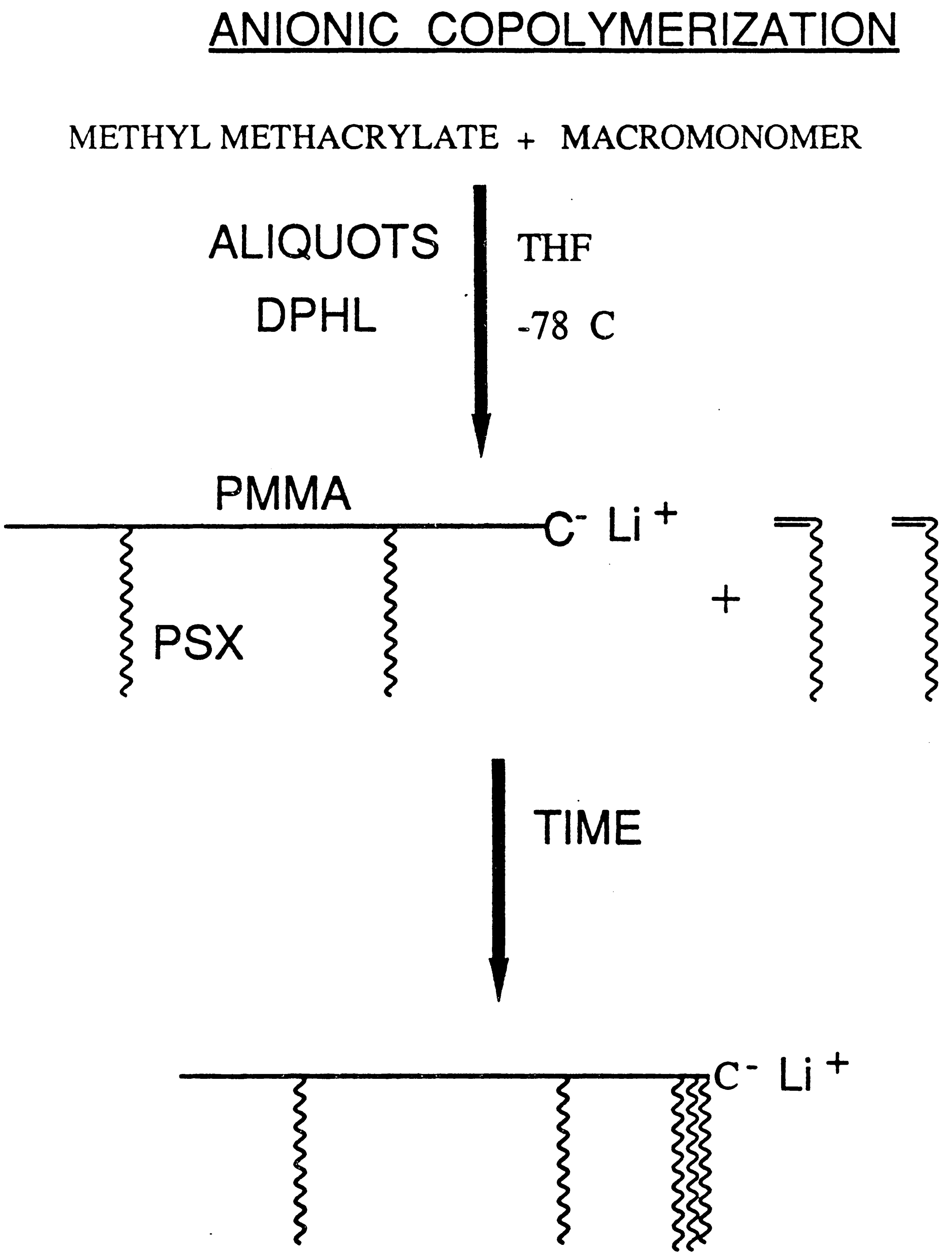
[312]. Extremely pure monomers may then be distilled from this titrated solution. The dropwise addition of these monomers to living polymerizations has been shown to be capable of producing very high molecular weight polymers with narrow polydispersities. Dropwise addition is necessary to achieve good mixing and to minimize any exotherm which helps to prevent side reactions. It has been found that the reactions are extremely fast and that complete monomer consumption in THF is achieved in seconds.

Macromonomers are not distillable so their purification to levels adequate for their continuous addition to a living polymerization is unlikely. However, under the proper conditions it should be possible to carry out the copolymerization of monomer and macromonomer to narrow polydispersity copolymer, with molecular weights of 100-200K desired. It was necessary to keep the exotherm from increasing the temperature above -65°C to prevent carbonyl attack. Solutions of 3-4 % solids were therefore used as it was found that at this concentration of monomer and initiator exotherms were controllable (to below -65°C). Next, it was necessary to add a living anionic initiator and diphenyl hexyl lithium was chosen, since it can initiate MMA with no side reactions. Aliquots were then added with time to the monomer- macromonomer solution while observing temperature via a thermocouple, as outlined in Scheme X. Exotherms start within 10 seconds after DPHL addition and continue for approximately 2 minutes. Then the temperature falls to -78°C again and the reaction is terminated.

Some of the early reactions produced materials with two to three narrow fractions from subsequent DPHL additions before the exotherm was noticed. Reaction was assumed to be rapid, but under these dilute conditions polymerization is relatively slow. Aliquot additions have to be spaced at least one minute apart to prevent this type of problem.

The analysis of these materials by NMR, GPC, Light scattering, SCFE, DSC, TGA, and TEM were also conducted.

NMR analysis indicated that 60- 70% of the macromonomer charged actually polymerized, as can be seen in Table 27. The reactivity ratios calculated for free radical copolymerizations indicate that macromonomers do not copolymerize as readily as a small monomer of similar structure due to the bulkiness of the macromonomer chain. This can be assumed to also be true for the case of an anionic copolymerization. If the copolymerization excludes some of macromonomer species, they will be present in solution after the polymerization has finished. However in the case of a living polymerization the possibility that



Scheme X. Anionic Copolymerization

Table 27

Molecular Weight Data for PMMA-g-PSX Prepared Anionically

Sample	<Mn>	MWD	WT% PSX	% Incorporated
28E 10K	154K	1.1	13%	40%
35A 5K	125K	1.3	33%	67%
35B 10K	116K	1.2	31%	62%
91B 10K			24%	60%

the living end will continue to react with time exists, which is not likely with free radical reactions. As shown in Scheme X, the situation where the end of the chain could continue to add macromonomer species and form highly branched comb structure exists. Another possibility is that as the polymerization proceeds the later formed graft co-polymer will be richer in macromonomer than the early formed copolymer. The difference between polymerization methods is that early formed and later formed copolymer in a free radical reaction are separate chains, since the chain growth lifetime is probably on the order of milliseconds to seconds. In a living polymerization the feed ratio is changing during the lifetime of the active chain end, and thus copolymer chains may be tapered in composition.

GPC measurements were very important to the analysis of these copolymers and important assumptions were made. It was assumed that no side reactions such as anionic attack on the siloxane chain were occurring or that the alkoxides in the system were not attacking the siloxane chains. This seems valid due to the lack in any case of a low molecular weight tail, which would occur with chain termination reactions.

The analysis then depended on the assumption that the backbone would have a narrow molecular weight distribution. Any broadening that would occur would be ascribed to a distribution of siloxane macromonomer units per backbone. The free radically synthesized materials have been theorized to have a distribution of chemical compositions dependent on the number of branches per backbone and the dispersity of backbone length. The anionic method eliminates the distribution of backbone lengths, and analysis of these copolymers for chemical composition heterogeneity would help elucidate the distribution function of the copolymers. If the dispersity of the anionic copolymers increased with siloxane content, there would be an indication that the composition heterogeneity were causing the broadening.

The analysis of these materials by PMMA standards indicated this trend, while analysis by the GPC with universal calibration and differential viscometer indicated that the materials were of narrow polydispersity (1.1- 1.3), even with siloxane contents of 40 weight percent, Table 27.

Confirmation of the absolute molecular weights were determined by membrane osmometry, and light scattering analysis, as with the free radical copolymers. Analysis of sample 35B showed that it had a number average molecular weight of 95,000g/mole and a weight average of 141,000 g/mole. An overall molecular weight distribution of 1.5

was determined with PMMA polydispersity of 2.3, and PSX dispersity of 2.1. It was concluded that a range of PMMA backbone chain lengths were present, along with a distribution of PSX chains per backbone.

The heterogeneity factors P/<Mw> were comparable to those for the free radical materials and Q/<Mw> values were a factor of two to five higher than for any of the free radical copolymers analyzed thus far. The interpretation of all of the data to provide a clear picture was then undertaken. Table 28 shows some typical chemical heterogeneity parameters for various free radical and anionic copolymers.

Several facts had to be considered. Firstly the copolymerization appears to have no side reactions and no low molecular weight tails, and secondly that macromonomer incorporation as with free radical copolymerizations is not efficient due to a lower reactivity of the macromonomer. This can be seen in Table 27 (in the last column) since typically only 60 -70% of the charged macromonomer is incorporated into the copolymer. Also of importance is our theory, that has foundation in the literature, that the macromonomer when present as the active chain end is hindered towards reinitiating monomer, in this case methyl methacrylate. The lower reactivity of the macromonomer also plays a role by steadily increasing

Table 28

Chemical Heterogeneity Parameters for PMMA-g-PSX Prepared Free Radically and Anionically

Sample	Description	P/<Mw>	Q/<Mw>
FREE RADICAL			
7K	10K 20 WT% PSX	0.105	0.021
7L	10K 29 WT% PSX	0.122	0.039
11J	10K 48 WT% PSX	0.102	0.047
11O	20K 25 WT% PSX	0.156	0.064
11Q	20K 43 WT% PSX	0.135	0.091
85B	10K 40 WT% PSX	0.041	0.019
ANIONIC			
35B	10K 31 WT% PSX	0.106	0.113

itself in the feed ratio by not being incorporated into the copolymer as readily as methyl methacrylate. If we extend this theory to the anionic copolymerization as well as the free radical copolymerization, then we have conditions where unequal reactivites of the chain ends can lead to non-uniform copolymerizations.

We can then imagine a case where homo-polymerization of methyl methacrylate is more rapid than copolymerization with macromonomer. With these conditions however increasing conversion improves the probability that the growing anion will react with a macromonomer, and thus slow its growth. With the proper kinetic conditions a fairly narrow molecular distribution is obtained, however considerable compositional heterogeneity has been incorporated not only into each individual chain because of the changing feed ratio, but also between chains due to the differences in kinetics between homo- and co-polymerization.

We can then reasonably explain the preparation of copolymers with narrow molecular weight distributions comprised of polydisperse backbones and a distribution of grafts / backbone. This is also necessary to explain the fact that the chemical heterogeneity is larger than for a random copolymer prepared free radically.

Super Critical Fluid Extraction was an important analysis technique for these polymers to determine their compositional heterogeneity. Samples with 10K grafts and compositions of 12, 25 and 41 weight percent siloxane were separated by SCFE. Table 29 summarizes the results of the NMR analysis of the fractions. A narrower distribution of compositions was determined to occur, in contrast to the free radical case. For example the anionic sample 91B may be compared to the free radical sample 81C, both of which have 10K grafts with similar siloxane contents. The anionic sample however has a much narrower range of compositions present than the free radical copolymer. All fractions of sample 91B appear to be identical both by NMR and GPC analysis.

The GPC traces of the fractions obtained from sample 91A are shown in Figure 56. There was a separation by composition as evident in Table 29, and the higher siloxane content fractions were of a lower molecular weight as evident in Figure 56.

SCFE was also used in an attempt to separate the materials with bimodal or trimodal distributions, prepared anionically. It was determined earlier that separation based on composition occured by SCFE. However in the case of the free radical materials it is difficult to determine whether separations occured due, either to composition or molecular weight alone or due to some combination of the

Table 29

NMR Analysis of SCFE Fractions of PMMA-g-PSX Prepared Anionically

NSF-16 SSII-91A, 10K Grafts, 41 WT% PSX

Fraction	FRAC. WT.	%PSX
1	0.17g	--
2	0.24g	53%
3	0.32g	54%
4	0.83g	55%
5	3.68g	36%

NSF-18 SSII-91B, 10K Grafts, 24 WT% PSX

Fractions	FRAC. WT.	%PSX
1	0.60g	29%
2	0.45g	22%
3	0.85g	23%
4	1.03g	24%
5	1.98g	21%

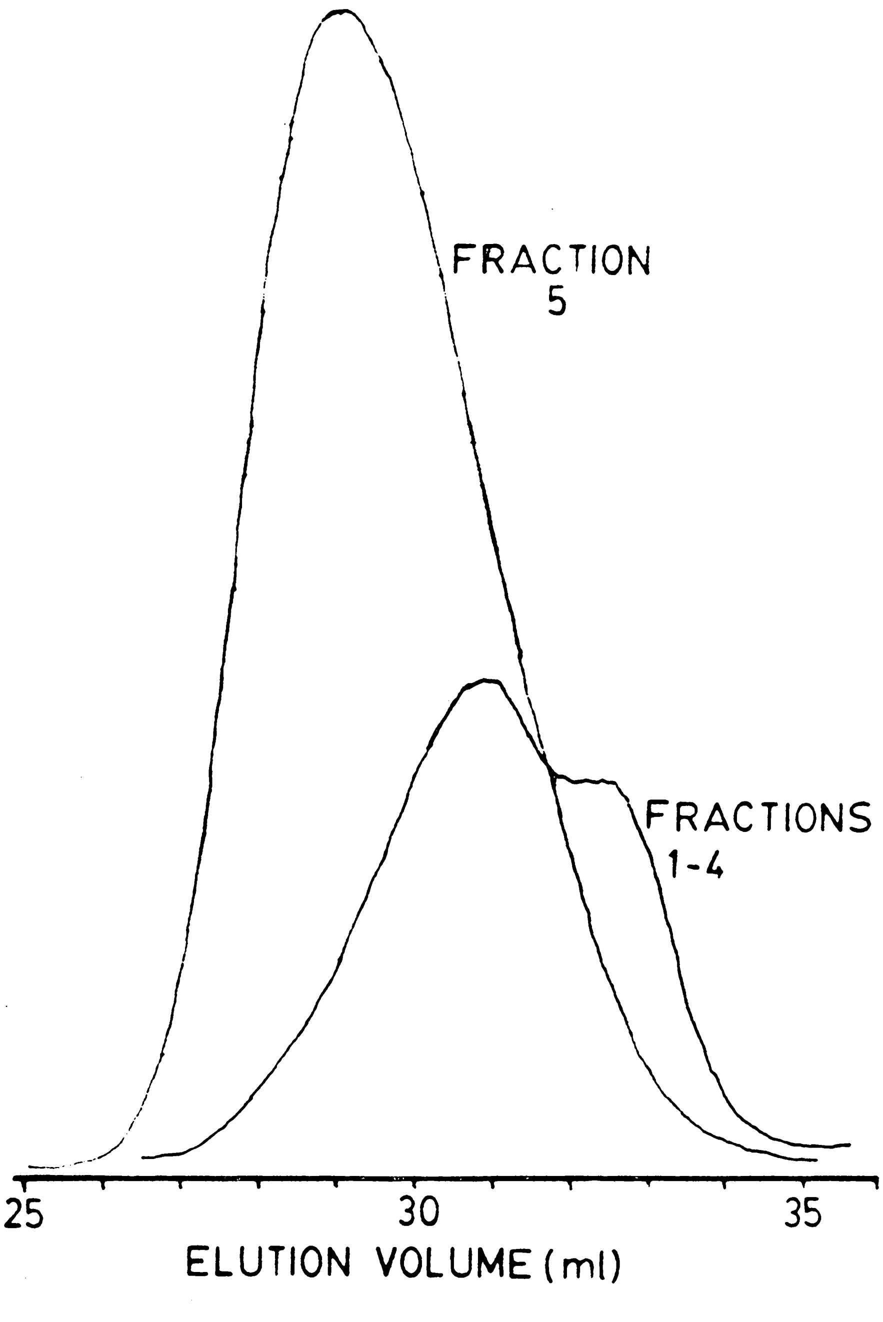


Figure 56. GPC of SCFE Fractions of PMMA-g-PSX Prepared Anionically

two. The anionic materials have been found to have a narrower distribution of compositions. Table 30 summarizes the NMR analysis of the fractions of bimodal samples, which were analyzed by GPC as well. Figures 56 and 57 summarize the GPC traces of samples NSF-17 and NSF-19. NSF-17 is a material with 10K grafts and approximately 12 wt% PSX overall. The fractions obtained show a narrow range of compositions, Table 30, and upon GPC analysis it can be seen that all fractions are monomodal, Figure 57. These fractions also represent the lower molecular weights present in the mixture. It was also found that the residue was bimodal and was mostly of the higher molecular weight species.

Sample NSF-19 with 1K grafts was found to be of narrow compositional heterogeneity as was the 1K free radical sample. GPC analysis, Figure 58, showed that again only the lower molecular weight peak was eluted through the SCFE experiment and the residue consisted mostly of the higher molecular weight material.

Analysis by DSC indicated that the anionically prepared materials fell into the proper Tg range for their composition and macromonomer molecular weight. This was important since any siloxane chain scission by alkoxides would lower the Tg due to the lower graft molecular weight and increased miscibility with PMMA.

Table 30

NMR Analysis of SCFE Fractions of Anionically Prepared PMMA-g-PSX

NSF-17 SSII-29A, 10K Grafts, 12 WT% PSX

Fraction	FRAC. WT.	%PSX
1	0.07g	--
2	0.21g	14%
3	0.37g	12%
4	0.47g	11%
5	1.31g	11%
6	0.94g	11%
7	0.78g	11%
Residue	0.5g	11%

NSF-19 SSII-35C, 1K Grafts, 29 WT% PSX

Fraction	FRAC. WT.	%PSX
1	0.13g	28%
2	1.75g	29%
3	1.03g	29%
4	1.83g	27%
5	0.70g	27%
Residue	0.2g	--

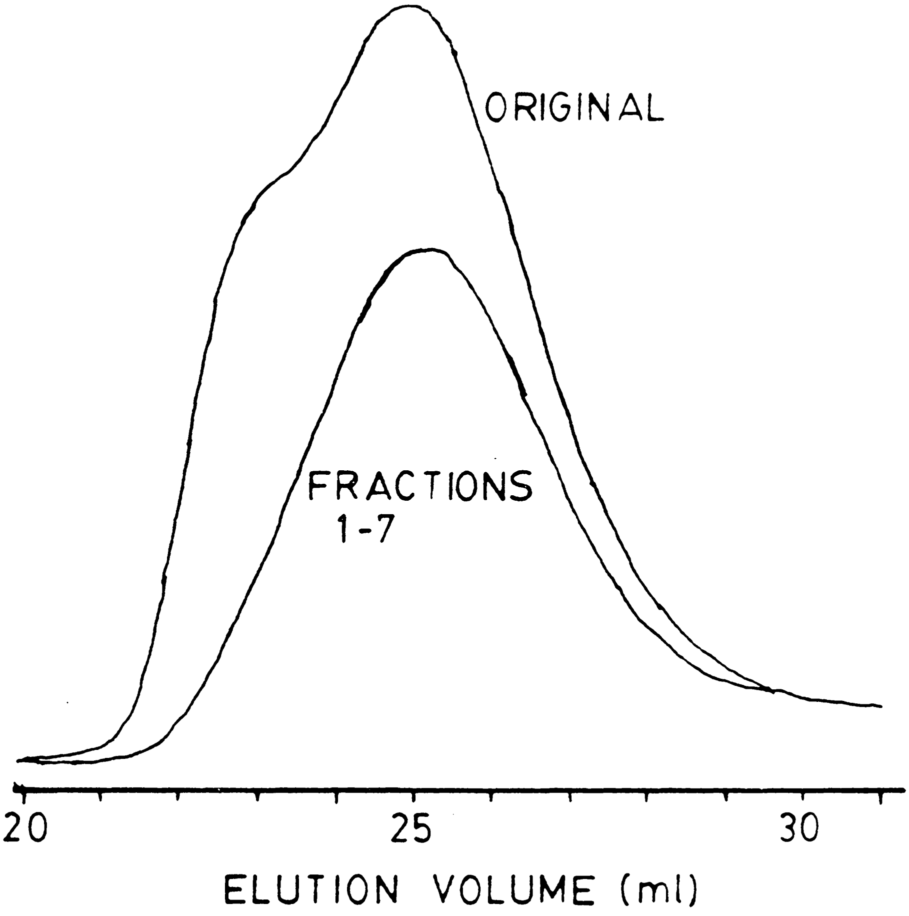


Figure 57. GPC of SCFE Fractions of PMMA-g-PSX Prepared Anionically

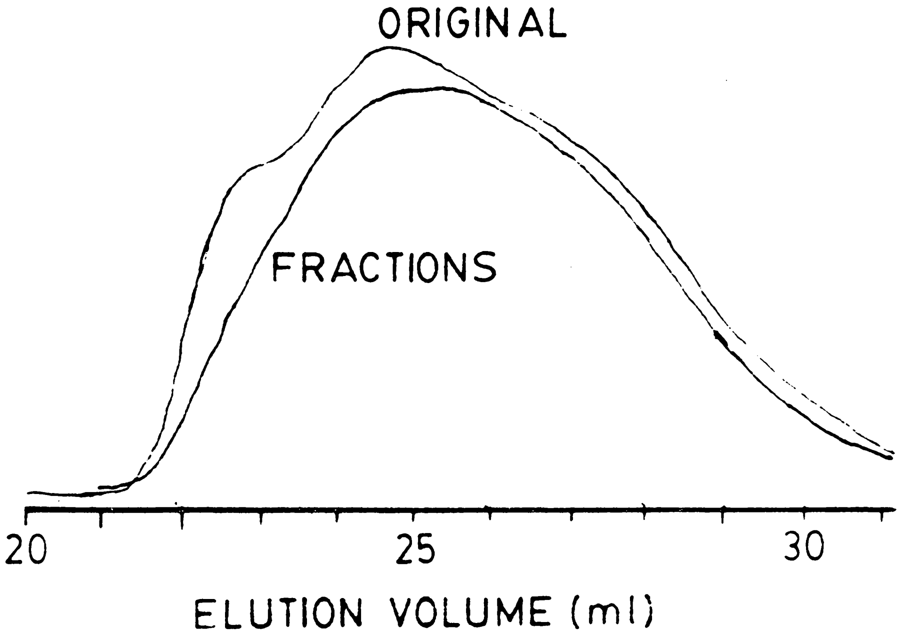


Figure 58. GPC of SCFE Fractions of PMMA-g-PSX Prepared Anionically

Copolymers prepared anionically were even more stable than the materials prepared free radically. Stabilities approaching 350°C were observed as shown in Figure 59. It is known that PMMA prepared anionically is more stable than PMMA synthesized free radically due to the difference in end group structures. The fact that the anionically synthesized materials are even more stable than the free radical copolymers is probably due to a small number of unstable links in the free radical materials. Even though they are very stable, the probability that some unstable links will be introduced free radically is enough to expect that the anionic copolymers should be more stable. Again a dependence of thermal stability on graft molecular weight was found.

TEM analysis of these copolymers was also undertaken and it was found that copolymers with 12 weight percent siloxane were of similar morpholgy to free radically synthesized materials. The free radical copolymers were noted to have a broad distribution of interdomain domain spacings which can be attributed to a broad distribution of backbone lengths between branches. The anionic copolymers also had a broad distribtuion of interdomain spacings. Copolymers with 10K grafts and 41 weight percent siloxane showed a lamellae morphology. Figure 60 shows the spherical morphology found in a copolymer with

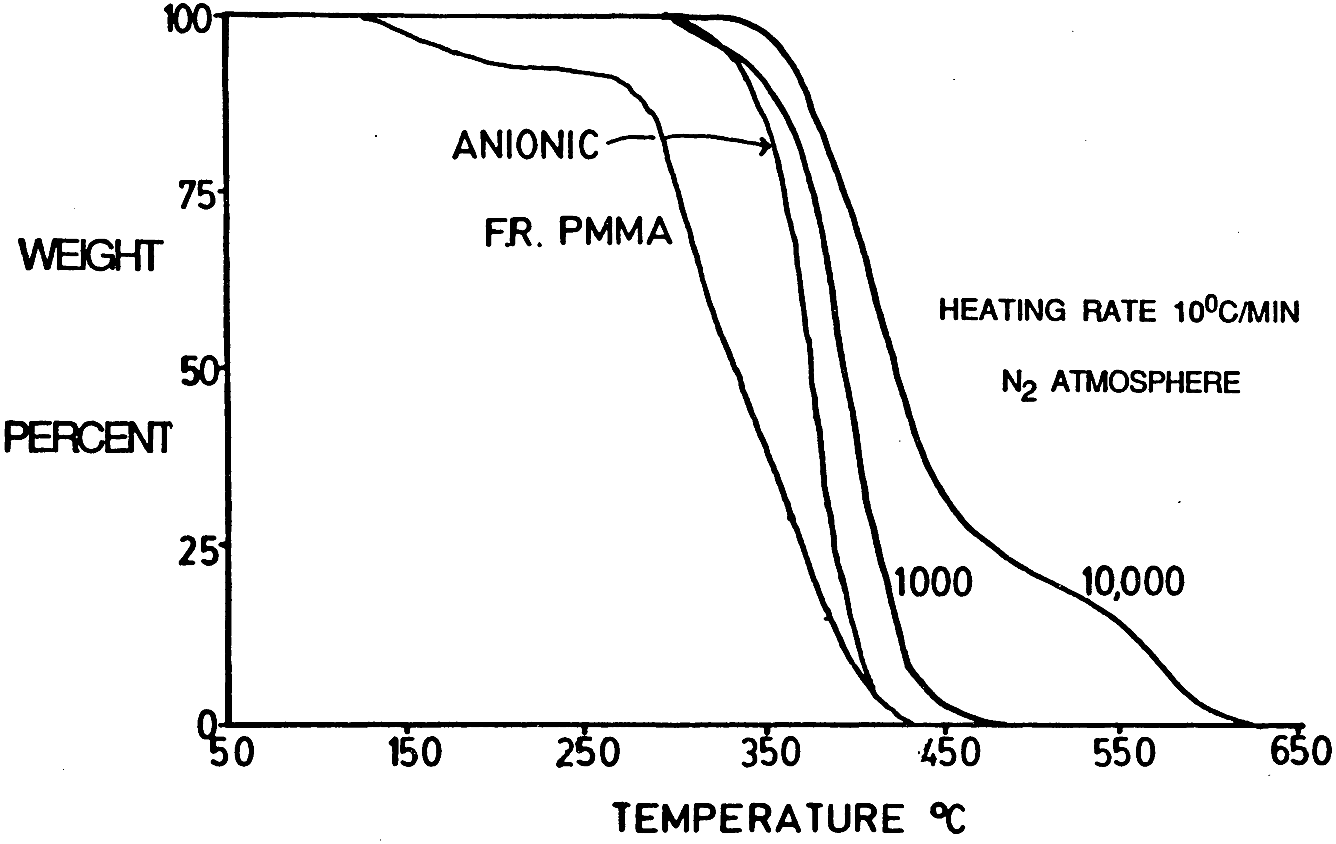


Figure 59. Thermal Gravimetric Analysis of PMMA-g-PSX Prepared Anionically as a function of PSX Molecular Weights (30 WT % PSX)

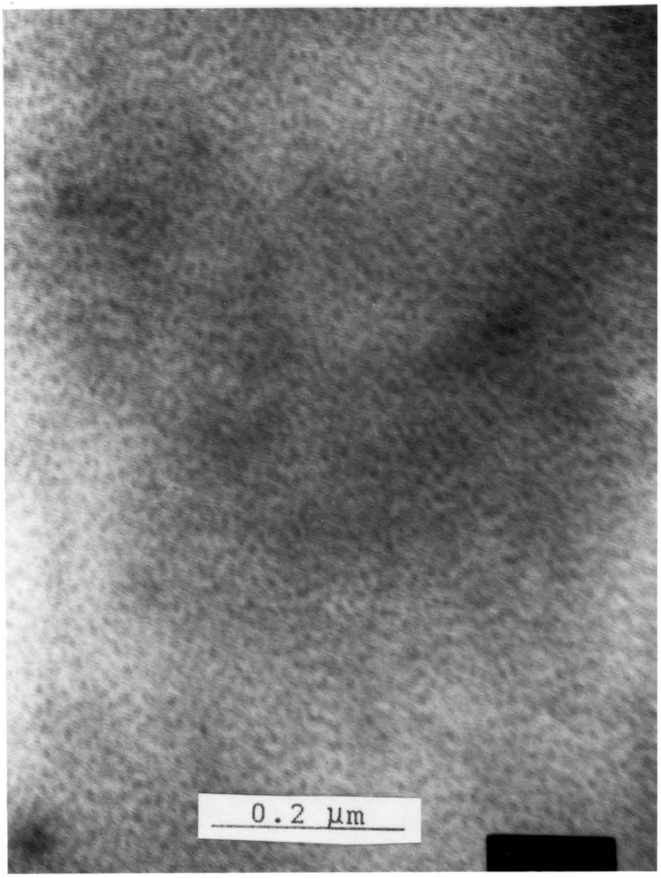


Figure 60. Morpholgy of PMMA-g-PSX Prepared Anionically
(12 WT% PSX)

approximately 15 weight percent siloxane. The domain sizes are similar to that found in the free radical copolymers of similar architecture. Figure 61 shows the bicontinuous morpholgy formed as the siloxane content is increased to 30 weight percent, and a lamellae morphology is shown for a material with 42 weight percent siloxane.

Copolymerizations with other methacrylate monomers such as i-butyl methacrylate, 2-ethylhexyl methacrylate, and N,N-dimethyl acrylamide were also carried out. Small changes in chemical structure were investigated to determine the possibilities of solubility and copolymer properties. Methacrylate homopolymers with low Tg's such as 2-ethylhexyl methacrylate are tacky materials, but copolymers with siloxane macromonomers are not. Since siloxanes tend to dominate the surface the methacrylate is prevented from forming a tacky bond. Copolymerization with acrylamides provided alcohol solubility to copolymers of i-butyl methacrylate or 2-ethylhexyl methacrylate with PSX macromonomers. Thus hydrophobic- hydrophilic copolymers were formed with solubility in hydrocarbon as well as alcoholic solvents.

Copolymers of methyl methacrylate or i-butyl methacrylate with PSX macromonomer and 4-Methacryloxybenzophenone were also synthesized. Polymer bound UV stabilizers are desired to stabilize light sensitive dyes

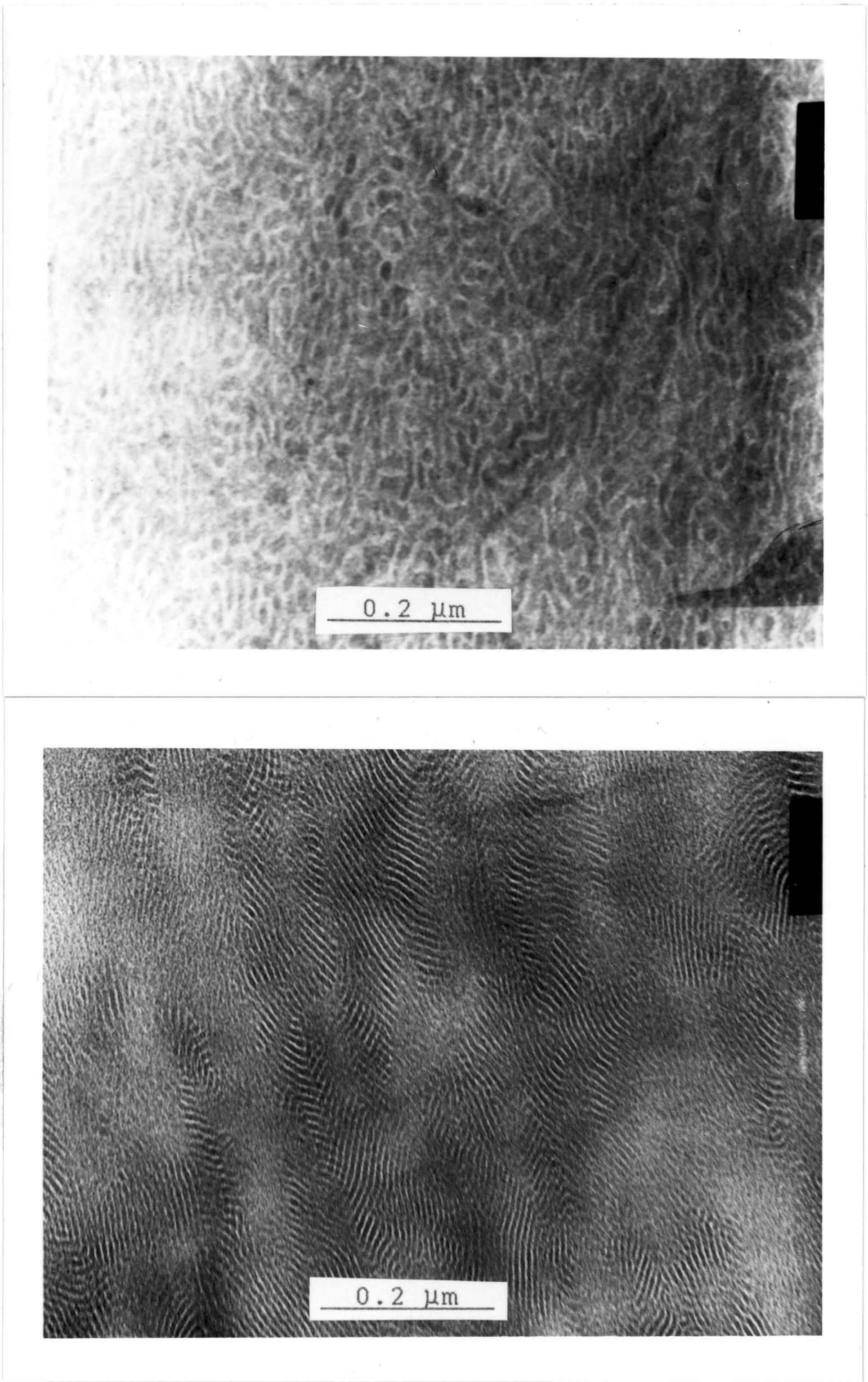


Figure 61. Morphology of PMMA-g-PSX Prepared Anionically (30 & 40 WT% PSX)

and sometimes other polymers. Since methacrylates are largely UV sensitive and good film forming materials, copolymers with UV protecting ability might very well be used as an overcoating to protect underlayers of less stable materials. To this end the methacrylate functional benzophenone derivative was synthesized and copolymerized free radically with i-butyl methacrylate and methyl methacrylate. Investigations into the long time stability of the i-butyl methacrylate materials were carried out at Johnson Wax.

Samples with varying benzophenone levels were synthesized. It has been suggested in the literature that the o-hydroxy compound formed by the Photo-Fries rearrangement is stabilizing to the thermal degradation of PMMA as well, probably acting as a phenolic inhibitor.

Poly(methyl methacrylate) copolymers were blended with PVC and interesting results obtained as will be detailed in the blend section.

V. RESULTS AND DISCUSSION

D. Styrenic- Siloxane Graft Copolymers: Synthesis and Characterization

Copolymerizations of the various siloxane macromonomers with styrene, p-methyl styrene, and t-butyl styrene were investigated. In general, greater problems with macrscopic phase separation during solution copolymerization occurred in the case of the styrenic monomers relative to the previously discussed methacrylate systems. Solubility parameters differences were apparently important since t-butyl styrene copolymerizations had minimal problems. Styrene has the greatest difference in solubility parameter from poly(dimethyl siloxane) and was the most difficult. The reactivity of the monomers was another factor to consider and it was observed that t-butyl styrene polymerized much faster free radically, probably due to the difference in structure and stabilization of its radical intermediate.

Styrene has a fairly low value of k_p/k_t, relative to the methacrylates. Thus the rate of termination is more comparable to the rate of propagation. Thus the solvent utilized must have a low chain transfer constant, as illustrated in Table 11. Benzene and cyclohexane have two of the lowest chain transfer constants for solvents which would be suitable for these systems. Cyclohexane is a theta solvent for poly(styrene) at 34°C and even though these polymerizations will be carried out at 65°C, it is a poor solvent system. However both solvents are good for poly(dimethylsiloxane) and the other substituted styrene monomers. Mixed solvents were often used for styrene copolymerizations in the current study, in order to maintain a homogeneous solution.

It was also necessary to initiate polymerizations at high solids (high monomer concentrations) levels to encourage high molecular weights. If phase separation started to occur, further dilution with solvent was conducted. Polymerizations at initial lower monomer concentrations led to lower molecular weights, as expected.

The graft co-polymers were typically worked up by adding the solutions to stirred methanol and later extracting with isopropanol. However t-butyl styrene copolymers provided a special problem since the solubility parameters of the two phases are similar. The graft copolymer was often soluble in solvents such as isopropanol that were used for poly(dimethylsiloxane) extraction. Low temperature extractions could be used to preferentially extract PSX homopolymer in favorable cases. Super Critical Fluid Extractions were also found to separate the siloxane oligomers when solvents could not be employed.

Characterization studies by NMR, GPC, DSC, TGA, ESCA, and TEM were employed. Table 31 summarizes the incorporation of siloxane macromonomer into the various styrene graft copolymers. It can be noted that very good agreement was achieved between charged and found siloxane content. The copolymerizability of the macromonomer methacrylate end group with the styrenic monomers would be expected to be better than with methacrylate monomers by a simple examination of the r1 and r2 values of copolymerizability of methacrylate and styrene monomers.

GPC of these materials confirmed that molecular weights of over 100,000 g/mole were obtained. Indeed, apparently very high molecular weight tails were often obtained.

DSC measurements of the upper and lower Tg's provided insight into the partial phase mixing behavior of the systems as a function of graft molecular weight, system composition, and differential solubility parameter.

In Figure 62, glass transition temperature is plotted versus siloxane content for poly(styrene-g-PSX) copolymers as a function of macromonomer molecular weight. Figures 63 and 64 demonstrate typical DSC traces for styrene-siloxane graft copolymers. Well developed microphase separation is indicated for the 5K and 10K systems while the 1K system

Table 31

NMR Analysis of Styrenic- Siloxane Graft Copolymers

Sample Description	Charged	Found
P(styrene-g-PSX)	20	19
P(styrene-g-PSX)	30	29
P(p-Methylstyrene-g-PSX)	10	8.5
P(p-Methylstyrene-g-PSX)	20	22
P(p-Methylstyrene-g-PSX)	30	35
P(t-Butylstyrene-g-PSX)	10	10
P(t-Butylstyrene-g-PSX)	20	20
P(t-Butylstyrene-g-PSX)	30	29

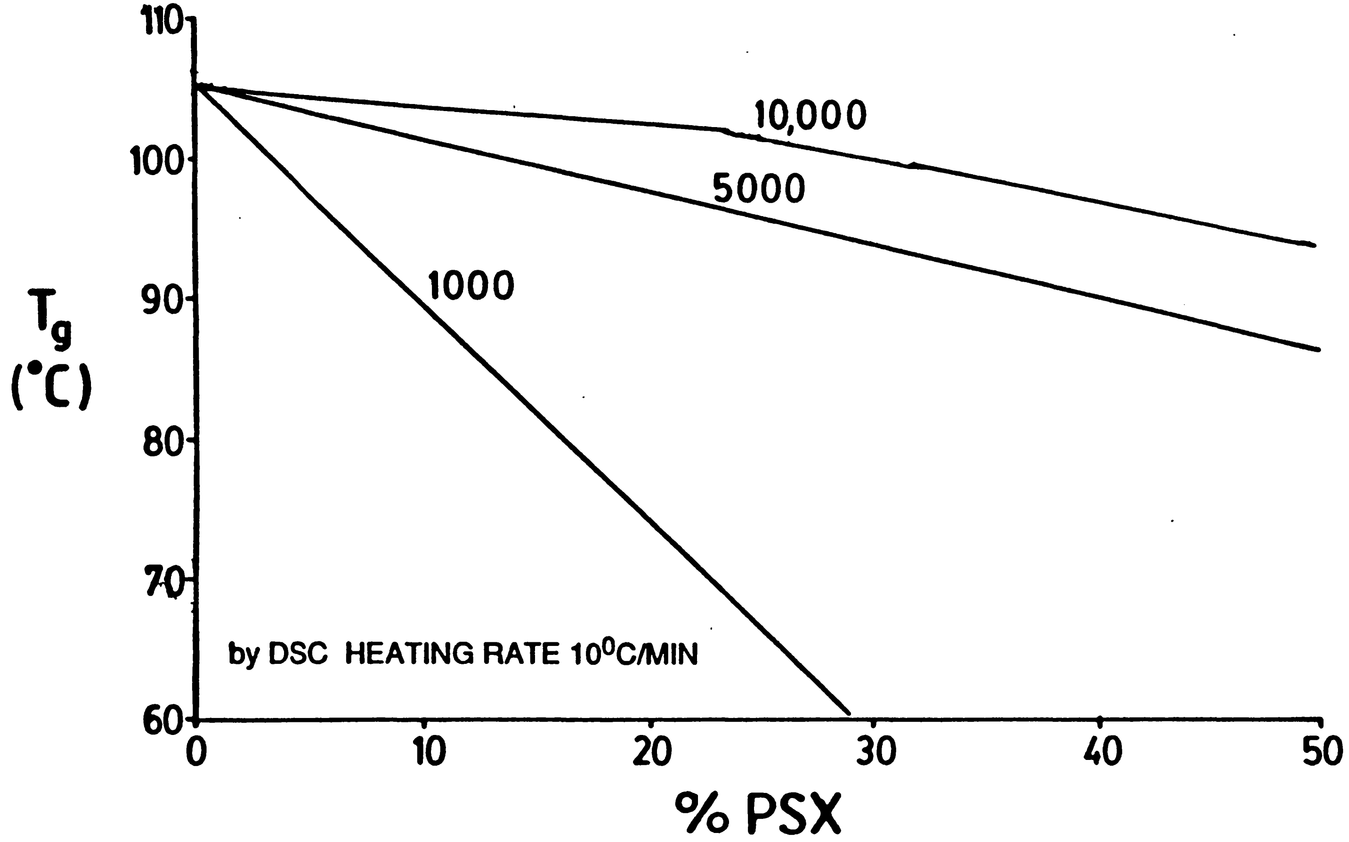


Figure 62. Glass Transition Temperatures of P(Styrene)-g-PSX Copolymers as a Function of Graft <Mn> and % PSX

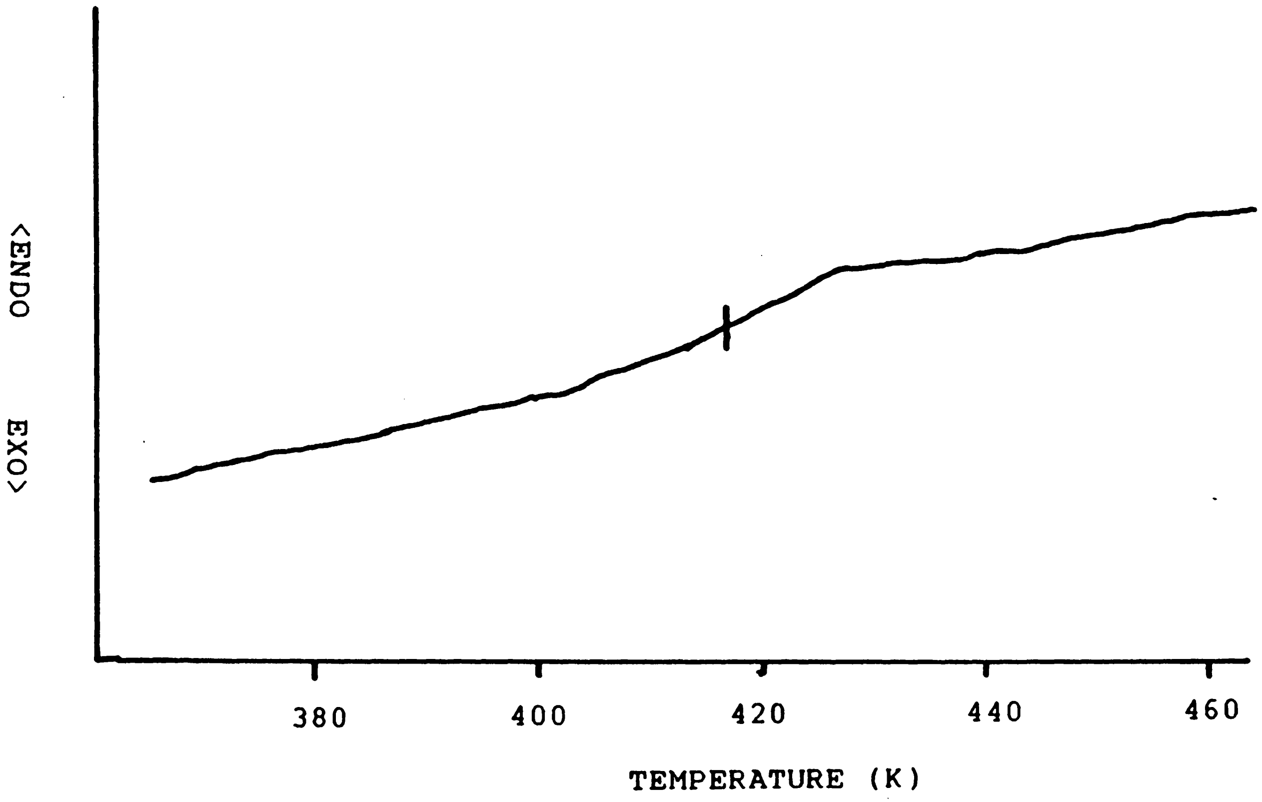


Figure 63. DSC of Styrene-Siloxane Graft Copolymer

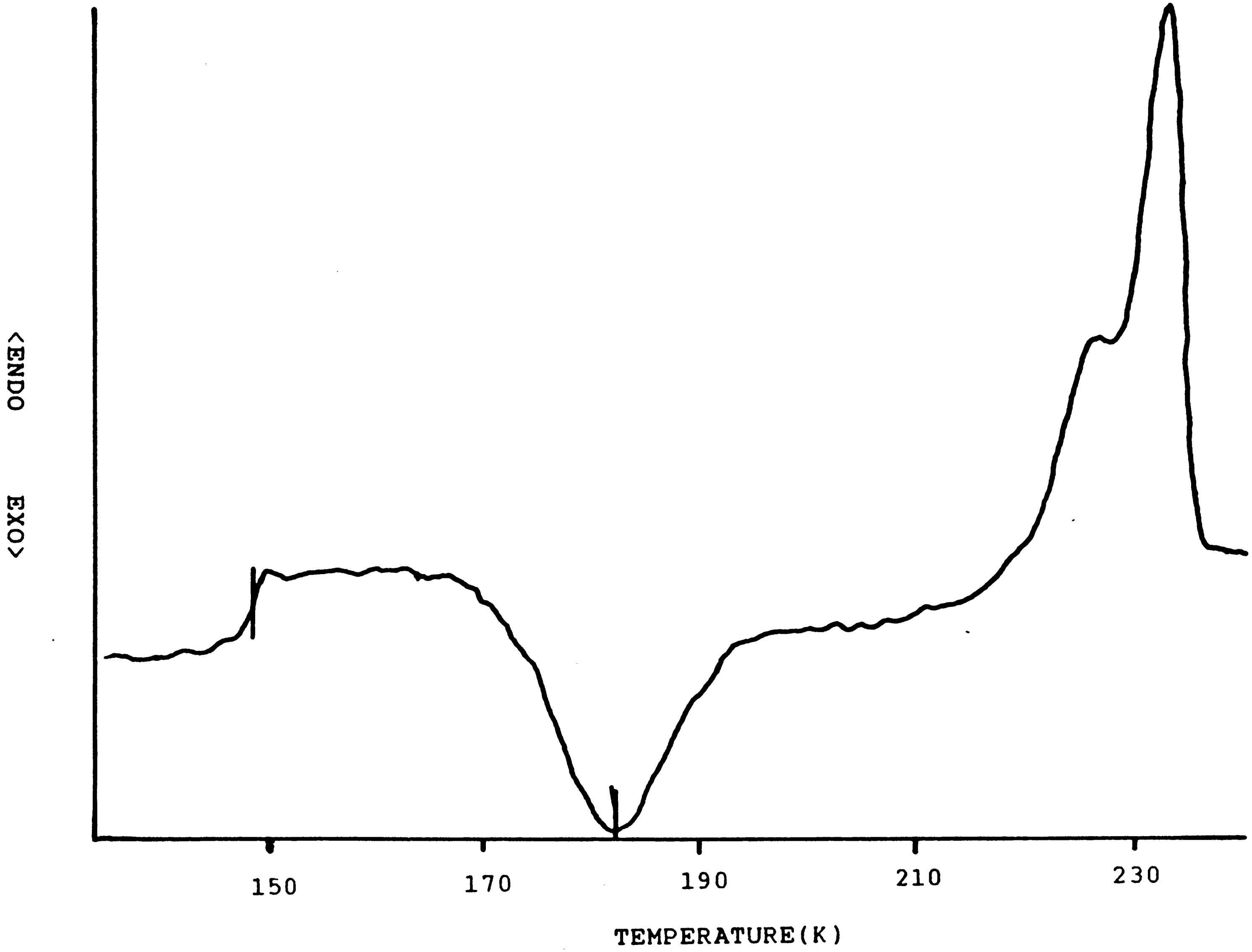


Figure 64. DSC of Styrene-Siloxane Graft Copolymer

seems to be fairly miscible. Only at high levels of siloxane does there appear to be mixing with the 5K and 10K systems, as was seen in the 10K and 20K systems with PMMA.

This can be compared to Figure 65, where the same plot for t-butyl styrene copolymers is shown. It is evident that much greater miscibility is present in this system, as would be expected by a much smaller difference in solubility parameters between poly(t-butyl styrene) and poly(dimethyl siloxane) relative to poly(styrene) and siloxanes. If the 1K copolymers are compared, one may note that over the same 30 wt% of siloxane plotted, the Tg of t-butyl styrene copolymers falls 65°C while the Tg of the styrene copolymer falls only 40°C. Also even the 5K and 10K graft copolymers seem quite highly [hase mixed even at low levels of siloxane.

Low temperature transitions of the siloxane phases were also determined and are presented in Table 32. It can be seen that the Tg of poly(dimethyl siloxane) (~-123°C) is observed for both 5K and 10K grafts in the styrene graft copolymers. However, poly(p-methyl styrene) copolymers show a tendency for mixing in the 5K graft sample. Poly(t-butylstyrene) graft copolymers show significant mixing in the 5K sample and possibly some mixing in the 10K graft copolymer. It is noteable that no

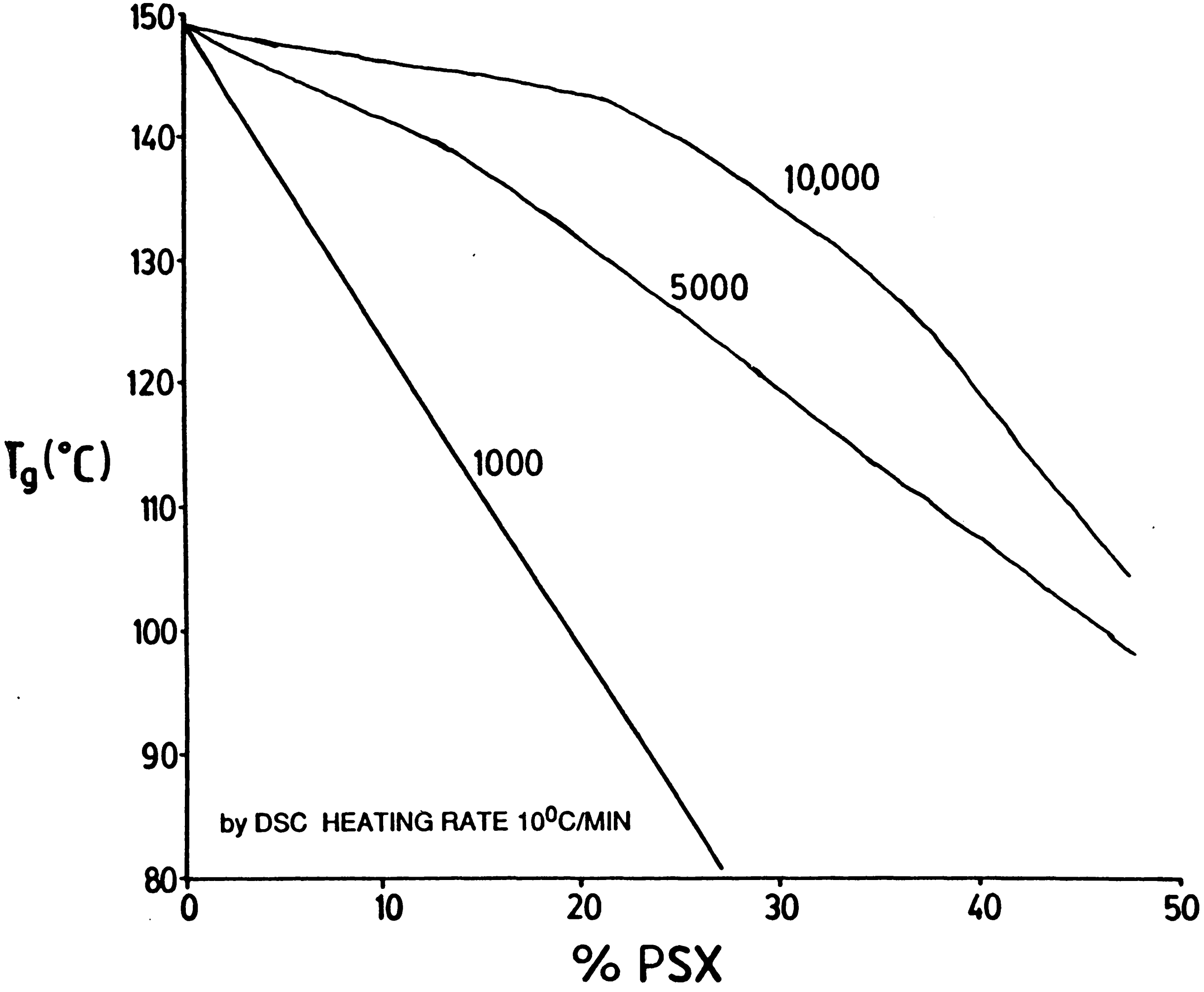


Figure 65. Glass Transition Temperatures of P(t-Butylstyrene)-g-PSX Copolymers as a Function of Graft <Mn> and % PSX

Table 32

Low Glass Transition Temperatures of Styrenic- Siloxane Graft Copolymers

Sample	Description	Tg°C
	PS-g-PSX	
34B	5K	-131
34C	10K	-117
	PPMS-g-PSX	
34E	5K	-106
34F	10K	-124
	PTBS-g-PSX	
16H	5K	- 95
16C	10K	-117

Copolymers Are Approximately 20 Weight Percent PSX

Total Molecular Weight ~100K

Tm's were observed for copolymers with less then 40% PSX.

TGA analysis of the styrenic copolymers indicated that anionic copolymers are more stable than the free radical materials. All of the siloxane containing materials are more stable than the homopolymers. No extremely large effects were seen probably due to the fact that the styrenics are not known to be unstable polymers. Unstable linkages that lead to free radical sites do not cause extensive chain depolymerization, as only monomers with disubstituted carbons such as the methacrylates undergo depolymerization to monomer. Other polymers degrade by other mechanisms, typically at much higher temperatures. Figures 66 and 67 are TGA's run in Nitrogen atmospheres, of some styrene and t-butyl styrene copolymers.

ESCA analysis of these graft copolymers was undertaken to investigate the anticipated surface domination by the poly(dimethyl siloxane) microphase. Poly(styrene) has a lower surface free energy than methyl methacrylate and the expected surface domination was not expected to be as great. The chance to study the effect of system miscibility was available as the various styrenes should mix with the siloxane to different extents and this might be reflected in the surface properties as well. Table 33 summarizes the siloxane composition at the

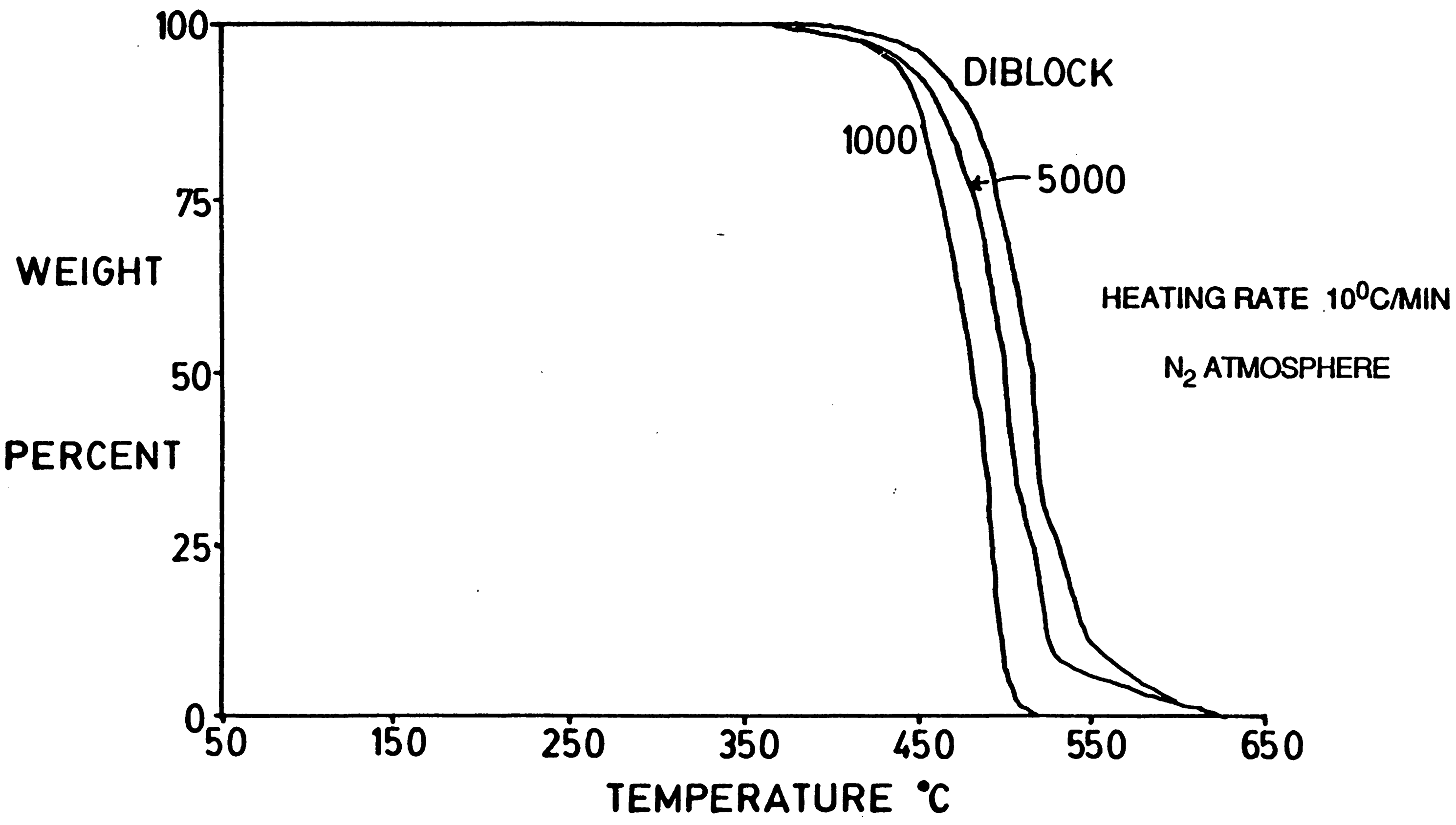


Figure 66. Thermal Gravimetric Analysis of Styrene-Siloxane Copolymers as a function of Architecture (18 WT % PSX)

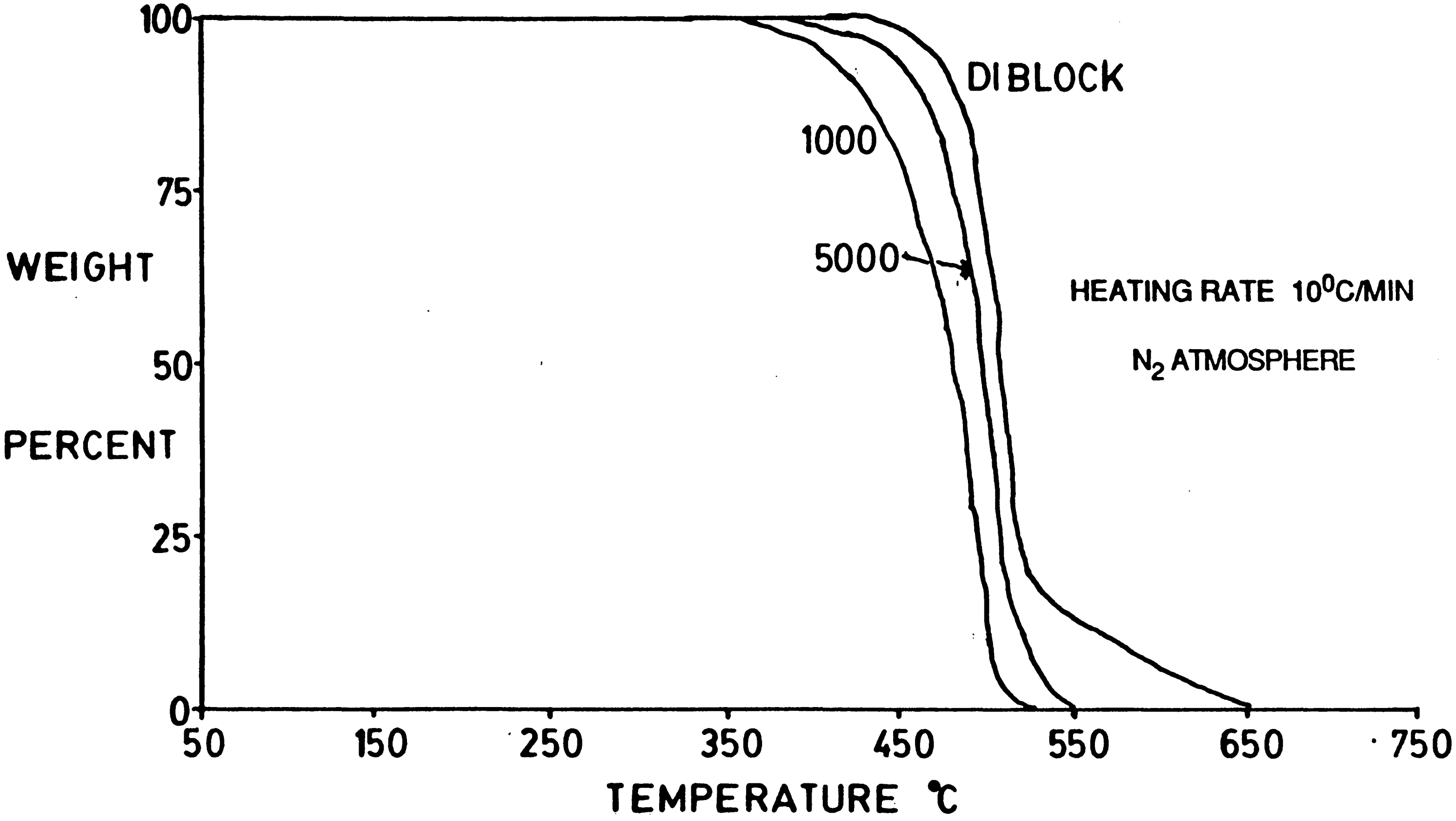


Figure 67. Thermal Gravimetric Analysis of t-Butylstyrene- Siloxane Copolymers as a Function of Architecture (18 WT % PSX)

Table 33

ESCA Study of Styrenic-Siloxane Block and Graft Copolymers (Copolymer Composition ~ 10 WT% PSX)

Copolymer	% PSX ANGLE 10°	30°	90°
P(Styrene-b-PSX) 100K-10K	91	80	52
P(Styrene-g-PSX) 1K	47	36	19
P(Styrene-g-PSX) 5K	68	59	35
P(Styrene-g-PSX) 10K	100	76	47
P(t-Butylstyrene-b-PSX)100K-10K	82	56	40
P(t-Butylstyrene-g-PSX) 1K	16	7	6
P(t-Butylstyrene-g-PSX) 5K	25	--	6
P(t-Butylstyrene-g-PSX) 10K	58	39	24

surface for some styrenic-siloxane copolymers. One observes that increasing graft molecular weights increase the surface domination as expected. The more miscible systems like t-butyl styrene also tend to show lower siloxane contents at the surface, again due to a miscibility effect.

TEM analysis of the styrenic copolymers indicated a trend similar to that noticed for PMMA copolymers. Domains of variable size were formed, with a certain tendency for "elongation" of the siloxane domains. Figure 68 shows TEM's of styrene-siloxane (10K grafts) graft copolymers, of approximately 20 weight percent siloxane. Figure 69 depicts TEM's of t-butyl styrene-siloxane (10K grafts) grafts, again of 20 weight percent siloxane. Slightly larger domains are formed with the poly(t-butyl styrene) copolymers, due to the smaller difference in solubility parameter and thus a lowering of the energy driving phase separation.

E. Styrenic- Siloxane Block Copolymers: Synthesis and Characterization

Styrenic- siloxane block copolymers were synthesized by the initiation of D3 with living polystyryl lithium species. The reaction initiation and propagation are largely the same as when initiated by butyl lithiums. Differences occur in the method used and in the possible

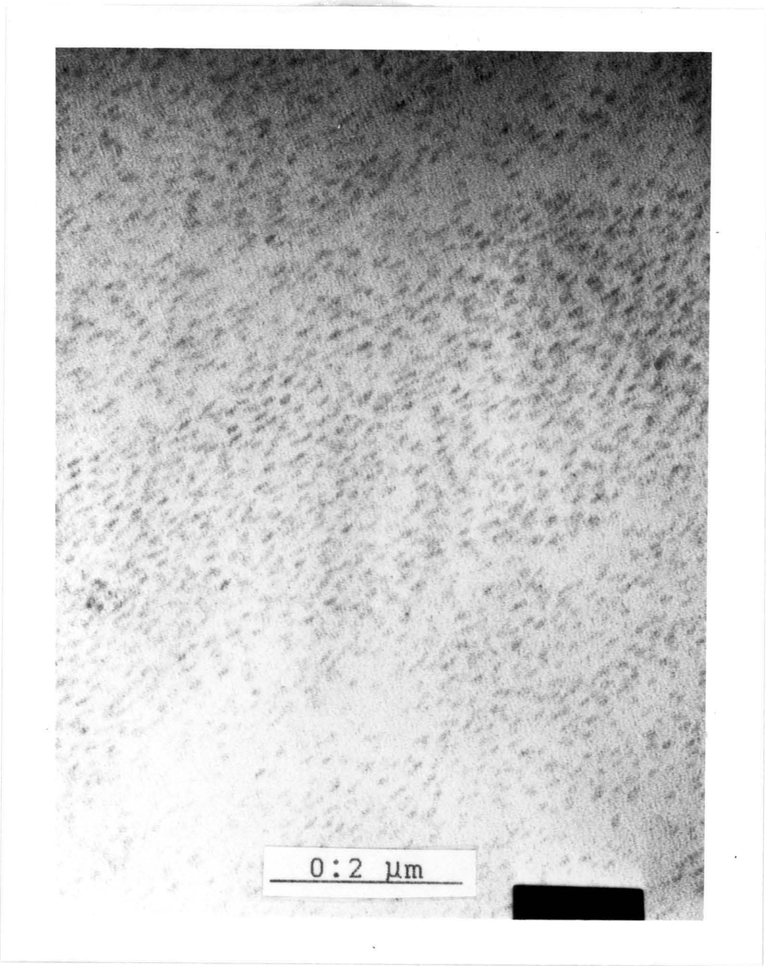


Figure 68. TEM's of Styrene-Siloxane Graft Copolymers

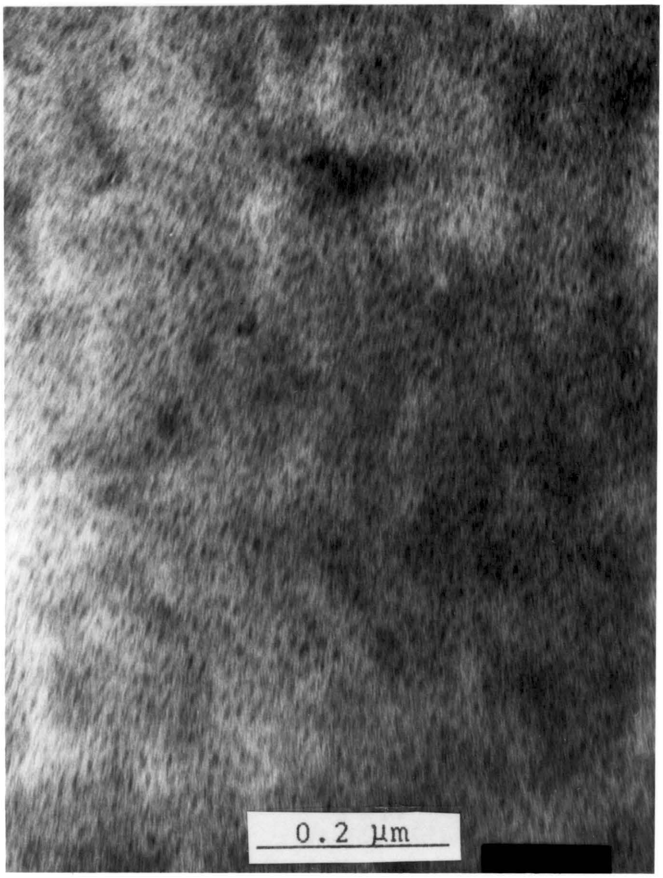


Figure 69. TEM's of t-ButylStyrene-Siloxane Graft Copolymers

formation of homopolymers of the two species.

The optimal method should produce pure diblock copolymers directly, however without high vacuum conditions contamination with some impurities is to be expected. The goal here was to be able to prepare block copolymers with styrene block molecular weights of 100-150,000 g/mole, and siloxane contents from 10-50 weight percent of the total copolymer. Molecular weights thus would range upward to 300,000 g/mole.

The addition of the siloxane monomer to a living anion requires that it be of extremely high purity, especially when synthesizing high molecular weights. Many impurities that terminate anionic polymerizations of styrenic monomers will not terminate siloxane polymerizations because they are much reactive with the relatively weak siloxanolate anion. This can be used to advantage by adding only a small portion of the siloxane monomer and once crossover to the siloxanolate occurs, adding the remaining monomer. This results in much cleaner block synthesis with no visible premature termination of styrenic homopolymer.

Formation of homopolymers of poly(dimethylsiloxane) is difficult to avoid completely. Two sources of alkoxides are present, one being in the original bottle of butyl lithium used, and the second source being that formed during the titration before polymerization. At low molecular weights the amount of alkoxides formed by titration is only a percent or two of the total butyl lithium concentration. However at molecular weights of 100,000 g/mole or higher, titrations requiring only 0.1 ml s-BuLi or less produce alkoxide concentrations comparable to the amount of butyl lithium used for initiation. It was found that by calculating the amount of alkoxides present as a fraction of the total an excess of D_3 could be added to compensate for the amount consumed in the formation of homopolymer and thus produce the copolymer of desired composition. Extraction with isopropanol was then used to remove the homo poly(diemthylsiloxane). Table 34 summarizes some typical data for calculated and obtained compositions of some styrenic copolymers.

The choice of solvents was also determined to play a role in the efficiency of crossover. Styrenic polymerizations in pure cyclohexane were first attempted, followed by addition of D3, however the crossover rate from styryl lithium was very slow. Typically 24 hours was needed, which allowed termination side reactions to occur. Addition of THF to the cyclohexane increased the rate of the crossover but also introduces the possibility of impurities which can terminate styryl anions. Polymerizations in pure THF at -78°C were found to be

Table 34

Incorporation of Siloxane into Styrenic-Siloxane Block Copolymers

Sample Description	Theory	Found
P(Styrene-b-PSX)	20	20
P(Styrene-b-PSX)	50	45
P(p-Methylstyrene)	20	19
P(t-Butylstyrene)	10	10
P(t-Butylstyrene)	40	42

optimal, since these conditions provide rapid crossover to siloxanolate and there is no need to add additional THF to the living styryl anion.

Figure 70 shows a GPC analysis of a di-block copolymer with narrow polydispersity, compared to a polystyrene GPC standard.

DSC analysis of these copolymers, as compared to the graft polymers, showed interesting trends. While the graft copolymers tend to show a depression in the upper glass transition temperature with increasing siloxane content, no depression occurs with the block copolymers, probably due to the extremely high block molecular weights. Low temperature transitions were more likely to be elevated in the block copolymers possibly due to greater mobility of a linear block, as opposed to the chain going in a branched graft linkage. Figure 71 shows a DSC transition for a styrene-siloxane block copolymer. Table 35 provides a summary of the glass transition temperatures for some styrenic-siloxane block copolymers. There is also a tendency for the t-butylstyrene copolymers to be more miscible than the styrenic copolymers as would be expected.

TEM analysis of films of these copolymers showed a more ordered structure than with any of the graft materials, Figures 72-73. Low siloxane copolymers had

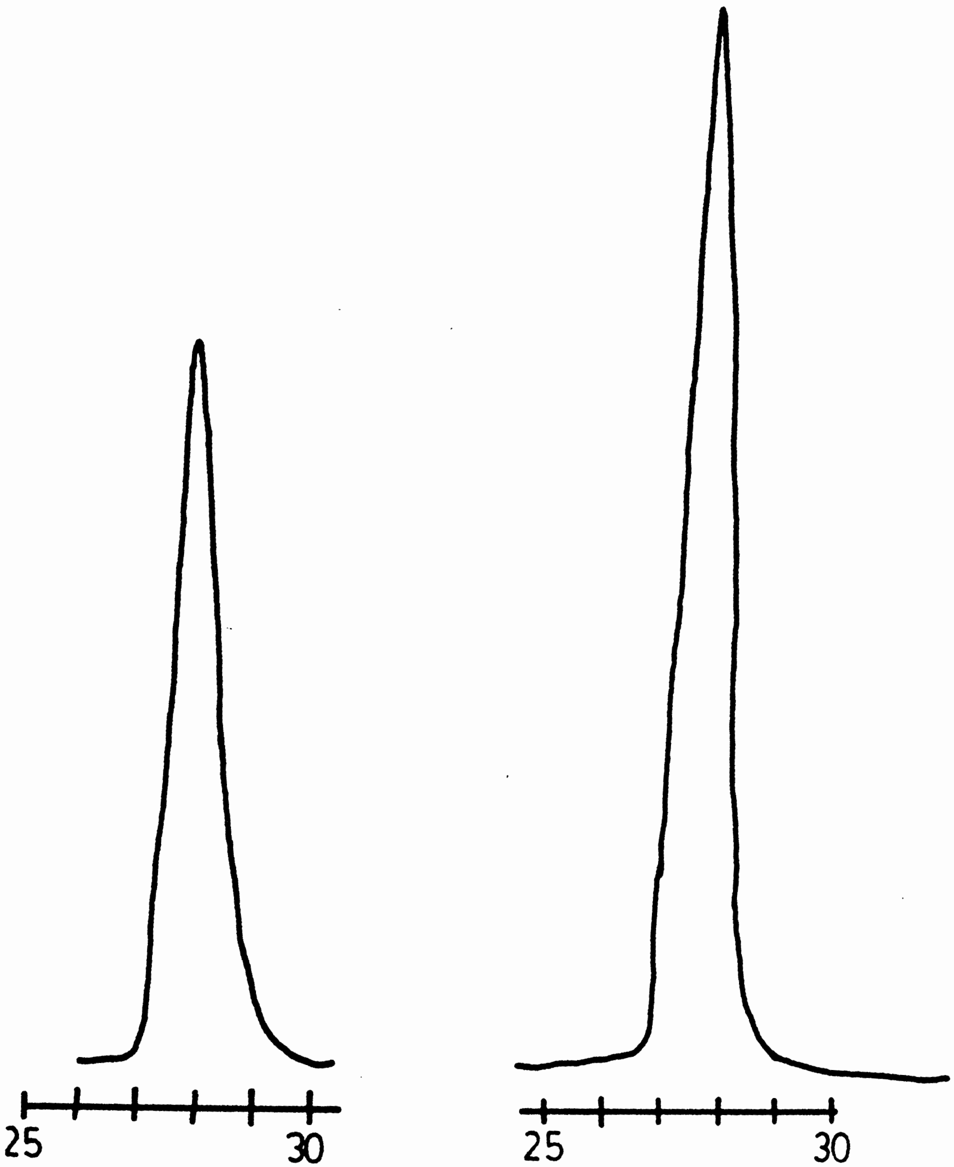


Figure 70. GPC Analysis of Styrene-Siloxane Block Copolymer

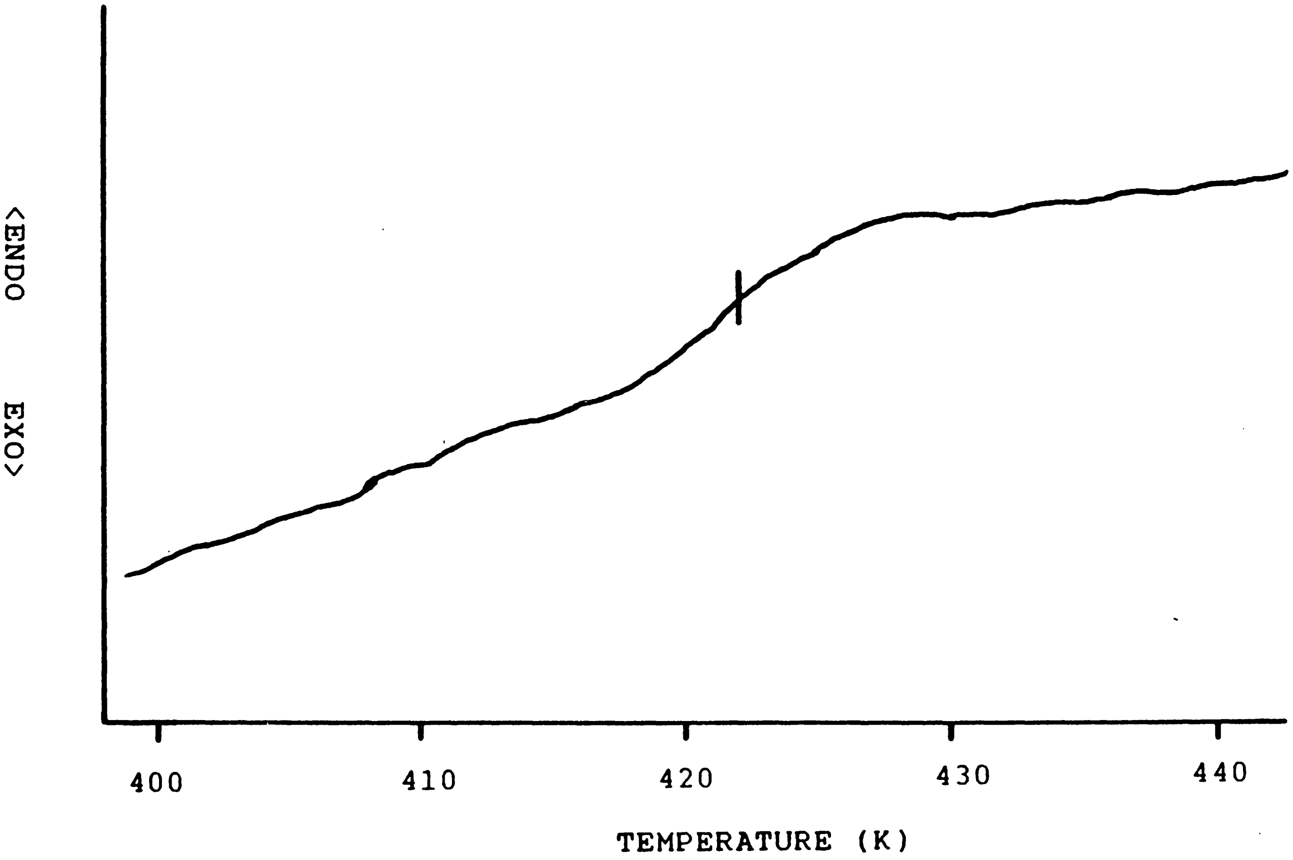


Figure 71. DSC of Styrene-Siloxane Block Copolymer

Table 35

Lower Glass Transition Temperatures of Styrenic-Siloxane Block Copolymers

Sample	Descriptiom	Tg°C	Tc°C	Tm°C
	PS-b-PSX			
30B	5K-5K	-122	-	-
39B	10K-10K	-124	-84	-53
39D	20K-20K	-125	-91	-40,-47
	100K-20K			
15C	PTBS-b-PSX	- 98	-	-
15F	PPMS-b-PSX	-113	-	-
18A	PS-b-PSX	-124	-	-
17C	PTBS-b-PSX 32% PSX	-118	-	-
17E	PTBS-b-PSX 55% PSX	-118	-105	-43
18D	PS-b-PSX 35% PSX	-116		--
18E	PS-B-PSX 45% PSX	-123	-	-43

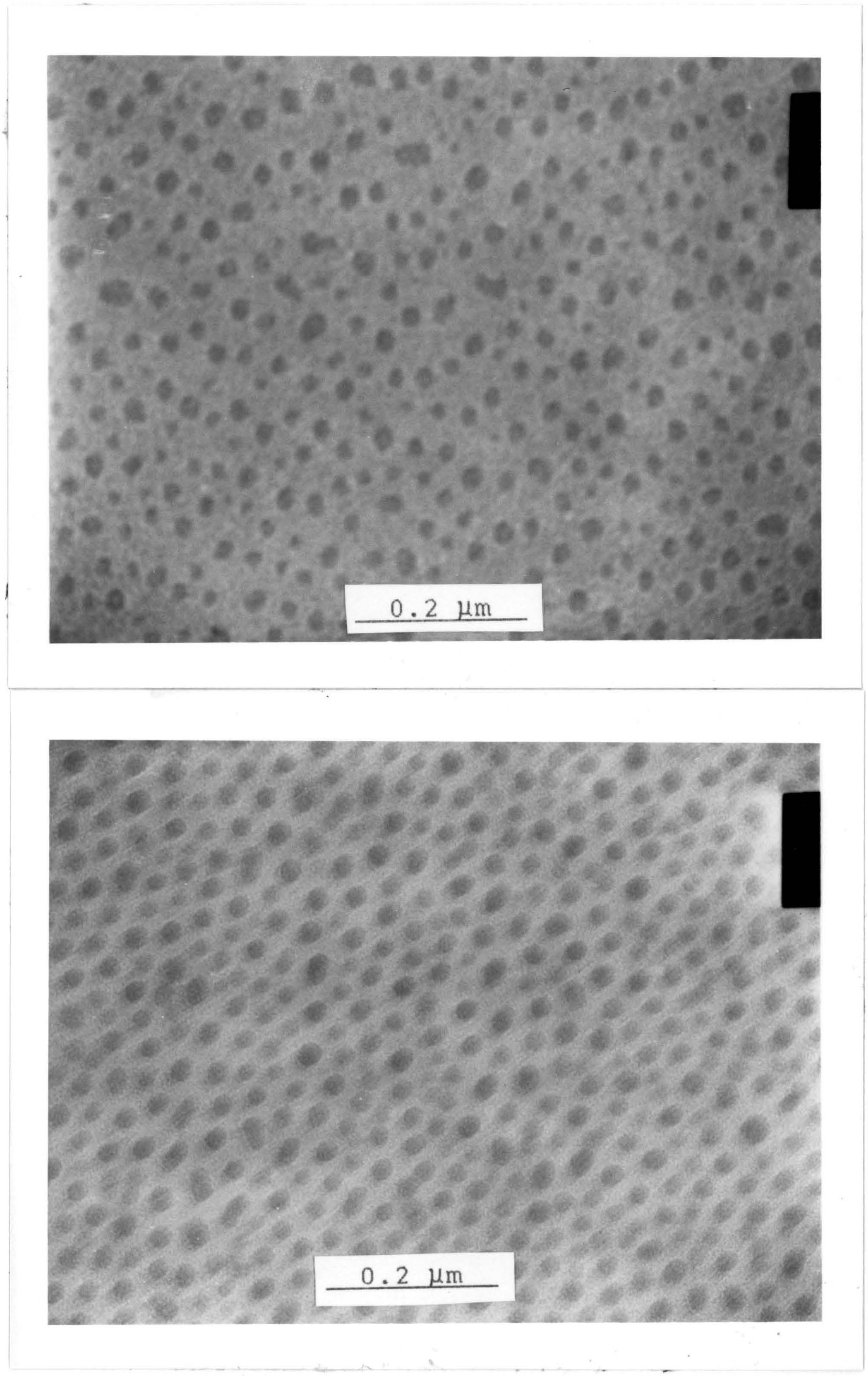


Figure 72. TEM's of Water Cast Styrenic- Siloxane Block Copolymers

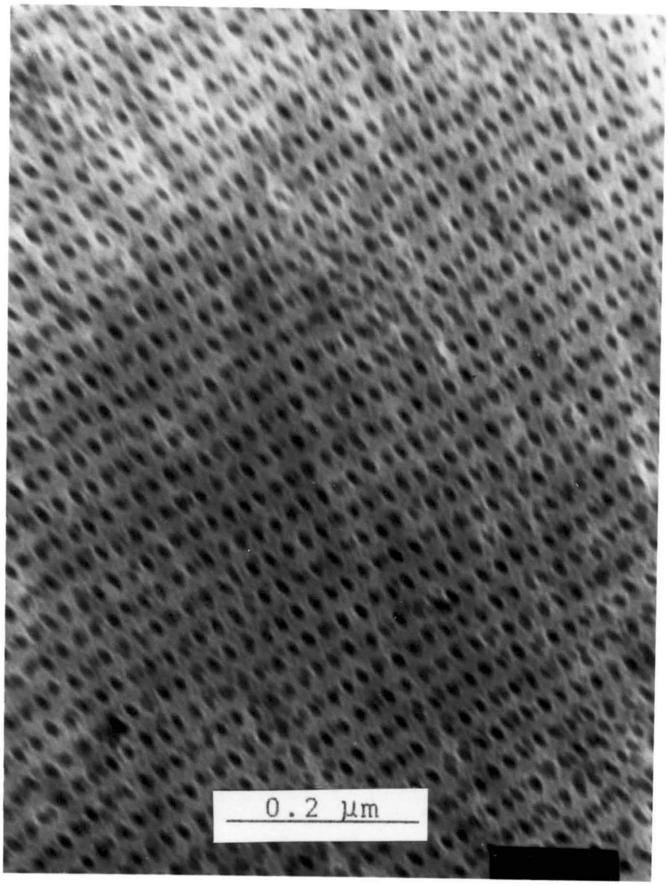


Figure 73. TEM's of Styrene- Siloxane Block Copolymer

spherical morphology with long range ordering of the domains into rows being evident and a much narrower distribution of domains sizes. This can be explained by the fact that narrow molecular weight distribution polymers are known to organize and pack in a more ordered way than copolymers with broad distributions, such as the graft materials. Domain sizes are more dependent on the film forming technique in the case of the styrenes than with methyl methacrylate copolymers. Water cast and slow cast films produced similar spherical morphologies with methacrylate copolymers. However, styrenic films cast onto water produced domain sizes considerably larger than when slow cast. In Figure 72 a comparison of water cast styrene and t-butyl styrene copolymers is provided with domain sizes of about 24 and 29nm. In contrast, Figure 73 shows the morpholgy formed by a slow cast formed poly(styrene-b-PSX) copolymer. The slow cast morpholgy has domains of approximately 11nm.. This evidence is very interesting, when considering the phase separation of these materials. High siloxane content materials show lamellae morphologies at various molecular weights ranging from 10K diblocks to 100K diblocks. Figure 74 represents a typical morpholgy of a diblock copolymer with about 50 weight percent siloxane.

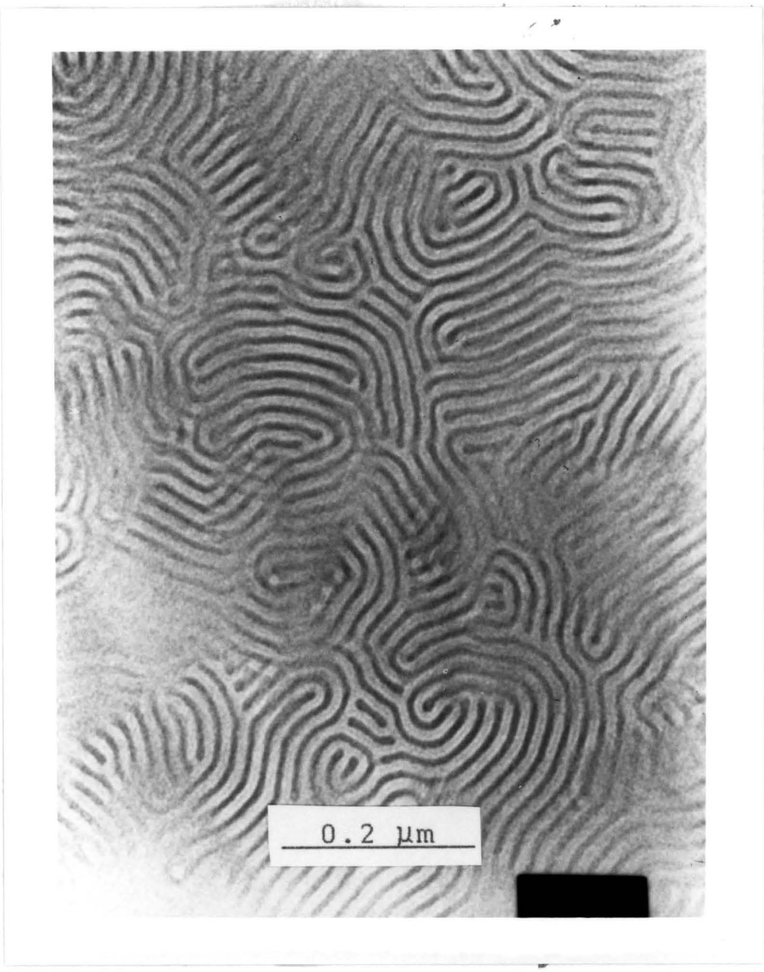


Figure 74. TEM of a 10K-10K Styrene-Siloxane Diblock Copolymer

F. Synthesis of Styrenic- Siloxane Diblock Macromonomers

The preparation of diblock macromonomers was simply a matter of terminating the above mentioned diblock siloxanolate anions with 3-Methacryloxypropyl-dimethylchlorosilane. Extraction with isopropanol had to be done at relatively low temperatures to prevent solubilizing the entire copolymer, since these were of low molecular weight and high siloxane content.

These macromonomers were analyzed by GPC and NMR, to confirm their structure and integrity. Copolymers of styrene and t-butyl styrene were prepared with styrenic molecular weights of 5K and 10K and siloxane molecular weights of 10K and 15K respectively. Thus 5K-10K and 10K-15K diblocks were prepared, and siloxane contents were calculated and found to be 66 weight percent and 60 weight percent siloxane respectively, after extraction. GPC's indicated that pure copolymer was present after extraction.

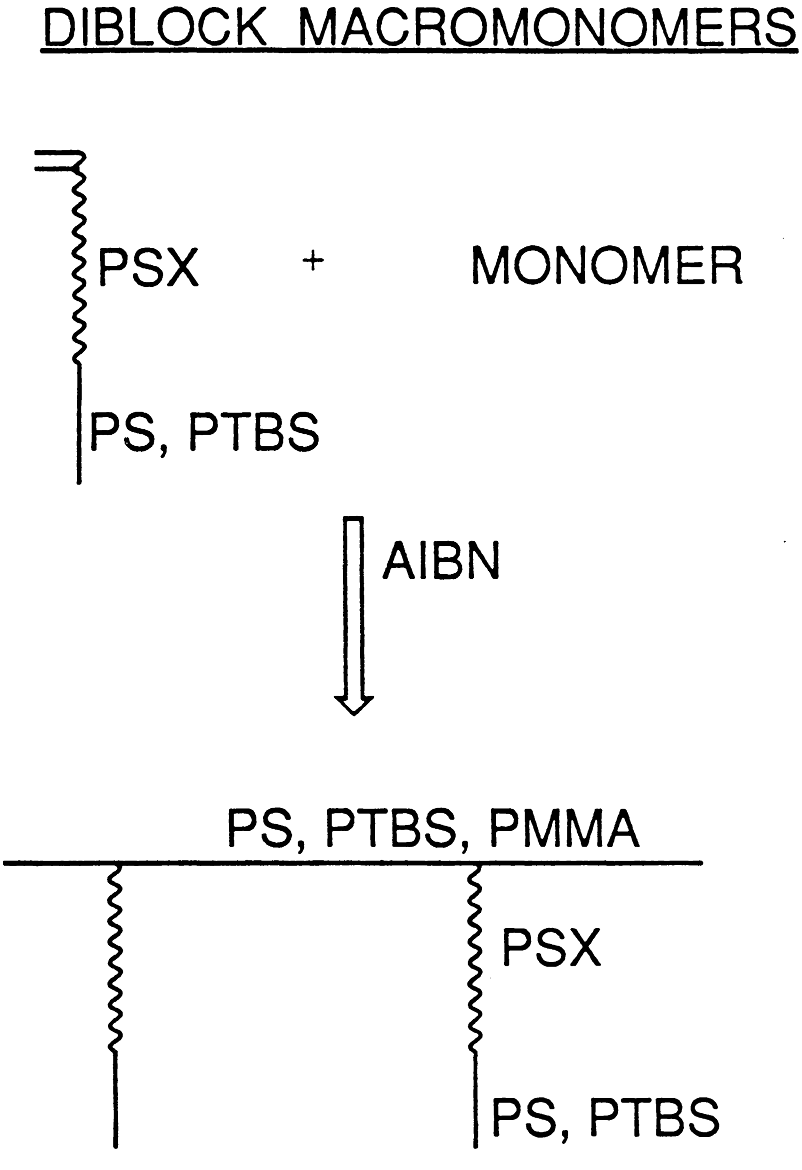
DSC showed that substantial miscibility occurred between the short diblocks as indicated in Table 36.

Scheme XI represents the structures formed from the copolymerization of these diblock macromonomers. The structure thus formed has a hard-soft-hard type linkage, and as such might have properties much different from a

Table 36

Glass Transition Temperatures of Styrenic-Siloxane Diblock Macromonomers

Sample	Tg°C
62A PS-b-PSX 5K-10K	80
62B PS-b-PSX 10K-15K	89
62C PTBS-b-PSX 5K-10K	100
62D PTBS-b-PSX 10K-15K	109



Scheme XI. Diblock Macromonomer Scheme

hard backbone with soft grafts. Materials wih high siloxane contents could be thermoplastic elastomers. Rubber toughening might also be more efficient with soft domains anchored at both ends.

G. Poly(Methyl methacrylate-g-(Poly(styrene-b-Poly(dimethylsiloxane)): Synthesis and Characterization

Styrene-siloxane diblock macromonomers were copolymerized with methyl methacrylate to prepare graft copolymers. Low molecular weight polystyrene and poly(methyl methacrylate) are known to be miscible. The low molecular weight poly(styrene) end block might provide miscibility with the PMMA matrix and change the morpholgy by anchoring both ends of the siloxane grafts. Even without miscibility of PMMA and PS the hard blocks anchoring the two ends of the siloxane chains will limit chain mobility and a three phase system might possibly form.

NMR analysis of the samples is summarized in Table 37. Fairly good agreement between charged and obtained incorporation was achieved. Ratios of styrene to siloxane agree with the original macromonomer, demonstrating the integrity of the "diblock graft".

DSC measurements indicated only the Tg of the PMMA as would be expected, since there is only about 5 weight

Table 37

NMR Analysis of PMMA-g-(PS-b-PSX)

Sample	Charged	NMR
66A 5K-10K Graft	20%	14%
66B 10K-15K Graft	20%	13%

percent of styrene in the system.

GPC indicated pure copolymer after extraction and that the molecular weights were approximately 100,000 g/mole.

TEM analysis of these copolymers showed a much more irregular morphology than a PMMA-g-PSX copolymer of similar composition, as can be compared in Figure 75. Perhaps a three phase system is present with poly(methyl methacrylate) and poly(styrene) phases indistinguishable. With the poly(styrene) forming a third phase it is much harder for the siloxane to form discreet and ordered phases, and instead an almost bicontinuous morpholgy is formed.

H. Poly(Styrene-g-(Poly(styrene-b-Poly(dimethylsiloxane)): Synthesis and Characterization

Copolymerizations of the styrene-siloxane diblock macromonomers with styrene monomer were carried out with two goals. One was to prepare copolymers with approximately 15-20 weight percent siloxane as comparisons to the PS-g-PSX copolymers and secondly materials with approximately 50 weight percent siloxane were desired for their elastomeric properties and for impact modification of styrene.

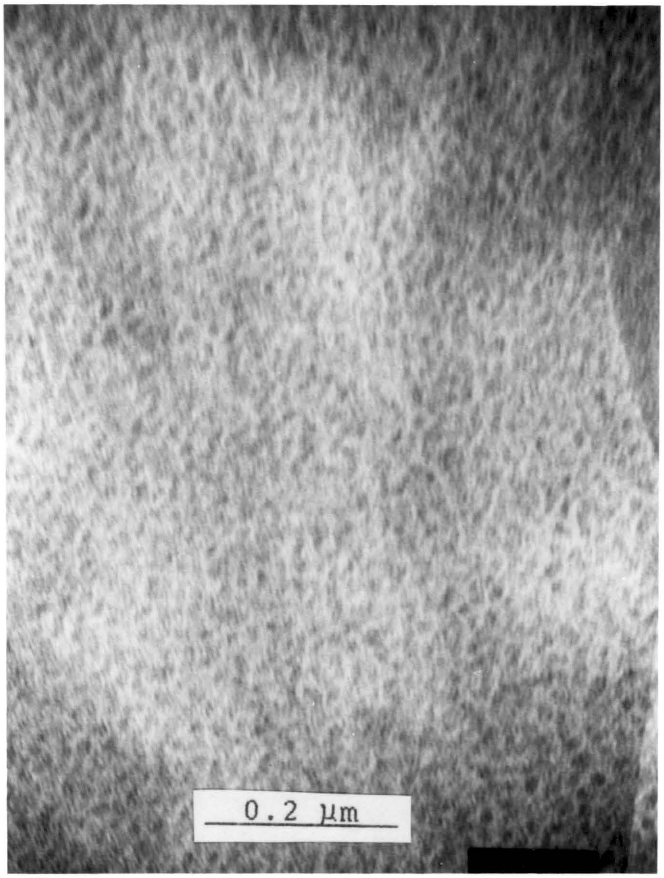


Figure 75. TEM of PMMA-g-(PS-b-PSX) 20 WT% PSX

The copolymers prepared with about 20 weight percent siloxane were extracted with hot isopropanol and hexanes to remove free diblock macromonomer. Characterization of the copolymers by NMR, DSC, GPC, and TEM were carried out. The incorporation was efficient as determined by NMR, and GPC.

DSC analysis showed a single transition at high temperature.

TEM provided insight into the morpholgy of these copolymers. As with the PMMA diblock graft copolymers a somewhat bicontnuous morpholgy is formed, as can be seen in Figure 76. Domains on the order of 10 nm. were observed.

The synthesis of copolymers with approximately 50 weight percent siloxane involves the copolymerization of the macromonomers which are only 60-66 weight percent siloxane with only small amounts of styrene monomer. This might be recognized as an inefficient procedure due to the extremely low concentration of polymerizable groups and therefore low efficiency of macromonomer incorporation, GPC confirmed this suspision. As Milkovich reported [124] the impact properties of his polymers were actually improved by the presence of unreacted diblock macromonomer. The tendency for these unreacted macromonomers to form larger domains may increase the

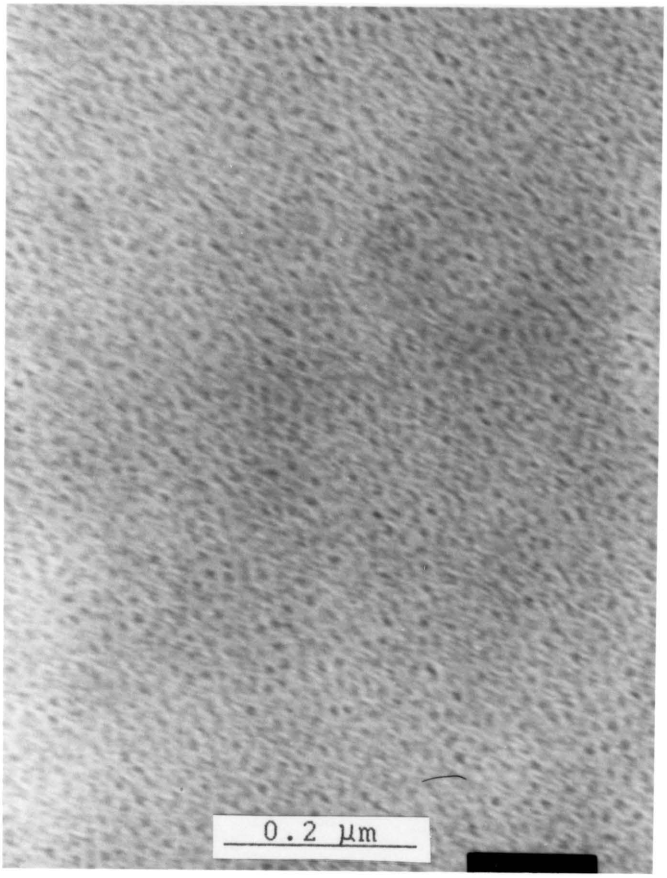


Figure 76. TEM of PS-g-(PS-b-PSX) 20 WT% PSX

impact properties.

These materials are not film forming due to the large amounts of unreacted diblock remaining in the system. Efforts to solution blend these copolymers with pure poly(styrene) resulted in immiscible blends.

I. Poly(t-Butylstyrene-g-(Poly(t-Butylstyrene-b-Poly(dimethylsiloxane)): Synthesis and Characterization

Copolymers were prepared from t-butyl styrene-siloxane diblock macromonomers and t-butyl styrene monomer. A series of copolymers were prepared with siloxane content being approximately 20 weight percent or 50 weight percent siloxane. Extraction of macromonomer here was achieved with isopropanol and NMR and GPC analysis concluded that macromonomer incorporation was achieved.

DSC indicted a single broadened transition at high temperature.

TEM showed a very poorly defined almost indistinguishable morpholgy at 20 weight percent siloxane.

Copolymers with 50 weight percent siloxane formed elastomeric films probably due to the higher efficiency of the copolymerization of t-butyl styrene with the macromonomer than in the case of styrene monomer. Blending of these copolymers with poly(t-butyl styrene) resulted in immiscible but still tougher films of poly(t-butylstyrene).

TEM showed that a bicontinuous morphology was formed as shown in Figure 77. Again the definition of phases is very poor due to the somewhat miscible phases.

J. Characterization of Blends of Poly(Methyl methacrylate-g- Poly(dimethylsiloxane)

Blends of PMMA-g-PSX with PMMA or PVC were cast from 5 w/v % solutions. PMMA blends were prepared from chloroform solutions, while PVC blends were cast from THF. Very slow evaporation rates were obtained by covering the cast solutions with watch glasses.

The methods of characterization were primarily based on the observation that clear or opaque films were produced, FTIR, DSC analysis of glass transition temperatures, and TEM analysis of morphology.

Blends with PMMA were partially undertaken as a method of further understanding the compositional heterogeneity that exists in a sample of copolymer. It has been discussed that homopolymer of the backbone may form and hence be present in the mixture of copolymers formed. Also applications of these graft copolymers as surface modifying agents might be possible at very low siloxane contents, by blending these copolymers with pure PMMA. The PMMA backbone would hopefully be compatable with the PMMA bulk and anchor the siloxane to the bulk, to provide long

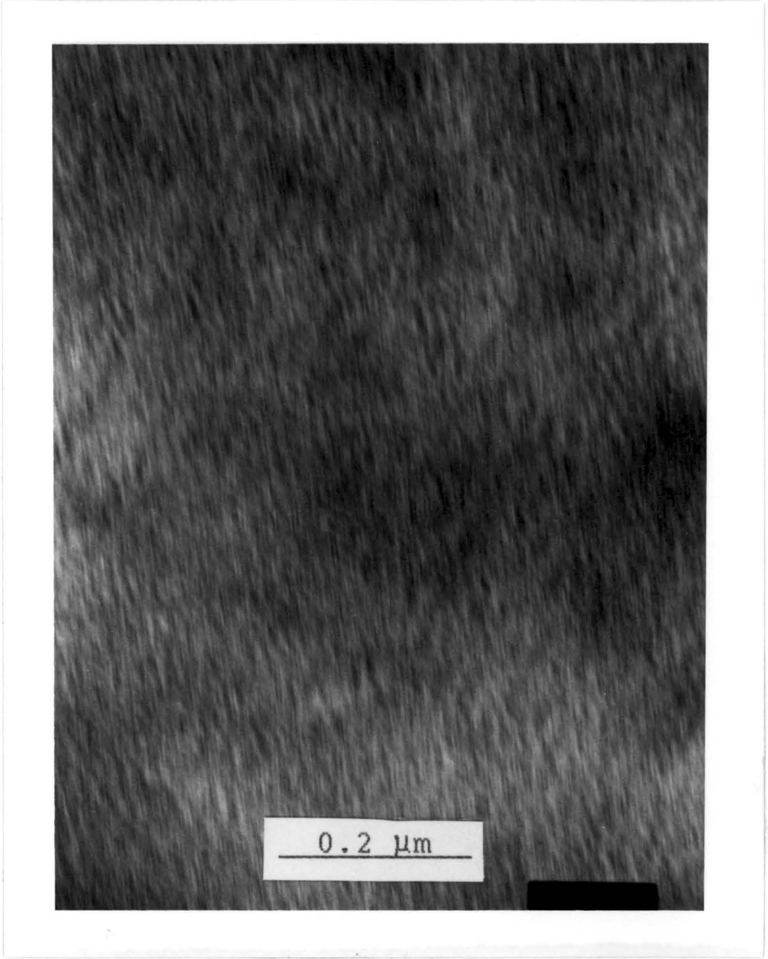


Figure 77. TEM of PTBS-g-(PTBS-b-PSX) 50 WT% PSX

term stability to the surface modification. An understanding of the blending properties of these copolymers was therefore desirable.

Samples with approximately 10 weight percent siloxane were made up as a standard for comparison by the TEM technique. The morphology of graft copolymers of about 10 weight percent siloxane could be compared to blends with the same composition but with varying siloxane content graft copolymer and graft molecular weights.

Table 38 presents a list of samples that were prepared and analyzed by TEM, as shown in Figures 78 through 80. It should be noted that sample 56C was prepared from sample 11Q which has a hexagonally packed rod morphology. The incompatability of this blend was checked by blending 11Q with several different PMMA samples of varying molecular weight, none of which provided a compatible blend.

Sample 11J which has a lamellae morpholgy does form a compatible blend with PMMA, while sample 88G also with 10K grafts and which has a lamellae morphology does not blend with PMMA. The morpholgy of the sample 56B (Figure 78) was very interesting from the point of view that the blend was miscible, but a spherical domain structure was not observed, but rather a metastable pattern of siloxane throughout the PMMA matrix.

Table 38

Summary of PMMA-g-PSX/ PMMA Blends (Blended with PMMA of Similar Molecular Weight to form 10 WT% PSX Overall)

Sample Description				Comments
56A	11G	42 WT% PSX	5K	Not Observeable
56B	11I	38 WT% PSX	10K	Bicontinuous
56C	11Q	43 WT% PSX	20K	Immiscible
56D	7F	23 WT% PSX	5K	Spherical
56E	7K	20 WT% PSX	10K	Spherical
56F	11N	17 WT% PSX	20K	Spherical

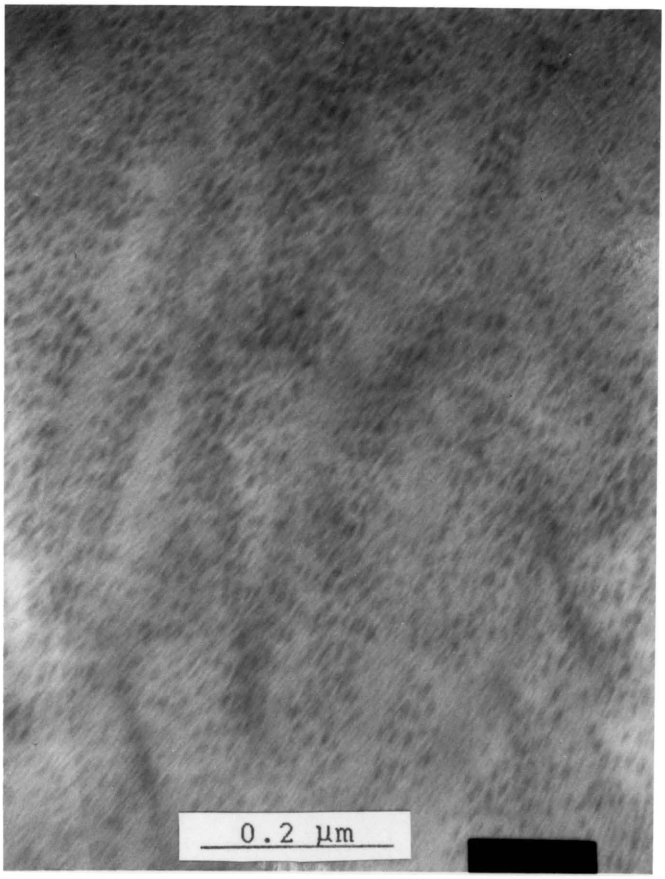


Figure 78. TEM of PMMA-g-PSX/ PMMA Blend 5K PSX

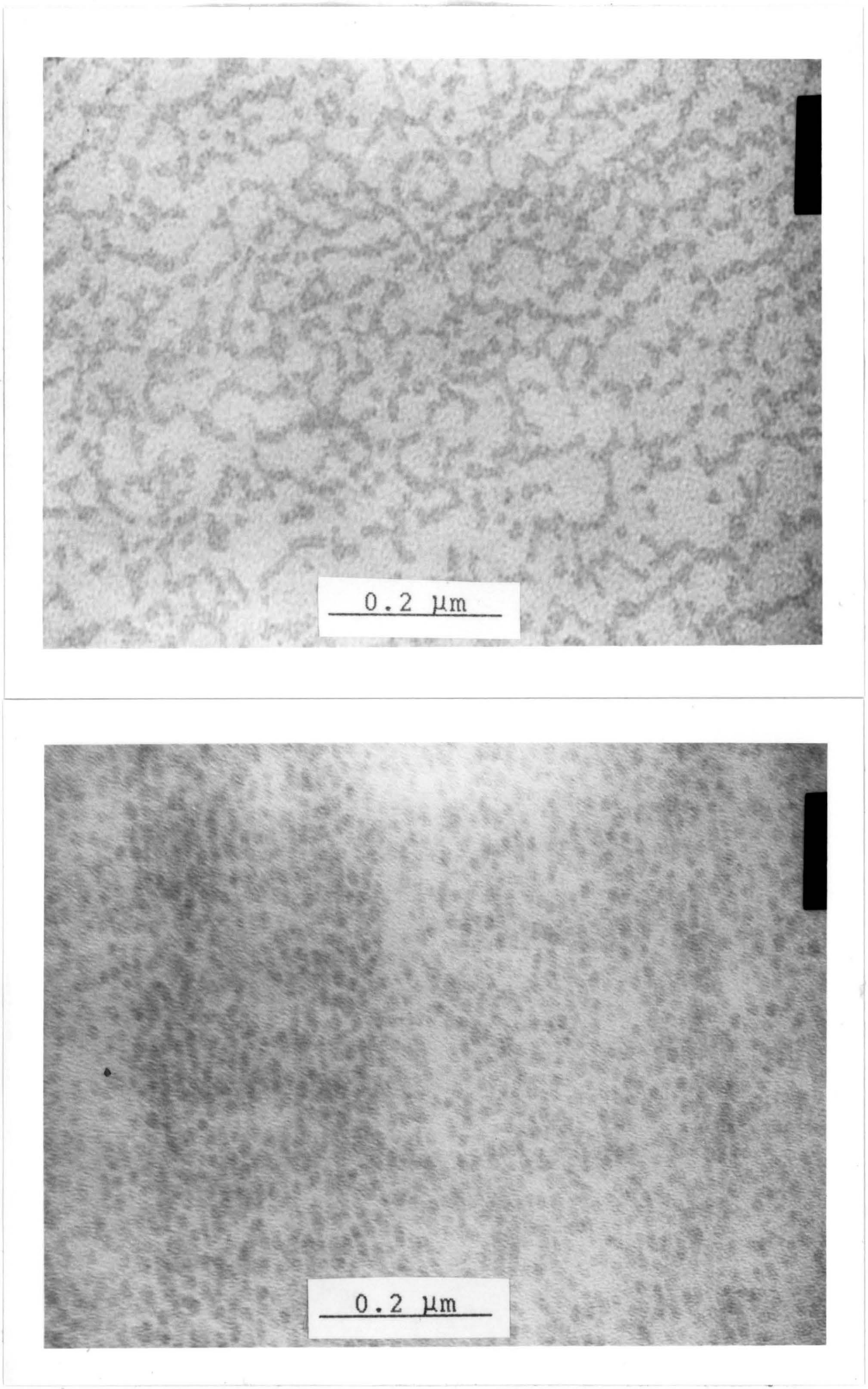


Figure 79. TEM of PMMA-g-PSX/ PMMA Blend 10K PSX

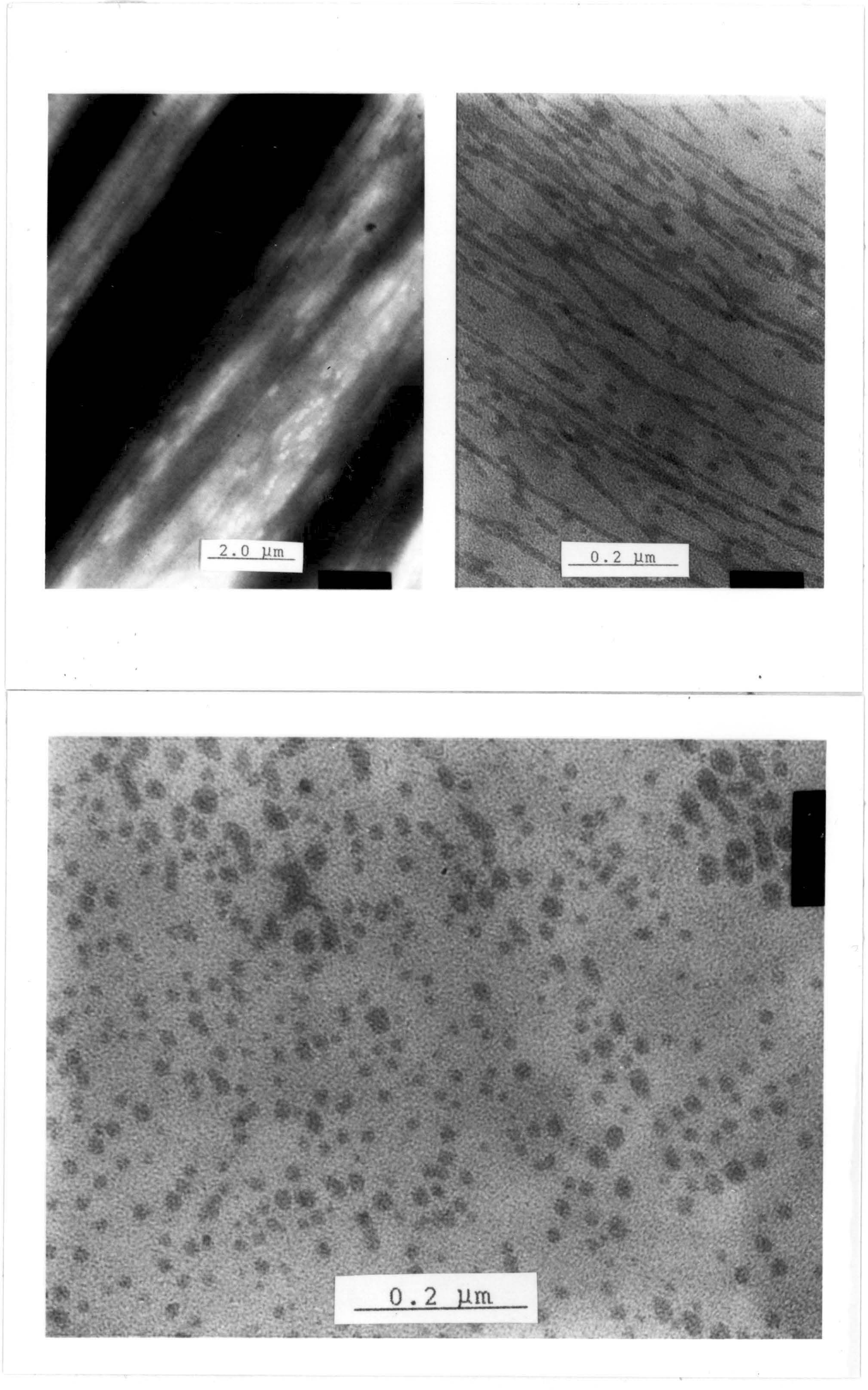


Figure 80. TEM of PMMA-g-PSX/ PMMA Blend 20K PSX

It was typical for copolymers with low siloxane content to blend back to a spherical morphology. Sample 56A blended from 11G with 5K grafts was also interesting since 11H (Figure 38) has a bicontinuous morphology and a suppressed Tg due to mixing, as we would expect 11G to have as well. There was no observeable morpholgy in this blend probably due to a large degree of phase mixing.

The series of spherical morphologies formed from the blending of lower composition copolymers are also interesting from the point of view that the domain sizes match that of the graft copolymers with the same graft molecular weights. It was also observed that domain sizes were independent of siloxane content. Higher siloxane contents produced only higher degrees of ordering with identical feature sizes. This would inidcate that the domain sizes were determined by the narrow molecular weight distribution grafts forming domains which then force the methacrylate to conform around the domains of PSX.

PMMA is miscible with several other polymers that make these copolymers useful for surface modification. One of these is PVC, whose polarized carbon-chlorine bond interacts with the ester carbonyl group of PMMA. This specific interaction probably enhances the compatability of the blends.

Early experiments with PMMA and PVC at higher levels of PMMA were shown to have a single Tg. FTIR spectra were run to show whether shifting of the PMMA carbonyl frequency occurred, showing the interaction of the carbonyl with the acidic proton of PVC. A minor shift of approximately 1.5 cm^{-1} occurred, with the carbonyl frequency of PMMA occurring at 1730.6 cm-1 while the carbonyl frequency in the blends was approximately 1732 cm-1.

There are however certain composition limits beyond which immiscible blends occur. For instance materials high in siloxane have not been succesfully blended. Also a certain limit on the amount of siloxane in the blend probably exists. While PMMA/PVC blends up to about a 50/50 weight composition. Even with materials low in siloxane immiscibility occurs above a siloxane content of approximately 5-10 wt% PSX.

VI. CONCLUSIONS

This investigation of the novel block and graft copolymers synthesized by a combination of anionic and free radical polymerizations has resulted in much more understanding of the structure- property relationships in graft copolymers. Specific conclusions are as follows:

1. The anionic alkyl lithium initiated polymerization of D_3 results in a living, non-equilibration polymerization. This allows for the preparation of polymers with controlled molecular weight, of narrow molecular weight distribution and controlled functionality.
2. Macromonomers were prepared by the termination of the anionic polymerization of siloxanes followed by termination with a methacrylate functional chlorosilane.
3. Copolymerizations of these macromonomers with styrenic and acrylic monomers proceeded free radically to yield well defined copolymers.
4. Anionic Copolymerizations at -78°C proceed to produce graft copolymers of relatively narrow molecular weight distributions.
5. Novel morphologies were observed in some instances indicating a very well defined nature of the copolymer.
6. Thermal stabilities exceeding those of typical free radical PMMA. It was suggested that that saturated end groups exist which probably result from an increase in the chain transfer rate when macromonomer units exist as the terminal chain unit.
7. Molecular weight distributions would also support a chain transfer reaction, since MWD increases with increasing siloxane content.

8. Compositional heterogeneity was also found to follow theoretical calculations as fractionated by Super Critical Fluid Extractions.

9. Blending of the copolymers was also informative as it was found that certain limits existed, and that surface domination could be achieved through blending.

VII. SUGGESTED FUTURE STUDIES

Many future directions exist for research efforts, several of which are reviewed below.

1. Further investigation of the morphologies of PMMA-g-PSX copolymers as a function of PSX graft molecular weight and MWD.
2. Further investigation into the effect of polymerization conversion on the chemical composition distributions.
3. Blends of the graft copolymers with PMMA, PVC, and PVF_2 to elucidate the ability of these materials to act as surface modifiers.
4. Copolymerizations of methyl methacrylate with other macromonomers to investigate the thermal stability and end group effects.
5. Diblock macromonomer investigations to determine the ability to prepare thermoplastic elstomers.
6. tert-Butyl methacrylate macromonomers which could be copolymerized with a low Tg material. These could then be hydrolyzed to form an ionomeric thermoplastic elastomer.

7. Styrene functional poly(dimethyl siloxane) macromonommer synthesis and copolymerization.

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APPENDIX 1

```
10 CLS
11 REM************************************************************************************
12 REM  This program will calculate molecular weight of polymers from GPC/SEC data
13 REM   Data from the calibration standards will be fit to both linear and cubic equations
14 REM  Programers include Pradip Das, Bob Dodson, Steve Smith, Jim Hoover and Paul Koning
15 REM************************************************************************************
20 K=0
30 DIM DIST(15),MW(15),PV(15),SAMDIS(50),H(50)
40 DIM A(7), R(5,5), T(5)
50 DIM HM(50),HOM(50),HM2(50),HM3(50),SAMVOL(50),SAMW(50)
60 PRINT "WARNING - INSURE THAT PRINTER IS ON"
70 IF K = 0 GOTO 100
80 INPUT "REPRINT LAST ANALYSIS ?", RLA$
90 IF RLA$ = "YES" OR RLA$ = "yes" OR RLA$ ="Y" OR RLA$ ="y" GOTO 2720
91 REM************************************************************************************
92 REM  Lines 100 thur 430 include input of experimental conditions and
93 REM  GPC/SEC data for the calibration standards.
94 REM************************************************************************************
100 INPUT "SAMPLE ID?",ID$
110 INPUT "DATE?",DA$
120 INPUT "INSTRUMENT?",INST$
130 INPUT "SOLVENT?",SOLV$
140 INPUT  "COLUMN TYPE ?",COL$
150 INPUT "STANDARD ?",STD$
160 INPUT "TEMPERATURE (centigrade) ?",TEMP
170 INPUT "FLOW RATE (ml/min) ?",FR
180 IF FR>0 GOTO 200
190 INPUT"ZERO IS INVALID,INPUT FLOW RATE",FR
200 INPUT "CHART SPEED (cm/min) ?",CSPEED
210 IF CSPEED >0 GOTO 230
220 INPUT"ZERO IS INVALID, INPUT CHARTSPEED",CSPEED
230 IF K=0 GOTO 260
240 INPUT "USE SAME STANDARDS ?",ANS$
250 IF ANS$ ="YES" OR ANS$="yes" OR ANS$="Y" OR ANS$="y" GOTO 1550
260 INPUT "HOW MANY STANDARDS ?",NSTD%
270 G1=0
280 G2=0
290 A(1) = NSTD%
291 A(2)=0
292 A(3) =0
293 A(3) =0
294 A(4) =0
295 A(5) =0
296 A(6) =0
297 A(7) =0
300 SV=0
302 T(1)=0
```

```
303 T(2) = 0
304 T(3) =0
305 T(4) =0
306 T(5) = 0
310 SY=0
320 V2=0
330 Y2=0
340 VM=0
350 IF NSTD% >0 GOTO 370
360 INPUT"ZERO IS INVALID, INPUT NUMBER OF STANDARDS",NSTD%
370 FOR I%=1 TO NSTD%
380 INPUT "ELUTION DISTANCE FOR STANDARD ?",DIST(I%)
390 IF DIST(I%) >0 GOTO 410
400 INPUT"ZERO IS INVALID, INPUT ELUTION DISTANCE",DIST(I%)
410 INPUT "MOL.WT. OF THE STANDARD ?",MW(I%)
420 IF MW(I%) >0 GOTO 440
430 INPUT"ZERO IS INVALID, INPUT MOLECULAR WEIGHT",MW(I%)
431 REM****************************************************************************************
432 REM  For calculation of the GPC/SEC calbration curve LOG(MW) is the "Y"
433 REM  value and  PV (peak elution vol.) the "X" value.
434 REM  Therefore  line 470 is the sum of "X", line 560 the sum of "Y"
435 REM line 570 the sum of "X**2", line 580 the sum of "Y**2"
436 REM line 590 the sum of "X*Y"
437 REM****************************************************************************************
440 PV=DIST(I%)/CSPEED*FR
450 DIST(I%) = DIST(I%)/CSPEED*FR
460 MW(I%)=LOG(MW(I%))
470 SV=SV+PV
480 FOR J% = 2 TO 7
490 A(J%) = A(J%) + DIST(I%)^(J%-1)
500 NEXT J%
510 FOR K% = 1 TO 4
520 R(K%,5) = T(K%) +MW(I%)*DIST(I%)^(K%-1)
530 T(K%) = T(K%) +MW(I%)*DIST(I%)^(K%-1)
540 NEXT K%
550 T(5) = T(5) + MW(I%)^2
560 SY=SY+MW(I%)
570 V2=V2+PV*PV
580 Y2=Y2+MW(I%)*MW(I%)
590 VM=VM+PV*MW(I%)
600 NEXT I%
610 FOR I% = 1 TO NSTD%
620 MF = EXP(MW(I%))
630 MF! = MF
640 PRINT I%,MF!,DIST(I%)
650 NEXT I%
660 INPUT "DO YOU WANT TO MAKE ANY CHANGES ?",ANS$
670 IF ANS$ ="N" OR ANS$="n" OR ANS$="NO" OR ANS$="no" GOTO 1010
680 INPUT "WHICH STANDARD, BY ITS I VALUE ",L%
690 PV = DIST(L%)
```

```
700 SV = SV- PV
710 FOR J% = 2 TO 7
720 A(J%) = A(J%) - DIST(L%)^(J%-1)
730 NEXT J%
740 FOR K% = 1 TO 4
750 R(K%,5) = T(K%) - MW(L%)*DIST(L%)^(K%-1)
760 T(K%) = T(K%) - MW(L%)*DIST(L%)^(K%-1)
770 NEXT K%
780 T(5) = T(5) - MW(L%)^2
790 SY = SY -MW(L%)
800 V2 = V2 - PV*PV
810 Y2 = Y2 - MW(L%) *MW(L%)
820 VM = VM - PV*MW(L%)
830 INPUT"INPUT CORRECT STANDARD MOLECULAR WEIGHT",MW(L%)
840 MW(L%) = LOG(MW(L%))
850 INPUT"INPUT CORRECT ELUTION VOLUME ",DIST(L%)
860 PV = DIST(L%)
870 SV = SV +PV
871 REM******************************************************************************
872 REM  Somewhere between here and line 1540 is the Thrid Order Regression fit.
873 REM  It's a bit messy, but it's in there!
874 REM  The program was translated from "SOME COMMON BASIC PROGRAMS  TRS-80 LEVEL
          II EDITION"
875 REM  By Steve Smith in NOV ' 85
876 REM******************************************************************************
880 FOR J% = 2 TO 7
890 A(J%) = A(J%) + DIST(L%)^(J%-1)
900 NEXT J%
910 FOR K% = 1 TO 4
920 R(K%,5) = T(K%) + MW(L%)*DIST(L%)^(K%-1)
930 T(K%) = T(K%) + MW(L%)*DIST(L%)^(K%-1)
940 NEXT K%
950 T(5) = T(5) + MW(L%)^2
960 SY = SY + MW(L%)
970 V2 = V2 + PV*PV
980 Y2 = Y2 + MW(L%)*MW(L%)
990 VM = VM +PV*MW(L%)
1000 GOTO 610
1010 FOR J% =1 TO 4
1020 FOR K% =1 TO 4
1030 R(J%,K%) = A(J% +K% -1)
1040 NEXT K%
1050 NEXT J%
1060 CLS
1070 FOR J% = 1 TO 4
1080 K% = J%
1090 IF R(K%,J%) < 0 OR R(K%,J%) >0 GOTO 1150
1100 K% = K% +1
1110 PRINT J%,K%
1120 IF K%<4  OR K%=4 GOTO 1090
```

```
1130 PRINT"NO UNIQUE SOLUTIONS"
1140 GOTO 3040
1150 FOR I% = 1 TO 5
1160 S = R(J%,I%)
1170 R(J%,I%) = R(K%,I%)
1180 R(K%,I%) = S
1190 NEXT I%
1200 Z= 1/R(J%,J%)
1210 FOR I% =1 TO 5
1220 R(J%,I%) = Z* R(J%,I%)
1230 NEXT I%
1240 FOR K% =1 TO 4
1250 IF K% = J% GOTO 1300
1260 Z= -R(K%,J%)
1270 FOR I% = 1 TO 5
1280 R(K%,I%) = R(K%,I%) + Z*R(J%,I%)
1290 NEXT I%
1300 NEXT K%
1310 NEXT J%
1320 D=NSTD%*V2-SV*SV
1330 IN=(V2*SY-SV*VM)/D
1340 Q=NSTD%*VM-SV*SY
1345 S = NSTD%*Y2 - SY^2
1350 T= (D*S)^ (.5)
1360 R= Q/T
1370 SLOPE=Q/D
1380 PRINT "LINEAR LEAST SQUARES: SLOPE = ", SLOPE
1390 PRINT "INTERCEPT =",IN
1400 PRINT "CORRELATION COEFFICIENT =",R
1401 PRINT
1402 PRINT "Cubit Fit"
1410 PRINT" CONSTANT =  "(R(1,5))
1420 FOR J% = 1 TO 3
1430 PRINT J%" DEGREE COEFFICIENT = "(R(J%+1,5))
1440 NEXT J%
1450 P=0
1460 FOR J% = 2 TO 4
1470 P = P+ R(J%,5)*(T(J%)-A(J%)*T(1)/NSTD%)
1480 NEXT J%
1490 Q= T(5) - T(1)^2/NSTD%
1500 Z= Q-P
1510 I = NSTD% -D -1
1520 J= P/Q
1530 PRINT"COEFFICIENT OF DETERMINATION = " J
1540 PRINT"COEFFICIENT OF CORRELATION = "(J^2)
1541 REM********************************************************************************
1542 REM  This is the end of the calculations for the calibration curve and the
1543 REM  begining of the data input for the MWD determination for the sample
1544 REM********************************************************************************
1550 INPUT" HOW MANY SAMPLE DATA ? ",NSAM%
```

```
1560 SUMHM=0
1570 SUMHMC=0
1580 SUMHM2=0
1590 SUMHMC2=0
1600 SUMHOM=0
1610 SUMHOMC=0
1620 SUMH=0
1630 SUMHC=0
1640 SUMHM3=0
1650 SUMHMC3=0
1660 IF NSAM% >0 GOTO 1680
1670 INPUT"ZERO IS INVALID, INPUT NUMBER OF SAMPLES",NSAM%
1680 INPUT"ELUTION DISTANCE INCREMENT",EDI
1690 Q=0
1700 FOR I%=1 TO NSAM%
1710 IF EDI =0 GOTO 1750
1720 IF Q=0 GOTO 1750
1730 SAMDIS(I%)=SAMDIS(I% -1) + EDI
1740 GOTO 1780
1750 INPUT "SAMPLE ELUTION DISTANCE ?",SAMDIS(I%)
1760 IF SAMDIS(I%)>0 GOTO 1780
1770 INPUT"ZERO IS INVALID, INPUT SAMPLE ELUTION DISTANCE",SAMDIS(I%)
1780 INPUT "PEAK HEIGHT ?",H(I%)
1790 SAMVOL=SAMDIS(I%)/CSPEED*FR
1800 SAMW=EXP(SAMVOL*SLOPE+IN)
1810 SAMWC = EXP( R(1,5) + R(2,5)*SAMVOL + R(3,5)*SAMVOL^2 +R(4,5)*SAMVOL^3)
1820 HM=H(I%)*SAMW
1830 HMC=H(I%)*SAMWC
1840 HOM=H(I%)/SAMW
1850 HOMC=H(I%)/SAMWC
1860 HM2=HM*SAMW
1870 HMC2=HMC*SAMWC
1880 HM3=HM2*SAMW
1890 HMC3=HMC2*SAMWC
1900 SUMHM=SUMHM+HM
1910 SUMHMC=SUMHMC+HMC
1920 SUMHM2=SUMHM2+HM2
1930 SUMHMC2=SUMHMC2+HMC2
1940 SUMHOM=SUMHOM+HOM
1950 SUMHOMC=SUMHOMC+HOMC
1960 SUMH=SUMH+H(I%)
1970 SUMHC=SUMHC+H(I%)
1980 SUMHM3=SUMHM3+HM3
1990 SUMHMC3=SUMHMC3+HMC3
2000 Q=1
2010 NEXT I%
2020 FOR I% = 1 TO NSAM%
2030 PRINT I%,SAMDIS(I%),H(I%)
2032 IF (I%/15) <> FIX(I%/15) GOTO 2040
2034 INPUT"PLEASE CHECK THIS DATA AND HIT RETURN TO CONTINUE",Z
```

```
2040 NEXT I%
2050 INPUT" DO YOU WANT TO MAKE ANY CHANGES ? ",ANS$
2060 IF ANS$ = "N" OR ANS$ = "n" OR ANS$="NO" OR ANS$="no" GOTO 2510
2070 INPUT "INPUT SAMPLE CHANGE BY ITS I VALUE",J%
2080 SAMVOL = SAMDIS(J%)/CSPEED*FR
2090 SAMW = EXP(SAMVOL*SLOPE +IN)
2100 SAMWC = EXP( R(1,5) + R(2,5)*SAMVOL + R(3,5)*SAMVOL^2 +R(4,5)*SAMVOL^3)
2110 HM =H(J%)*SAMW
2120 HMC =H(J%)*SAMWC
2130 HOM =H(J%)/SAMW
2140 HOMC =H(J%)/SAMWC
2150 HM2 = HM*SAMW
2160 HMC2 = HMC*SAMWC
2170 HM3 = HM2*SAMW
2180 HMC3 = HMC2*SAMWC
2190 SUMHM = SUMHM - HM
2200 SUMHMC = SUMHMC - HMC
2210 SUMHOM = SUMHOM - HOM
2220 SUMHOMC = SUMHOMC - HOMC
2230 SUMH = SUMH - H(J%)
2240 SUMHC = SUMHC - H(J%)
2250 SUMHM3 = SUMHM3 - HM3
2260 SUMHMC3 = SUMHMC3 - HMC3
2270 INPUT" INPUT CORRECT SAMPLE ELUTION DISTANCE ",SAMDIS(J%)
2280 INPUT"INPUT CORRECT SAMPLE HEIGHT ", H(J%)
2290  SAMVOL = SAMDIS(J%)/CSPEED*FR
2300 SAMW = EXP(SAMVOL*SLOPE +IN)
2310 SAMWC = EXP( R(1,5) + R(2,5)*SAMVOL + R(3,5)*SAMVOL^2 +R(4,5)*SAMVOL^3)
2320 HM = H(J%)*SAMW
2330 HMC = H(J%)*SAMWC
2340 HOM = H(J%)/SAMW
2350 HOMC = H(J%)/SAMWC
2360 HM2 = HM*SAMW
2370 HMC2 = HMC*SAMWC
2380 HM3 = HM2*SAMW
2390 HMC3 = HMC2*SAMWC
2400 SUMHM = SUMHM + HM
2410 SUMHMC = SUMHMC + HMC
2420 SUMHM2 = SUMHM2 + HM2
2430 SUMHMC2 = SUMHMC2 + HMC2
2440 SUMHOM = SUMHOM + HOM
2450 SUMHOMC = SUMHOMC + HOMC
2460 SUMH = SUMH +H(J%)
2470 SUMHC = SUMHC +H(J%)
2480 SUMHM3 = SUMHM3 + HM3
2490 SUMHMC3 = SUMHMC3 + HMC3
2500 GOTO 2020
2510 AVGMN=SUMH/SUMHOM
2520 AVGMNC=SUMHC/SUMHOMC
2530 AVGMW=SUMHM/SUMH
```

```
2540 AVGMWC=SUMHMC/SUMHC
2550 AVGMZ=SUMHM2/SUMHM
2560 AVGMZC=SUMHMC2/SUMHMC
2570 AVGMZ1=SUMHM3/SUMHM2
2580 AVGMZC1=SUMHMC3/SUMHMC2
2590 PD!=AVGMW/AVGMN
2600 PDC!=AVGMWC/AVGMNC
2610 CLS
2620 PD! = FIX(PD! * 100) * .01
2630 PDC! = FIX(PDC! * 100) * .01
2640 MN1!=FIX(AVGMN*.01)*100
2650 MNC1!=FIX(AVGMNC*.01)*100
2660 MWX!=FIX(AVGMW*.01)*100
2670 MWXC!=FIX(AVGMWC*.01)*100
2680 MZ!=FIX(AVGMZ*.01)*100
2690 MZC!=FIX(AVGMZC*.01)*100
2700 MZ1!=FIX(AVGMZ1*.01)*100
2710 MZC1!=FIX(AVGMZC1*.01)*100
2711 REM ***********************************************************************
2712 REM                              Output to printer
2713 REM ***********************************************************************
2720 LPRINT ,,"GPC ANALYSIS"
2730 LPRINT
2740 LPRINT ,"SAMPLE:", ID$
2750 LPRINT ,"DATE:", DA$
2760 LPRINT ,"SOLVENT:", SOLV$
2770 LPRINT ,"STANDARD:", STD$
2780 LPRINT ,"COLUMNS:", COL$
2790 LPRINT ,"TEMPERATURE:", TEMP
2800 LPRINT ,"FLOW RATE (ml/min):", FR
2810 LPRINT ,"CHART SPEED (cm/min):", CSPEED
2820 LPRINT
2830 LPRINT"LINEAR ANALYSIS"
2840 LPRINT ,"<Mn> =", MN1!
2850 LPRINT ,"<Mw> =", MWX!
2860 LPRINT ,"<Mz+1> =", MZ1!
2870 LPRINT
2880 LPRINT ,"POLYDISPERSITY =", PD!
2890 LPRINT
2895 LPRINT "Correlation Coefficient for linear fit = ",R
2900 LPRINT
2910 LPRINT
2920 LPRINT
2930 LPRINT"CUBIC FIT"
2940 LPRINT ,"<Mn> =", MNC1!
2950 LPRINT ,"<Mw> =", MWXC!
2960 LPRINT ,"<Mz+1> =", MZC1!
2970 LPRINT
2980 LPRINT ,"POLYDISPERSITY =", PDC!
2990 LPRINT
```

```
2995 LPRINT "Correlation Coefficient for Cubic fit = ",(J^2)
3000 LPRINT
3010 LPRINT
3020 K=1
3030 GOTO 80
3040 END
```

APPENDIX 2

```
10 CLS
20 INPUT "NUMBER OF MONOMER TYPES ?",ST
30 FOR I= 1 TO ST
40 PRINT " ID OF MONOMER"I
50 INPUT NID$(I)
60 NEXT I
70 FOR I = 1 TO ST
80 PRINT "MOLECULAR WEIGHT OF MONOMER"I
90 INPUT MW(I)
100 NEXT I
110 FOR I= 1 TO ST
120 PRINT"NUMBER OF HYDROGENS INTERGRATED ON MONOMER"I
130 INPUT H(I)
133 IF H(I) > 0 GOTO 140
136 H(I) = 1
140 NEXT I
150 INPUT"HOW MANY SAMPLES ?",NS%
160 FOR I% = 1 TO NS%
170 FOR J% = 1 TO ST
180 PRINT"INTENSITY OF MONOMER"J%
190 INPUT IN(J%)
200 NEXT J%
210 INPUT"SAMPLE ID ?",ID$
220 SMP =0
230 FOR I = 1 TO ST
240 MP = IN(I)/H(I)
250 SMP = SMP + MP
260 NEXT I
270 FOR I = 1 TO ST
280 M(I) = (IN(I)/H(I))/SMP
285 M(I) = FIX(M(I)*10000)/100
290 NEXT I
300 SWP =0
310 FOR I = 1 TO ST
320 WP = IN(I)*MW(I)/H(I)
330 SWP = SWP + WP
340 NEXT I
350 FOR I =1 TO ST
360 W(I) =(IN(I)*MW(I)/H(I))/SWP
365 W(I) = FIX(W(I)*10000)/100
370 NEXT I
380 IF ST>2 GOTO 440
390 IF I%>1 GOTO 410
400 LPRINT"SAMPLE ID                    WT% "NID$(2)"              MOLE%"NID$(2)
410 LPRINT ID$"                      "W(2)"              "M(2)
420 NEXT I%
430 GOTO 490
440 LPRINT
```

```
450 LPRINT"SAMPLE ID "ID$
455 FOR I = 1 TO ST
460 LPRINT NID$(I) "= "M(I)"MOLE%", "= " W(I)"WEIGHT %"
470 NEXT I
480 GOTO 420
490 INPUT"WOULD YOU LIKE TO DO MORE SAMPLES ?",ANS$
500 IF ANS$ = "YES" OR ANS$ = "yes" OR ANS$ = "Y" OR ANS$ ="y" GOTO 10
510 END
```