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Daniella J. Fisher

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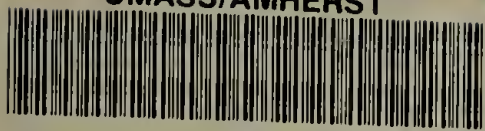
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INVESTIGATIONS OF THE LEWIS ACID-INITIATED
POLYMERIZATIONS OF p-SUBSTITUTED- α -METHYLSTYRENES

A Dissertation Presented

By

DANIELLA J. FISHER

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 1985

Polymer Science and Engineering

Daniella J. Fisher



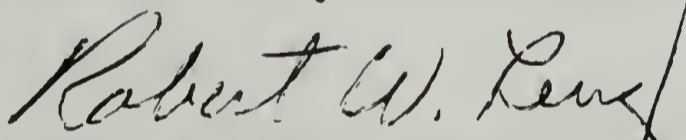
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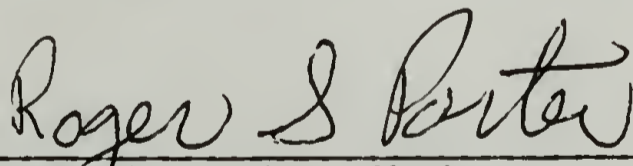
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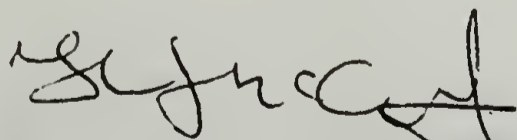
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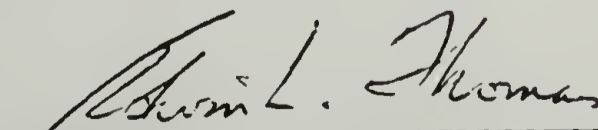
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ACKNOWLEDGEMENTS

I would like to express my appreciation and gratitude for the guidance provided by my advisor Professor Robert W. Lenz during my tenure at the University of Massachusetts. The advice and help were invaluable. Thanks are also extended to Professors Roger S. Porter and Thomas J. McCarthy for their insight and valuable suggestions as committee members and for their parts in providing a challenging and rewarding research atmosphere.

It is impossible to name all the people who have enriched my life, but several deserve mention. First, my parents, whose nurturance and encouragement helped to establish my goals, and Wayne, whose love and perspective sustained me while attaining my goals. Thanks are due to Richard Grant for the preparation of figures and to Craig Trask for technical assistance. Steve Arnold, Jim Capistran, Carl Sullivan, Bret Vanzo, and many other research group members combined to furnish enlightening staff meetings. A special thank you must be extended to John Smith and Victoria White for their friendship.

ABSTRACT

Investigations of the Lewis Acid-Initiated
Polymerizations of p-Substituted- α -methylstyrenes

September 1985

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The cationic polymerization reactions of p-chloro-, p-fluoro-, and p-methoxy- α -methylstyrene, using tin tetrachloride as the Lewis Acid initiator, were studied. Precipitation studies showed that the abrupt variations in molecular weight and yield for the p-chloro and p-fluoro polymers and in tacticity for the p-chloro polymer, as found in previous studies, were caused by precipitation of the polymers from the reaction solution. In homogeneous media, variations of solvent polarity resulted in smooth changes in the tacticity of the p-chloro polymer, while the tacticity of the p-fluoro polymer remained insensitive. Both polymers were highly syndiotactic under polar conditions. These results are consistent with stabilization of the propagating carbenium ion by the p-fluoro substituent and with propagation by free ions and solvated or contact ion pairs. The p-chloro and p-methoxy polymers were found to follow first-order Markov

statistics. The p-fluoro polymer, at first appearing to be Bernoullian, could not unambiguously be assigned. Propagation was much faster than initiation for the p-chloro monomer. Studies using a tritiated water tracer showed that water could not be totally removed from methylene chloride by conventional methods and that "stopping experiments" are inadequate for determining the role of water in the initiation reaction. Dessicants for the polymerization were evaluated. Optimum polymerization conditions for p-methoxy- α -methylstyrene were determined. Variation of the polymerization temperature affected the number average molecular weights and tacticities of the p-methoxy polymers. Activation energies for the degree of polymerization were calculated. The coefficient for chain transfer to monomer and the ratio of termination to propagation at -85°C were calculated. The polymerization of the p-methoxy monomer was neither living nor long-lived based on sequential monomer addition studies.

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C H A P T E R I

INTRODUCTION

Many polymers have been prepared from olefinic and cyclic monomers by a cationic mechanism. The most common initiators are Lewis Acids. Although used industrially, not much is known about the polymerization of olefinic monomers initiated by Lewis Acids. This lack of knowledge is due mainly to the high reactivity of carbocations. Consequently, direct observation of the active carbocation by conventional methods is hindered. Information about the reaction mechanisms in cationic polymerization processes must come from indirect observations of the physical characteristics of the polymers.

Previous studies in this laboratory [1-4] have looked at the polymerizations of substituted α -methylstyrenes in an attempt to correlate changes in substituents with changes in polymerization mechanisms. The most recent study [5] dealt solely with p-substituted- α -methylstyrenes. The α -methylstyrene monomer is a good candidate for study because the presence of the α -methyl and phenyl groups imparts stability to the subsequent carbocation. Thus, the occurrence of side reactions is decreased. It is the intent of this work to answer some of the questions raised in the previous studies indicated and to add to the knowledge of the behavior of p-substituted- α -methylstyrenes in cationic polymerization.

The polymers formed from p-substituted- α -methylstyrenes are easily characterized. Most importantly, proton nuclear magnetic resonance, $^1\text{H-NMR}$, can be used to determine the tacticities of these polymers. Polymer tacticity can be related to the type of active center present in the polymerization.

One side reaction of importance in cationic polymerization is chain transfer. The variation of the polymerization temperature can be used to determine conditions under which chain transfer is absent. Once chain transfer is eliminated, it may be possible to force long-lived behavior in some of these monomers and to eventually prepare block copolymers by a cationic mechanism.

A brief literature review covering the concepts pertinent to the current study is presented. The following chapters deal with initiation, propagation, and chain transfer in cationic polymerization, as well as the possibility of long-lived behavior. Recommendations for future work prompted by the results reported here are included in the final chapter.

Literature Review

Terminology

The nomenclature adopted in this work is defined here. Much debate has arisen in the literature over the use of two sets of terms. The first controversy involves the use of "carbenium ion" versus

"carbonium ion" to describe the propagating carbocation. "Carbenium ion" is preferred by researchers to denote the trigonal, sp^2 -hybridized carbon, as in the classical ion, CH_3^+ [6]. "Carbonium ion" is taken to mean a non-classical, pentavalent carbon, such as CH_5^+ . In this work, carbenium ion and carbocation are used interchangeably to denote the propagating center in cationic polymerization.

The second controversy is over the terms "catalyst" and "initiator". By definition, a catalyst remains unconsumed in the course of a reaction. Since most species that induce cationic polymerization are indeed consumed during the reaction, the more correct term of initiator will be used. Similarly, "coinitiator" is preferred over "cocatalyst". Where applicable, initiator is used for the Lewis Acid and coinitiator for the added carbenium-ion source. This convention is the reverse of that adopted by Kennedy [7,8].

The term "living" is reserved for those systems that exhibit behavior identical to the classical, living anionic polymerizations [9]. The term "long-lived" will be used for systems that show behavior similar but not identical to the classical, living systems.

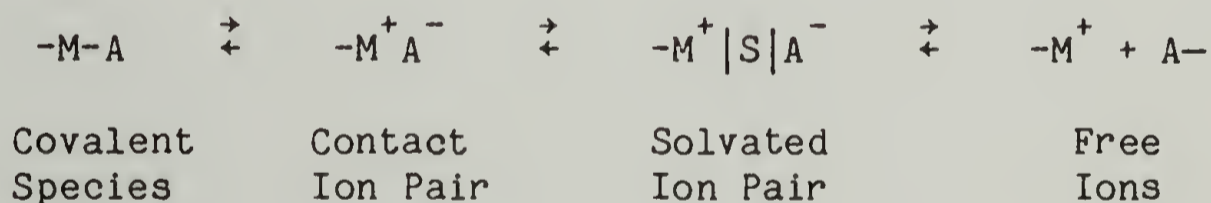
Carbenium ions and ion pairs

The chemistry of the polymerization of carbenium ions has been extensively reviewed [7,8,10-16]. However, complete characterization of the initiation, propagation, and termination processes involved in

the cationic polymerization of olefinic monomers remains elusive. Attainment of a stable carbenium ion that can be observed and manipulated depends on two factors, the stabilizing effect of substituents and the interaction of the counteranion.

Variation of substituents has proven to be successful in some cases. Higashimura and coworkers [17,18] have prepared polymers of p-methoxystyrene which exhibit long-lived behavior during polymerization initiated by iodine. Stopped flow techniques were used by Pepper [19], Sawamoto [20], and Cotrel [21] to directly observe the carbenium ion generated from p-methoxystyrene. The behavior of p-methoxy- α -methylstyrene is considered in Chapter V.

The role of the counteranion is hard to determine. The range of interaction of the counteranion is often represented by the Winstein spectrum [9,22]:



Conceivably, the polymerization media can contain several of the species shown above. Covalent species are not usually found in polymerizations initiated by Lewis Acids, but have been identified in pseudocationic polymerizations [23].

At the other end of the spectrum, free ions are also not usually found in Lewis Acid initiated systems. Free ions are produced from Y

radiation initiated polymerizations and are extremely fast.

Propagation rate constants, k_p , are on the order of 10^6 - 10^8 [24].

The distribution of ion pair species in a polymerization can be influenced by solvation. The effect of solvent polarity has been addressed previously [5,25,26] and will be considered more fully in Chapter II.

Stability of the counteranion must be considered. Several examples of termination of the polymer chain by collapse of or combination with the counteranion are known [8]. The theory of hard and soft acids and bases (HASAB) has been applied by Heublein [27] to determine the stability of ion pairs generated in cationic polymerization.

In this work, only tin tetrachloride, SnCl_4 , was used as initiator to avoid the variable of counteranion differences. The polymerization solvent was also kept constant except for studies involving solvent variations.

Water Coinitiation

When Lewis Acids are used without deliberately added coininitiator to induce polymerization, the identity of the counteranion is in doubt. This arises from the uncertainty of the initiation process and of the role of water. The many proposals made concerning the need for a coininitiator with Lewis Acids have been well reviewed by Kennedy [8]. Stopping experiments [8,28,29] have been used to attempt to determine

the necessity of water in initiation. The results of these experiments are in doubt due to the uncertainty in determining the presence of water in the reaction systems. The detection of trace quantities of water in cationic polymerization systems and the applicability of stopping experiments are considered in Chapter IV.

Tacticity and chain statistics

The changes in polymer tacticity with variation of the reaction conditions can offer insight into the nature of the propagating center. The tacticities can easily be obtained by $^1\text{H-NMR}$ [2,30] with the use of $^{13}\text{C-NMR}$ [31] and $^{19}\text{F-NMR}$ [2] also being reported. The correlation of polymer chain tacticities with a propagating species is considered in Chapter II.

For most polymerizations, propagation can be characterized as being either a Bernoulli trial or a first-order Markov process. In short, addition of a monomer unit is either unaffected, Bernoulli trial, or profoundly affected, first-order Markov, by the previous monomer addition. These processes are more fully defined and considered in Chapter III.

Chain transfer

Chain transfer and termination are the two side reactions most often encountered in cationic polymerization that prevent the formation of "living" systems. Modes of unintentional termination of

the propagating chain have been reviewed [7] and are not considered in this work. Chain transfer and the effects of temperature on it have been addressed by several researchers.

The influence of temperature on chain transfer can be understood by considering the activation energy for the degree of polymerization for a cationic mechanism [32]:

$$E_{DP} = E_p - E_{term} - E_{ct} \quad (1)$$

The activation energies for termination and transfer are larger than that for propagation. Thus a decrease in the reaction temperature increases the degree of polymerization.

Ideally, a temperature should exist where both termination and chain transfer are absent. In practice, termination most often is always present in cationic polymerization of olefinic monomers, but chain transfer can be "frozen out" by variation of temperature. The point at which control of the degree of polymerization switches from chain transfer domination to termination domination can be determined by observing changes in the slope of an Arrhenius plot [30]. Such changes have been observed for the polymerizations of isobutene [33] and α -methylstyrene [34]. The temperature and chain transfer effects for the polymerization of the p-methoxy monomer are considered in Chapter V.

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C H A P T E R I I
THE EFFECTS OF SOLVENT POLARITY AND REACTION
HOMOGENEITY ON THE POLYMERIZATION

Introduction

Solvent Polarity and Ion Pairs

The solvation state of the carbocationic active center influences polymerization rates and the molecular weights, yields, and physical properties of the polymers formed. Many researchers have studied the above properties and rates in order to identify the active species and the mechanism of propagation in the cationic polymerization of olefins.

Variation of solvent polarity has been used to study the polymerization rates of several monomers. In the cationic polymerization of styrene initiated by trifluoromethanesulfonic acid at 0°C, the polymerization rate increased greatly with increasing dielectric constant of the solvent mixture [1]. This increase in rate was attributed to a change in mechanism from propagation by contact ion pairs or covalent species in low polarity environments to propagation by solvated or free ions in high polarity environments. A similar effect in rate was reported for the polymerization of α -methylstyrene initiated with boron trifluoride etherate [2].

Reaction rates for cationically-initiated polymerizations, however, are difficult to measure because the lifetimes of carbocations are very short [3]. Gross reaction rate constants may be obtained by dilatometry, but detection of the actual propagating species is necessary to assign specific propagation rate constants for free ions and solvated or contact ion pairs. Thus, measurement of reaction rate is not a reliable method of determining the identity of the active ion pair for the polymer in this study.

Tacticity, Ion Pairs, and Mechanism

Kunitake and Aso [4] studied the tacticities of polymers of α -methylstyrene prepared in solvent mixtures of varying dielectric constant. They proposed the model of propagation shown in Figure 1. Assuming the preferred conformation at the carbocationic center as shown in the figure, increased solvation of the ion pair would favor "front-side" attack of the incoming monomer and lead to a syndiotactic addition. Conversely, "back-side" attack and isotactic addition would occur with contact ion-pairs. Thus, it follows that polymerization in high polarity solvents should yield polymers with high syndiotactic content.

To test the applicability of this model to the polymerization of p-substituted- α -methylstyrenes, p-chloro and p-fluoro- α -methylstyrene were polymerized in mixtures of methylene chloride and n-hexane with SnCl_4 or TiCl_4 as initiators in a recent study [5]. The results were

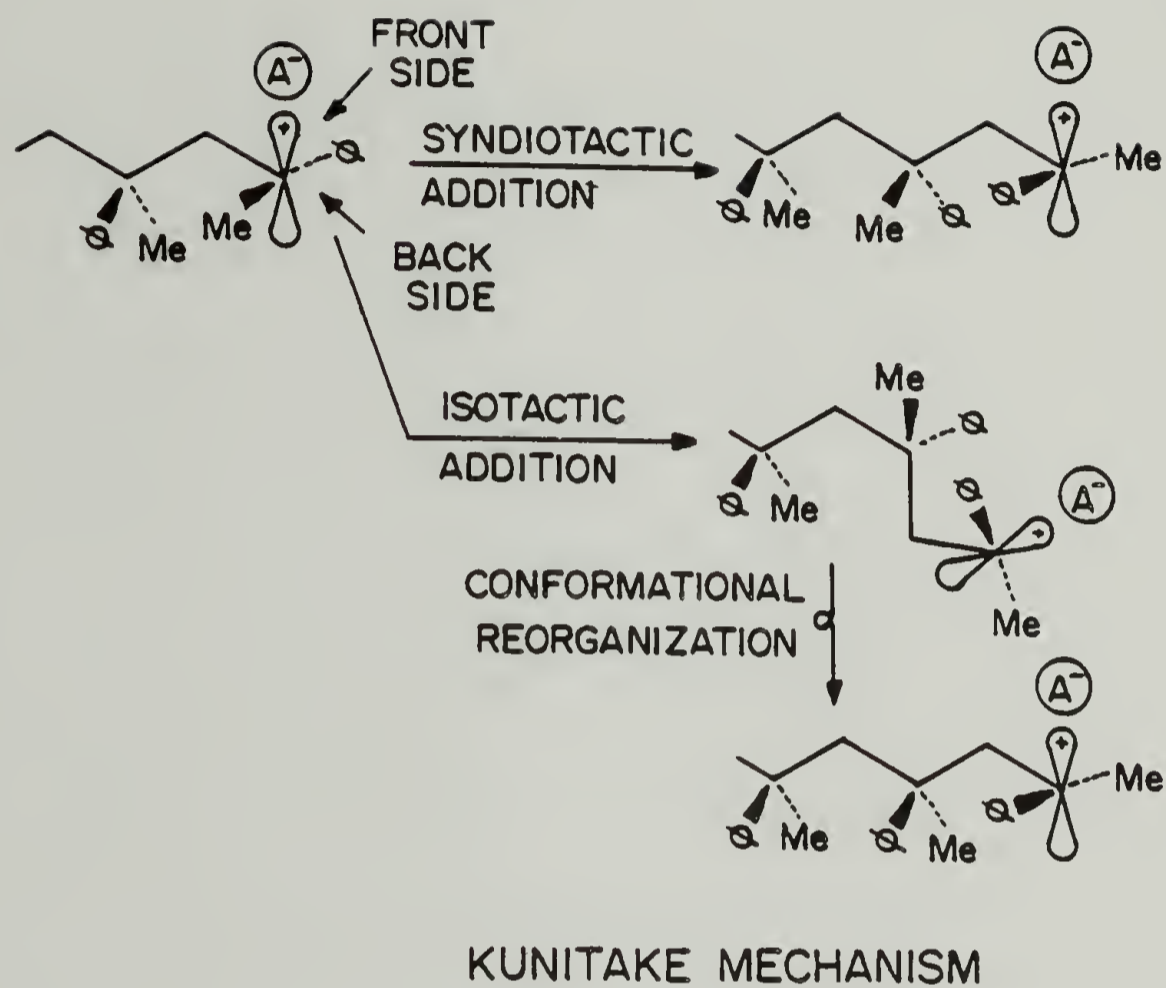


Figure 1. Mechanism for propagation according to [4].

surprising. The p-chloro polymer showed sharp tacticity changes over a narrow range of dielectric constants, as shown in Figure 2, while the tacticity of the p-fluoro polymer was insensitive to polarity changes. The disparity between the polymers was attributed to different electron donating and withdrawing powers of the p-chloro and p-fluoro substituents. The question of why the p-chloro showed such an abrupt change in the tacticity, however, remained unanswered. The high syndiotactic contents at high polarity and increased heterotactic and isotactic contents at low polarity agreed with the mechanism in Figure 1, but the tacticity change was not smooth as expected.

Similar behavior has been observed [6] in the polymerization of α -methylstyrene in several solvent mixtures of varying polarity. Large changes in tacticity occurred at low polarity when the reaction mixture became heterogeneous. Those workers claimed that the physical interaction of neighboring phenyl groups alone, which are important in heterogeneous media, influenced the attack of the incoming monomer and that under homogeneous conditions, solvation of the carbocation plays no role in determining tacticity. Thus, it is important to show that the phenomena in the previous study [5] were obtained under heterogeneous conditions and to observe the tacticities of polymers obtained in homogeneous media in solvent mixtures with a range of dielectric constants similar to those of methylene chloride and n-hexane. Both the p-chloro and p-fluoro polymers are soluble in 100% toluene at -78°C in concentrations similar to those used for

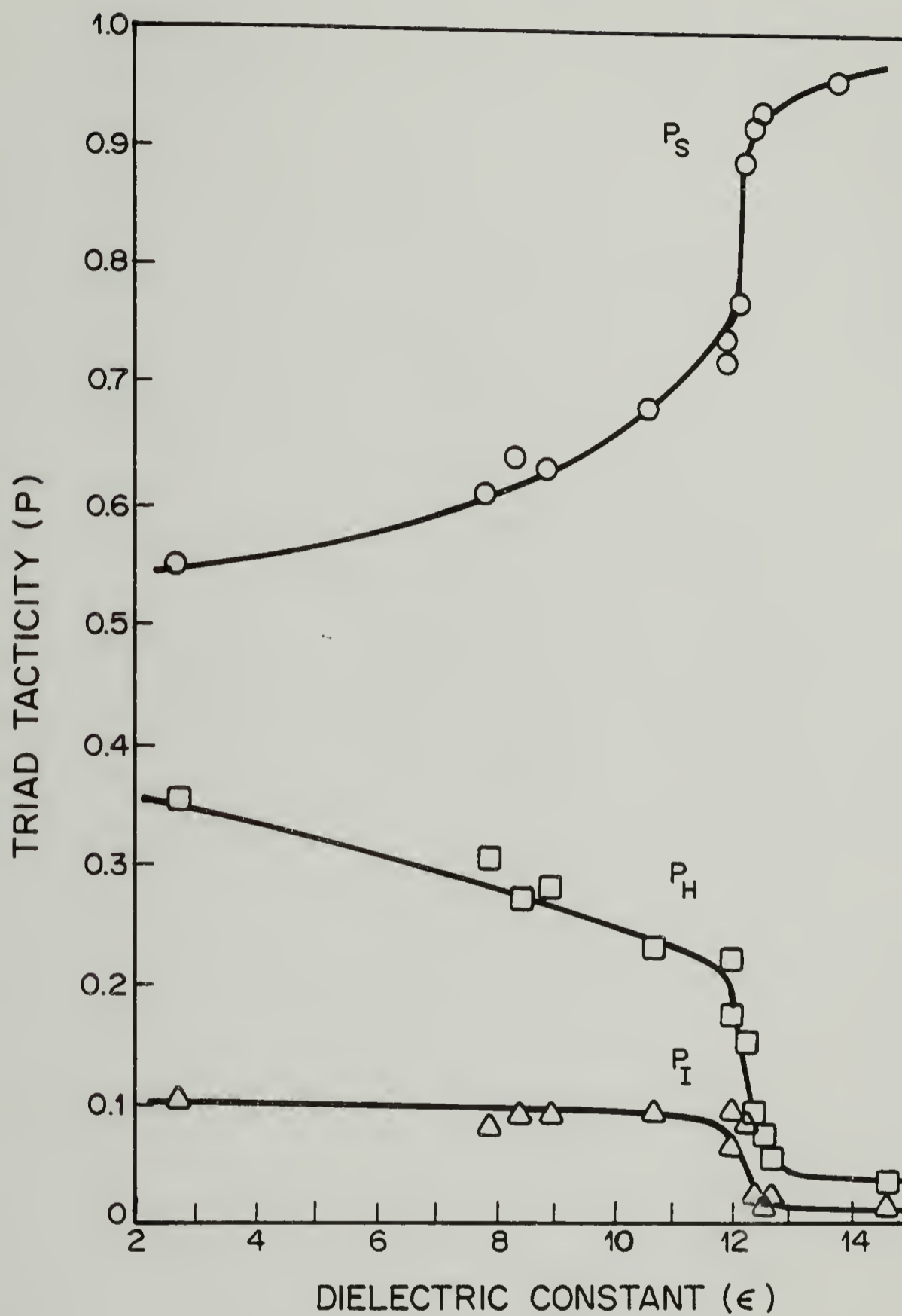


Figure 2. Effect of solvent polarity on the tacticities of poly(p-chloro- α -methylstyrene) prepared in methylene chloride/n-hexane mixtures.

polymerization. Toluene has a dielectric constant of 2.6 at -78°C , which is comparable to the dielectric constant of 2 for hexane at -78°C . The equations used to calculate the dielectric constants of the solvent mixtures are [7]:

$$\text{Methylene Chloride} \quad \epsilon = \frac{3320}{T} - 2.24 \quad (1a)$$

$$\text{n-Hexane} \quad \epsilon = 2.35 - \frac{T}{625} \quad (1b)$$

$$\text{Toluene} \quad \epsilon = 2.438 \text{ invlog}(-0.455 \times 10^{-2}T) \quad (1c)$$

Where T = temperature, K

Tacticity Determination by Nuclear Magnetic Resonance Spectroscopy

The tacticities of polymers of α,α -disubstituted olefins, especially α -methylstyrene, have been extensively studied by nuclear magnetic resonance (NMR). High resolution spectrometers with high temperature capability furnish well-resolved triad data for the α -methyl proton resonance of poly(α -methylstyrene) and related polymers. The controversy arising over the assignment of triads has been decided in favor of Brownstein, et al [8]. The peak assignment in this work follows the convention of assigning isotactic, heterotactic, and syndiotactic triads in order of increasing field strength.

Proton NMR furnishes well-resolved spectra for both the p-chloro and p-fluoro polymers as shown in Figures 3 and 4, respectively.

Rate of Initiation

For a living polymer, the degree of polymerization equals the ratio of the monomer concentration to the initiator concentration. In such cases, initiation of all chains occurs simultaneously, unintentional termination is absent, and the molecular weight distribution of the resultant polymer is monomodal [9]. Several cationic polymerizations have yielded polymers with molecular weight distributions less than the most probable distribution of 2.0 ($1 \leq \bar{M}_w / \bar{M}_n \leq 2.0$) [10]. In a series of papers by Pepper, et al [11-13], near monomodality was attributed to extremely fast initiation relative to propagation for the polymerization of styrene with sulfuric acid as initiator. It has been stated, however, that fast initiation with slow propagation is an unlikely scenario for most cationic polymerizations [10].

To test the possibility of extremely fast initiation in the present systems, monomer and initiator can be mixed together in equimolar amounts under the conditions of polymerization. If initiation is indeed very fast compared to propagation, only very short oligomers should be formed.

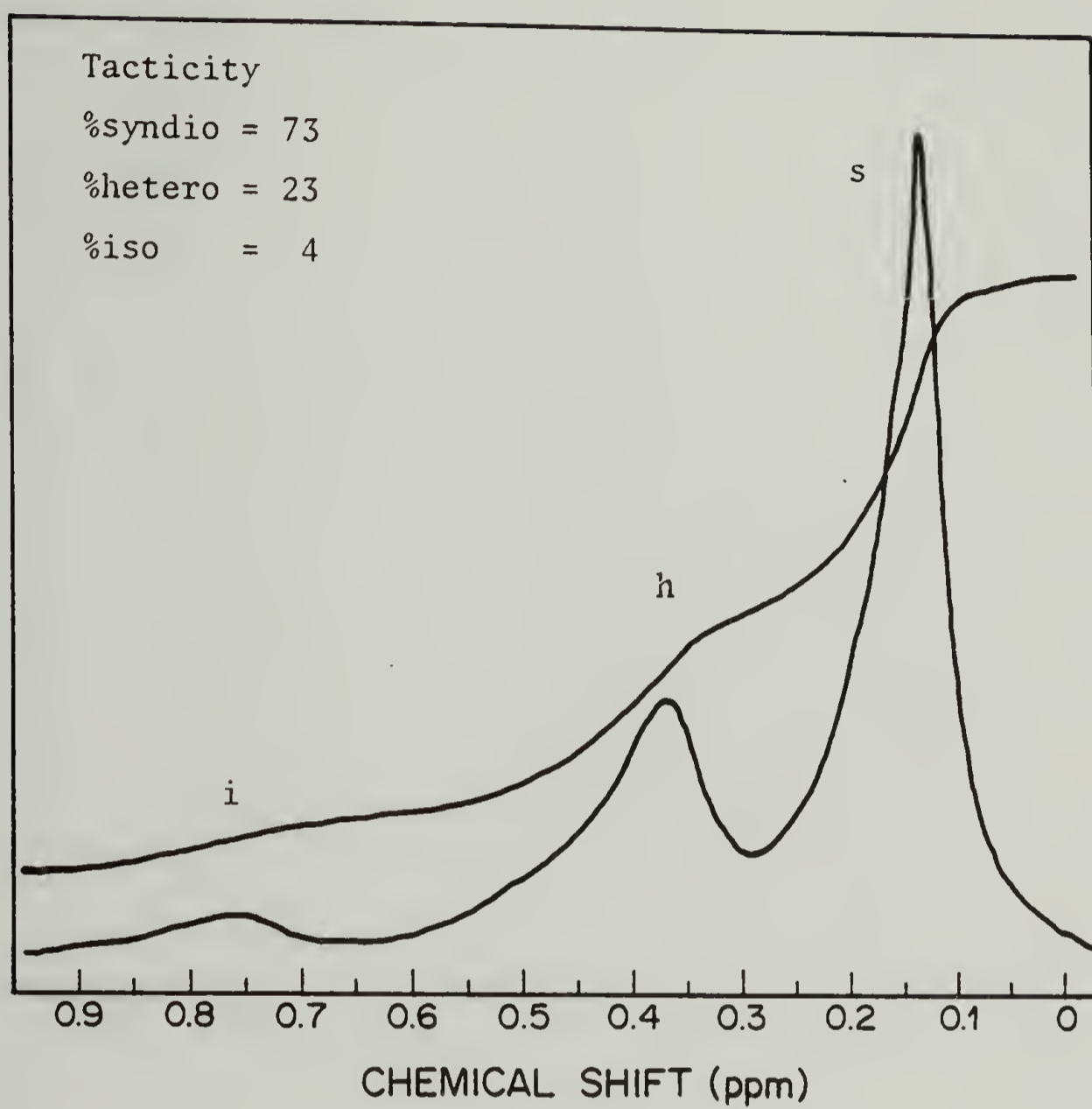


Figure 3. Proton NMR of poly(p-chloro- α -methylstyrene).

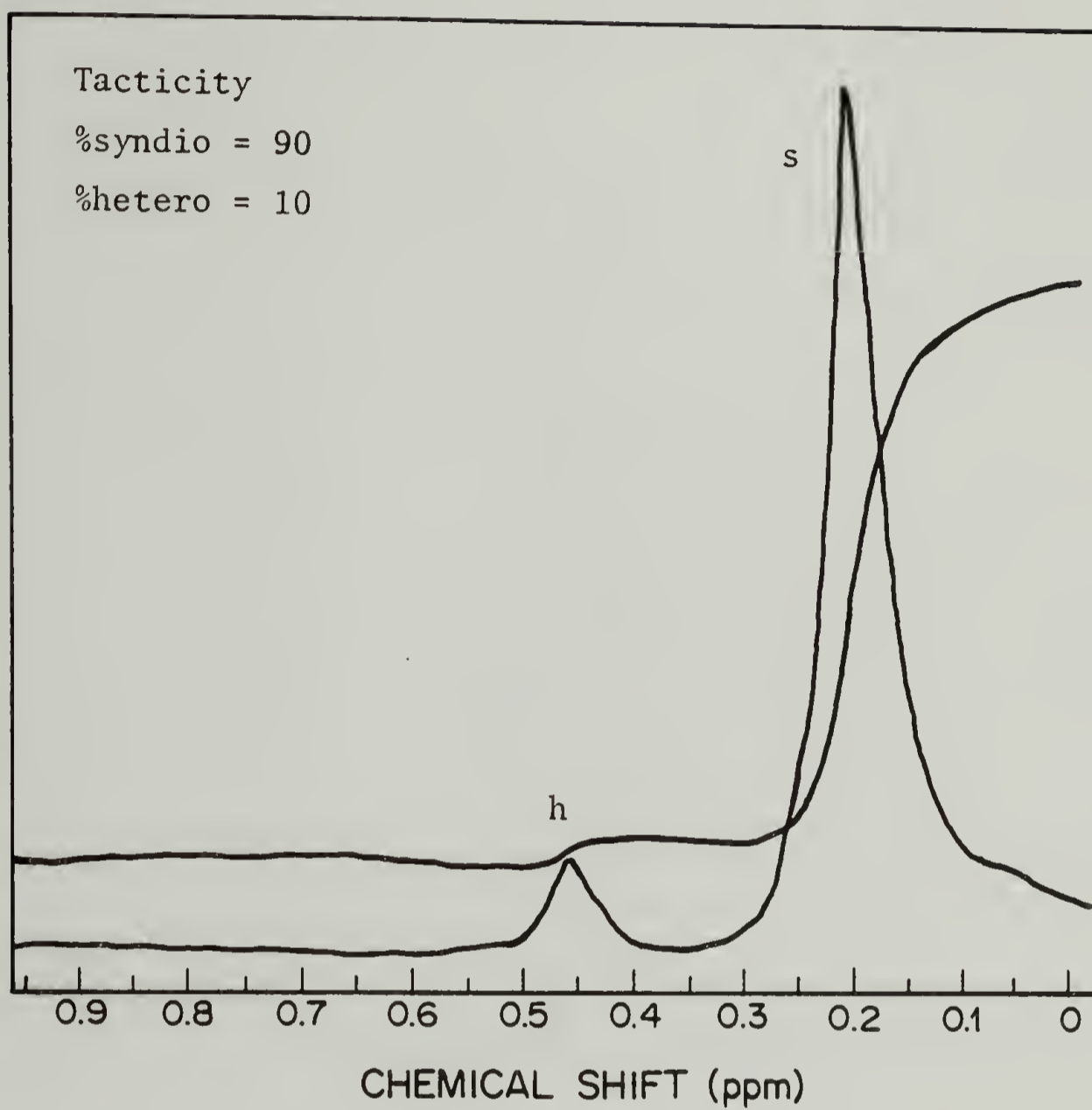


Figure 4. Proton NMR of poly(p-fluoro- α -methylstyrene).

Experimental

Purification of Solvents

All of the solvents, high purity grade, were fractionally distilled, and the middle fraction was dried as described below. All solvents were freshly distilled from dessicant before use.

Methylene chloride. Solvent was refluxed for 24 hours over CaH_2 under an atmosphere of dry argon, followed by distillation onto 3A molecular sieves (activated in vacuo at 300°C for 24 hours). Purity and water content were determined by GC (Chromosorb 101 column) just prior to use.

n-Hexane. Solvent was refluxed for 24 hours over CaH_2 under an atmosphere of dry argon, followed by distillation onto activated 3A molecular sieves. Purity and water content were determined by GC.

Toluene. Solvent was refluxed for 24 hours over CaH_2 and distilled under argon onto sodium metal. Benzophenone was added to the distillate. The toluene was then refluxed over the resulting sodium-benzophenone ketal. Purity and water content were determined prior to use by GC (15% FFAP column).

Purification of p-Chloro- α -methylstyrene

The monomer as obtained from Aldrich, 97%, was purified by preparative HPLC on a Waters 500LC with silical gel cartridge, toluene

solvent. The monomer was then distilled from CaH_2 , distilled twice more, then freshly distilled before use (b.p. = 43°C , 1 mm Hg).

Synthesis and Purification of p-Fluoro- α -Methylstyrene

The monomer was synthesized by the method of Seymour [14]. Distillation was the same as that used for the p-chloro monomer.

The purities of both monomers were 99.9% as determined by GC (Chromosorb 102 column) and LC (μ -porasil column).

Purification of Initiator

Anhydrous tin tetrachloride was distilled under dry argon prior to use. 0.5 ml of SnCl_4 was transferred by purged, gas tight syringe with stainless steel needle to a 100 ml volumetric flask, which was previously fitted with a stopcock, heated under vacuum, and filled with argon. Methylene chloride, dried as described above, was then distilled into the volumetric flask. The solution was 0.043 M in SnCl_4 .

Polymer Precipitation Studies

10 mg of polymer were dissolved in 25 ml of CH_2Cl_2 at the desired temperature. Hexane was added by buret until a cloud point was reached as determined by comparison with a blank, isothermal polymer solution.

Polymerization Reactions

All polymerizations were carried out under dry argon in 100 ml round bottom flasks, which had been heated under vacuum. The flasks were equipped with a stir bar and an 11 mm Wheaton neck capped with a PTFE-backed silicon rubber septum. The flasks were filled with monomer and solvent and cooled to -78°C . Polymerization was initiated with SnCl_4 solution delivered by a purged, gas tight syringe through the septum. The reactions were quenched with 5 ml of cold methanol. The polymers were precipitated by dripping into methanol, redissolved in CH_2Cl_2 , filtered, and reprecipitated. The polymers were dried to constant weight in vacuo at 50°C .

The homogeneous and heterogeneous reactions were 0.40 M in monomer and 8.0×10^{-4} M in initiator. The equimolar reactions were 0.44 M in both monomer and initiator.

Polymer Characterization

Gel permeation chromatography. Weight and number average molecular weight moments were determined in THF solution at 25°C on a Waters 201 GPC with styragel columns. The reported molecular weights are relative to polystyrene standards.

Nuclear magnetic resonance spectroscopy. Triad tacticities were determined on a Varian XL-300 NMR (300 MHz) in 10% (W/V) toluene- d_8 solution at 80°C with p-dioxane as internal standard. The relative areas of the integrations of the α -methyl proton resonances were used.

Results and Discussion

Precipitation Studies

The data collected in Table 1 show the results of the addition of n-hexane to methylene chloride solutions of both the p-chloro and p-fluoro polymers. Molecular weights of both polymers were comparable. In all cases, precipitation of the polymer was caused by the addition of n-hexane. At -78°C , precipitation occurred at 26 weight percent added n-hexane for the p-chloro polymer and at 33 weight percent for the p-fluoro polymer. These levels of added n-hexane are comparable to those at which abrupt changes in polymer properties occurred in the previous study [5]. Thus, it is most likely that the carbocationic active center is in a highly nonpolar swollen polymer environment for levels of n-hexane greater than 26 and 33 weight percent for the p-chloro and p-fluoro polymers, respectively.

Heterogeneous Reactions

p-Chloro- α -methylstyrene. Reactions 28 and 29 in Table 2 were carried out in a mixture of 73 weight percent methylene chloride and 27 weight percent n-hexane ($\epsilon = 11.2$) and in pure methylene chloride, respectively. Reaction 29 remained homogeneous over the reaction time of five minutes. As expected Reaction 28 became heterogeneous immediately after initiation, and the amount of precipitated polymer increased over the course of the reaction. The yield of the polymer

TABLE 1

Effect of n-hexane on solutions of polymers in methylene chloride

POLYMER	T°C	WT. % HEXANE AT CLOUD POINT	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
<u>p</u> -Chloro	24	29	624,000	516,000	1.12
	4	28	"	"	"
	-78	26	"	"	"
<u>p</u> -Fluoro	24	36	790,000	470,000	1.70
	4	35	"	"	"
	-78	33	"	"	"

TABLE 2

Visual observation of polymerization media

POLYMER	REACTION NUMBER	%CH ₂ Cl ₂ ^a	%HEXANE	YIELD %	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
p-Chloro	29	100	0	93	715,000	619,000	1.16
	28	73	27	13	334,000	282,000	1.18 ^b
p-Fluoro	65	100	0	96	550,000	310,000	1.78
	45	73	27	14	882,000	556,000	1.60 ^b

a. Weight percent

b. Non-homogeneous

obtained in Reaction 28 is only 13 weight percent. There are three possible explanations for decreased yield relative to Reaction 29.

1. Termination of the kinetic chain occurs upon precipitation or swelling.
2. Propagation proceeds through a contact ion pair.
3. Propagation becomes diffusion controlled.

The first explanation can be ruled out on the basis of the data collected in Table 3. The conversion of the polymerization with time was studied at -78°C at a value of $\epsilon = 11.3$. If termination of the kinetic chain occurs, then conversion should remain constant with time. Clearly this is not the case as seen in Table 3.

The molecular weights of the polymers also increase with time thereby further weakening the argument of kinetic chain termination. The polymer of Reaction 31 has a lower peak molecular weight than that of Reaction 32, but this is understandable since all reactions were batch polymerizations. It should be noted that growth proceeded through two species as shown in Figure 5. With time, the lower molecular weight peak became absorbed into the larger peak.

Bimodal molecular weight distributions are indicative of the presence of two propagating species. At the value of $\epsilon = 11.3$, it is

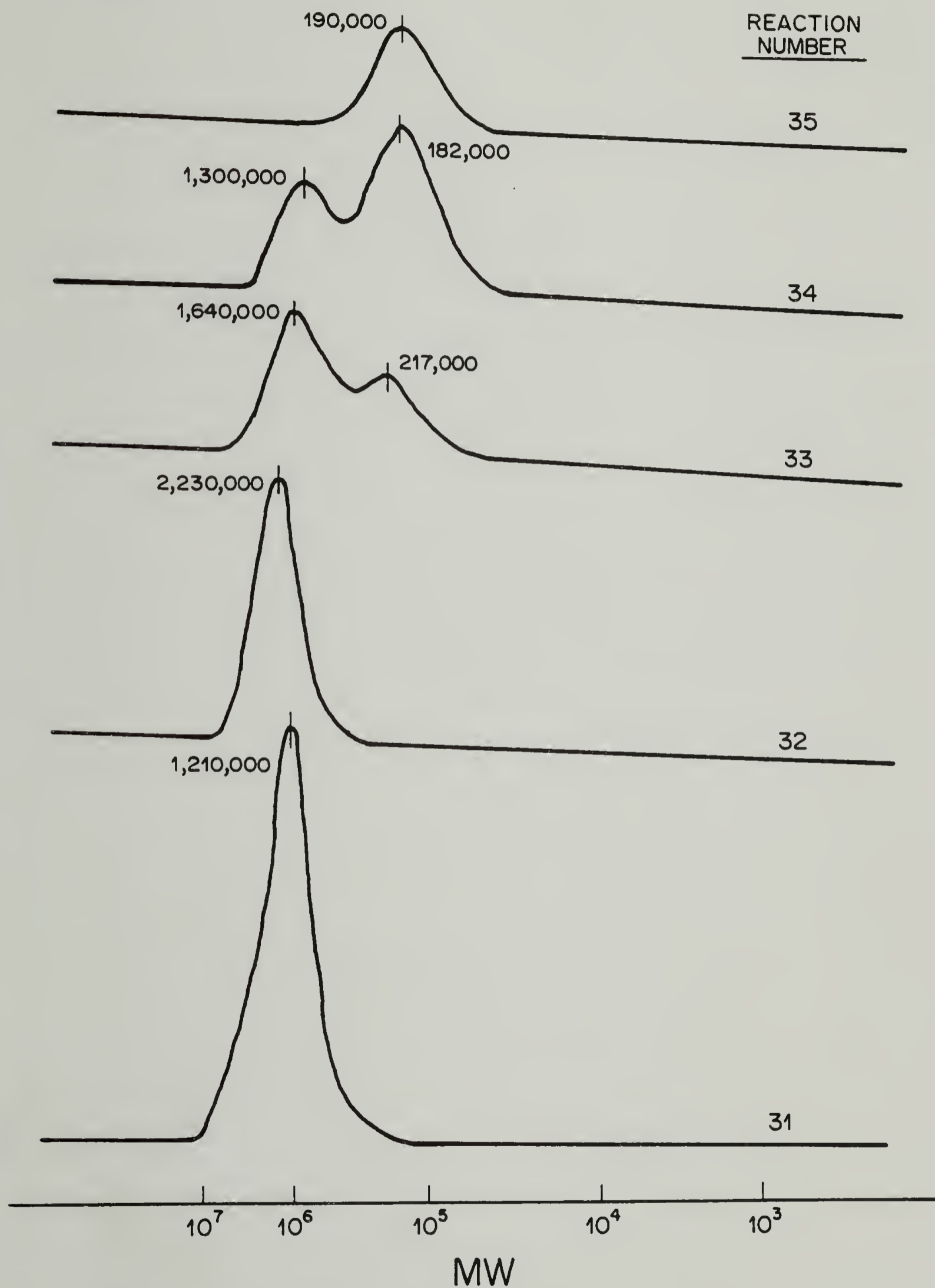
TABLE 3

Polymerization of p-chloro- α -methylene initiated by SnCl_4 at $\epsilon = 11.3$

REACTION NUMBER	TIME (MIN)	YIELD %	TRIAD TACTICITY				PEAK(S)		
			P_S	P_H	P_I	σ			
35	1	0.1	-	-	-	-	-	190,000	1.24
34	5	4.0	.81	.14	.05	.120	1,300,000	182,000	2.84
33	10	9.0	.82	.14	.04	.110	1,640,000	217,000	2.69
32	20	33.0	.91	.08	.01	.050	2,230,000	-	1.42
31	45	41.0	.81	.13	.06	.135	1,210,000	-	1.63

Figure 5. GPC for poly(p-chloro- α -methylstyrene) prepared in methylene chloride/n-hexane at $\epsilon = 11.3$.

GPC



possible that the two species, solvated ion pairs and contact ion pairs, coexist. Triad tacticities did not vary significantly with conversion. It must be noted that the triad tacticities reported in Table 3 are for the entire distribution of each polymer and were similar to the results obtained at comparable values of ϵ for the data shown in Figure 2. By using preparative GPC, Jonte [5] separated the high and low molecular weight fractions of bimodal polymers of p-fluoro- and p-bromo- α -methylstyrene. For both polymers, the low molecular weight fractions were heterogeneous and the high molecular weight fractions were highly syndiotactic.

p-Fluoro- α -methylstyrene. In Table 2, Reaction 45 shows that the p-fluoro polymer also precipitates from solution with n-hexane in the polymerization solvent mixture, and the amount of precipitate increased with time. The yield was also low at 14 weight percent.

Polymerizations carried out at -78°C at $\epsilon = 11.3$ in a mixture of methylene chloride and n-hexane are presented in Table 4. Molecular weights increased with time and all distributions were monomodal. The triad tacticities were highly syndiotactic and remained constant with time.

Homogeneous Reactions for p-Chloro- α -methylstyrene).

Tacticity. Table 5 contains results for the polymerization of p-chloro- α -methylstyrene, initiated by SnCl_4 , in mixtures of methylene chloride and toluene. All reactions were homogeneous. As is seen,

TABLE 4

Polymerization of p-fluoro- α -methylstyrene by SnCl_4 at $\epsilon = 11.3$

REACTION NUMBER	TIME (MIN)	YIELD %	TRIAD TACTICITY				\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
			P_S	P_H	P_I	σ			
45	5	14	.94	.06	0	.03	882,000	556,000	1.6
46	10	23	.90	.10	0	.05	970,000	613,000	1.6
47	20	63	.92	.08	0	.04	1,220,000	650,000	1.9
48	30	94	.90	.10	0	.05	1,550,000	910,000	1.7

TABLE 5

Effect of solvent composition on the cationic polymerization of p-chloro- α -methylstyrene, in methylene chloride/toluene mixtures, initiated by SnCl_4

REACTION NUMBER	SOLVENT COMP. (WT. %)		ϵ^a	YIELD %	TRIAD TACTICITY			σ^b
	CH_2Cl_2	TOLUENE			P_S	P_H	P_I	
56	100	0	14.8	88	.91	.09	0	.04
57	98	2	14.6	57	.89	.11	0	.06
58	83	17	12.7	37	.87	.13	0	.06
59	60	40	9.9	6	.85	.15	0	.08
63	13	87	4.2	- ^c	.79	.18	.03	.12
64	5	95	3.2	- ^c	.73	.23	.04	.16

a. Calculated dielectric constant of solvent mixture

b. Calculated from triads: $\sigma = P_I + 1/2P_H$

c. Obtained after one hour reaction time.

the polymer obtained in 100% methylene chloride is highly syndiotactic. As the amount of toluene in the solvent mixture increased, the syndiotactic triad content decreased and the heterotactic content increased. Very small amounts of isotactic triads were formed. These fairly smooth changes in tacticities are shown in Figure 6 and contrast sharply with the results shown in Figure 2. Such smooth variations in tacticity do agree with the mechanism of Kunitake and Aso shown in Figure 1.

Steric hindrance between adjacent phenyl groups in the polymer is severe. Thus, it is not surprising that isotactic triads are difficult to form and amounts greater than 5 percent were observed only for polymers obtained in highly swollen, non-polar environments. From Table 5, Reaction 59, prepared at a value of $\epsilon = 9.9$, gave a polymer with 85 percent syndiotactic, 15 percent heterotactic, and 0 percent isotactic triads. Conversely, the reactions in Table 3, prepared at a value of $\epsilon = 11.3$, gave polymers with lower syndiotactic and higher heterotactic and isotactic triads than Reaction 59. Theoretically the higher ϵ value used for Reactions 35 through 31 should have produced polymers with higher syndiotacticity than that of Reaction 59. It follows that the carbocationic center is experiencing an environment which is more polar than expected from the levels of solvents used.

The difficulty of forming isotactic sequences in these polymers can be illustrated by calculating the average sequence lengths of the

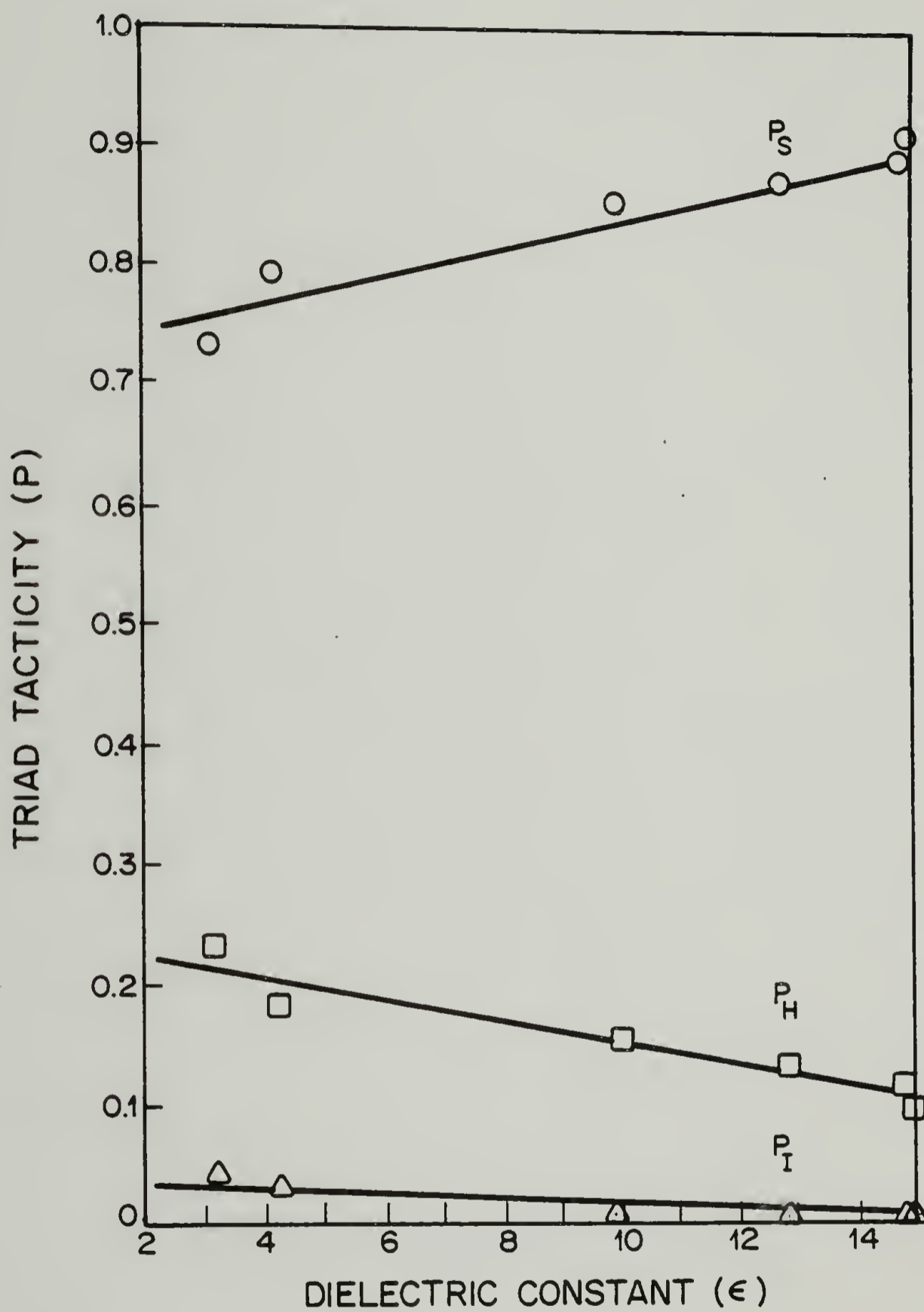


Figure 6. Effect of solvent polarity on the tacticities of poly(p-chloro- α -methylstyrene) prepared in methylene chloride/toluene mixtures.

isotactic and syndiotactic units from triad tacticity data according to Equations 2a and 2b [15].

$$\mu_{(I)} = \frac{p_{(I)}}{p_{(S)} + P_S} \quad (2a)$$

$$\mu_{(S)} = \frac{p_{(S)}}{p_{(I)} + P_I} \quad (2b)$$

Table 6 contains the results for the polymers reported in Table 5. It is seen that syndiotactic sequences are fairly long and decrease with decreasing solvent polarity and that isotactic sequences are less than two over the range of solvent polarities studied.

Molecular weight and yield. The molecular weights and yields of the polymers obtained from the reactions in Table 5 decreased with decreasing values of the dielectric constant of the solvent mixture as indicated in Table 7 and Figure 7. All molecular weight distributions were monomodal in contrast to those of the p-chloro polymers obtained in methylene chloride/n-hexane mixtures in Table 3. The lower yields are expected for a change in mechanism from fast propagation by free carbocations to relatively slow propagation by contact ion pairs.

TABLE 6

Tacticity sequence lengths in polymers obtained from the cationic polymerization of *p*-chloro- α -methylstyrene in methylene chloride/toluene mixtures

REACTION NUMBER	POLYMER TACTICITIES				CALCULATED SEQUENCE LENGTHS		
	SYNDIOTACTIC ^a		ISOTACTIC ^a		ISOTACTIC	SYNDIOTACTIC	ϵ^c
	$P(S)$	P_S^b	$P(I)$	P_I^b	$\mu(I)$	$\mu(S)$	
56	.96	.91	.04	0	0.8	24	14.8
57	.94	.89	.06	0	1.2	16	14.6
58	.94	.87	.06	0	0.8	16	12.7
59	.92	.85	.08	0	1.1	12	9.9
63	.88	.79	.12	.03	1.3	10	4.2
64	.84	.73	.16	.04	1.4	7	3.2

a. Dyads

b. Triads

c. Calculated dielectric constant of solvent mixture

TABLE 7

Molecular weights of poly(p-chloro- α -methylstyrene)
prepared in methylene chloride/toluene mixtures

REACTION NUMBER	ϵ	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
56	14.8	2,200,000	1,260,000	1.75
57	14.6	1,820,000	1,040,000	1.75
58	12.7	1,700,000	992,000	1.71
59	9.9	692,000	349,000	1.99
63 ^a	4.2	245,000	90,400	2.71
64 ^a	3.2	255,000	101,000	2.52

a. Obtained after one hour reaction time.

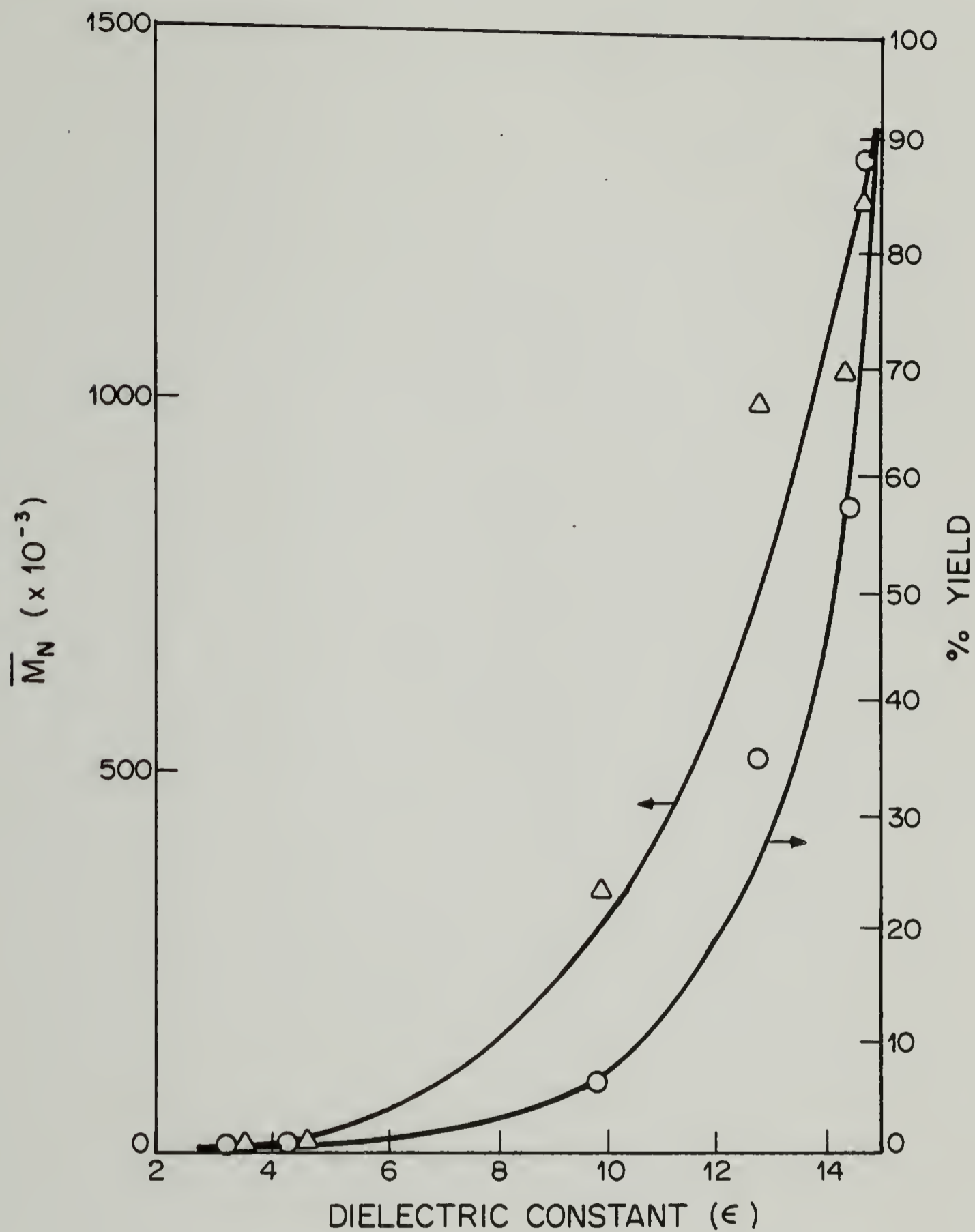


Figure 7. Effect of solvent polarity on the number average molecular weights and yields of poly(p-chloro- α -methylstyrene) prepared in methylene chloride/toluene mixtures.

It is also possible that chain transfer to toluene occurs. Chain transfer to solvent would account for the increase in \bar{M}_w/\bar{M}_n and for the decrease in the yields of polymers rather than a change in mechanism to propagation by contact ion pairs and subsequently lower propagation rates. Chain transfer to toluene is known for the polymerization of styrene. However, one would expect no increase in the molecular weights of high polymer present over time. Reactions 63 and 64 were obtained after one hour reaction time. Identical reactions carried out for five minutes produced no methanol insoluble fractions. Another possible cause for the increase in \bar{M}_w/\bar{M}_n as toluene is added to the solvent mixture is the increased incidence of chain transfer to monomer as the propagation rate decreases. The contact ion pairs present in systems with low polarity would propagate more slowly than free ions.

Studies by Higashimura [6] and those in Table 3 show no changes in triad tacticity levels with conversion at a constant value of dielectric constant of the polymerization solvent. Therefore, the tacticities obtained for the polymers of Reactions 63 and 64 may be directly compared with those of Reactions 56 through 59 for solvent effects.

Homogeneous Reactions for p-Fluoro- α -methylstyrene

Tacticity. Table 8 contains results for the polymerization of p-fluoro- α -methylstyrene, initiated by SnCl_4 , in mixtures of methylene

TABLE 8

Effect of solvent composition on the cationic polymerization of p-fluoro- α -methylstyrene, in methylene chloride/toluene mixtures, initiated by SnCl_4

REACTION NUMBER	SOLVENT COMP. (WT. %)		ϵ^a	YIELD %	TRIAD TACTICITY			σ^b
	CH_2Cl_2	TOLUENE			P_S	P_H	P_I	
65	100	0	14.8	96	.88	.12	0	.06
66	98	2	14.6	14	.90	.10	0	.05
67	83	17	12.7	0.2	.90	.10	0	.05
71	13	87	4.2	- ^c	.93	.07	0	.04
73	5	95	3.2	- ^c	.87	.13	0	.08

a. Calculated dielectric constant of solvent mixture

b. Calculated from triads: $\sigma = P_I + 1/2P_H$

c. Obtained after one hour reaction time

chloride and toluene. All reactions were homogeneous. Reactions 71 and 73 were obtained after a reaction time of one hour. The tacticities of the polymers obtained from Reactions 71 and 73 are directly compared with those of Reactions 65 through 67 for solvent effects based on the reasons given in the previous section. As with the case of the p-fluoro polymer obtained in methylene chloride/n-hexane mixtures, the tacticities remained insensitive to changes in the dielectric constant of the polymerization solvent. All polymers were highly syndiotactic.

The difference in reaction solvent effect on the tacticities of the p-fluoro and p-chloro polymers may be a result of the difference in the electron contributing or withdrawing properties of the substituents on the active growing center. The p-fluoro substituent, with a σ^+ value of -0.07 [16], can act as an electron donor. The resulting resonance interaction on the developing carbocationic center would decrease the positive charge at that center and favor free ion formation. Conversely, the p-chloro substituent has a σ^+ value of +0.11 and acts as an electron withdrawer. Thus, the positive charge is increased at the carbocationic center and the formation of solvated or contact ion pairs is favored. Highly polar solvents would permit the existence of free or solvated carbocations for both monomers, while decreasing the solvent polarity would affect the p-chloro polymer to a greater extent.

It is also instructive to look at the stereotactic sequence lengths for the p-fluoro polymers. As shown in Table 9, the isotactic lengths remain less than two. In contrast to the p-chloro polymer, the syndiotactic sequence lengths remain constant.

Molecular weight and yield. As seen in Table 10 and Figure 8, the molecular weights and yields decrease with decreasing values of dielectric constant of the solvent analogous to the results for the p-chloro monomer. All molecular weight distributions were monomodal in contrast to the bimodal distributions prepared previously [5] in methylene chloride/n-hexane mixtures. The ratio of \bar{M}_w/\bar{M}_n increased as the amount of toluene in the solvent mixture increased. Again, chain transfer to toluene may be present as discussed for the p-chloro polymer in the previous section.

Equimolar Reactions

The results for the reactions of equimolar amounts of p-chloro- α -methylstyrene and tin tetrachloride in toluene at -78°C are presented in Table 11. The monomer concentrations were similar to those used for the polymerization reactions of Table 5. In both Reactions 103 and 105, high molecular weight polymers were obtained, and the molecular weights and distributions were similar. Propagation is thus much faster than initiation for these systems.

It should be noted that the triad tacticities of the polymers were similar to those obtained from Reactions 63 and 64 in Table 5.

TABLE 9

Tacticity sequence lengths in polymers obtained from the cationic polymerization of p-fluoro- α -methylstyrene in methylene chloride/toluene mixtures

REACTION NUMBER	POLYMER TACTICITIES				CALCULATED SEQUENCE LENGTHS		
	SYNDIOTACTIC ^a $P(S)$	SYNDIOTACTIC ^b P_S	ISOTACTIC ^a $P(I)$	ISOTACTIC ^b P_I	ISOTACTIC $\mu(I)$	SYNDIOTACTIC $\mu(S)$	ϵ^c
65	.94	.88	.06	0	1.0	16	14.8
66	.95	.90	.05	0	1.0	19	14.6
67	.95	.90	.05	0	1.0	19	12.7
71	.96	.93	.04	0	1.3	24	4.2
73	.94	.87	.06	0	0.8	16	3.2

a. Dyads

b. Triads

c. Calculated dielectric constant of solvent mixture

TABLE 10

Molecular weights of poly(p-fluoro- α -methylstyrene)
prepared in methylene chloride/toluene mixtures

REACTION NUMBER	ϵ	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
65	14.8	550,000	310,000	1.78
66	14.6	377,000	202,000	1.85
67	12.7	85,100	38,500	2.21
71 ^a	4.2	119,000	49,000	2.43
73 ^a	3.2	63,600	40,700	1.56

a. Obtained after one hour reaction time

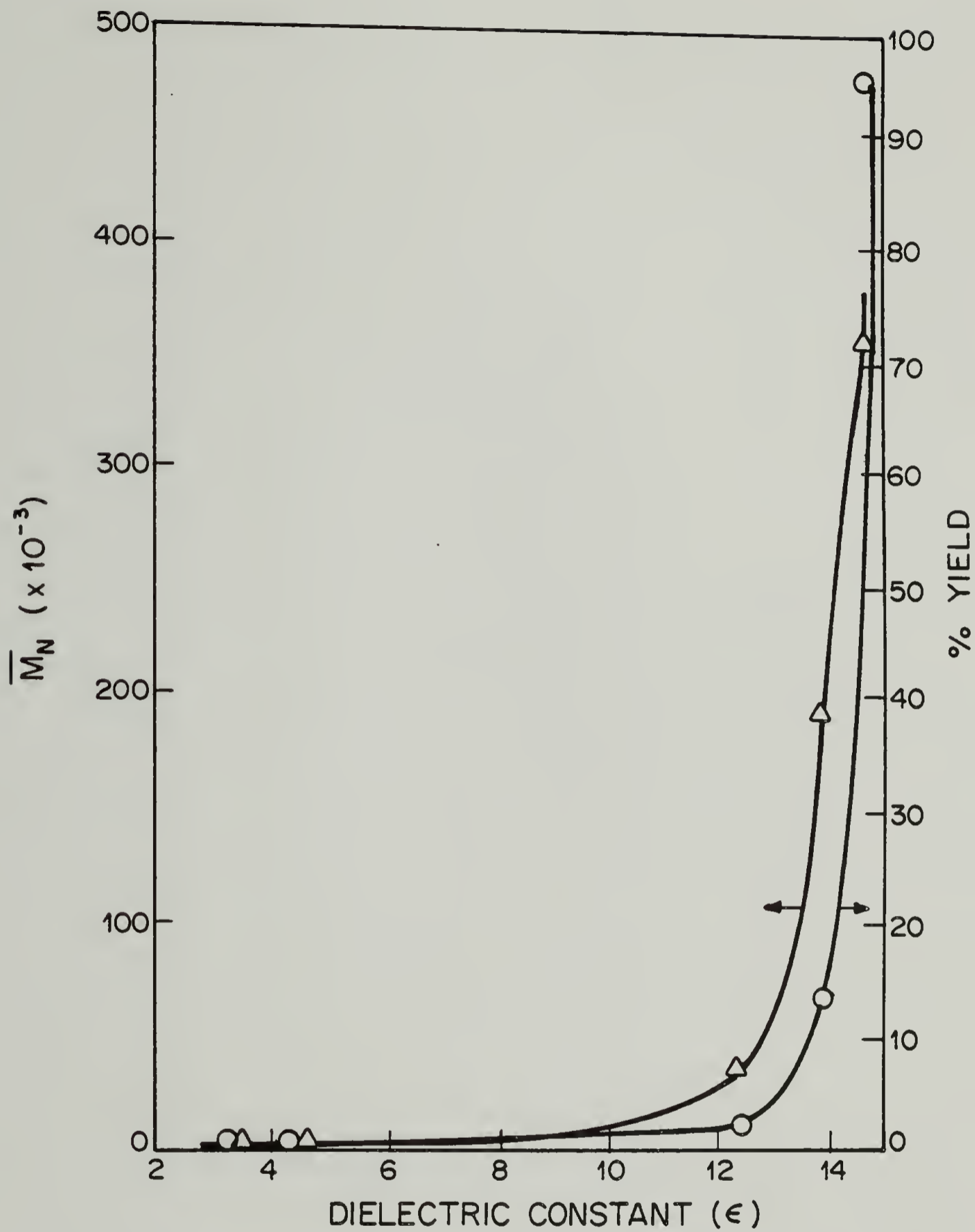


Figure 8. Effect of solvent polarity on the number average molecular weights and yields of poly(*p*-fluoro- α -methylstyrene) prepared in methylene chloride/toluene mixtures.

TABLE 11

Reactions of equimolar amounts of p-chloro- α -methylstyrene
and tin tetrachloride in toluene at -78°C

REACTION ^a NUMBER	YIELD %	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	TRIAD TACTICITY		
					P _S	P _H	P _I
103	74	1,950,000	1,280,000	1.52	.73	.21	.06
105	88	1,840,000	1,090,000	1.69	.70	.27	.03

a. 103 = initiator added to monomer; 105 = monomer added to
initiator

Conclusions

1. The abrupt changes present in the tacticities and molecular weights of the polymers prepared in mixtures of methylene chloride and n-hexane were due to precipitation of the polymer from solution during polymerization.
2. The polymers may be propagating in a highly non-polar, polymer environment when n-hexane is present in the polymerization solvent.
3. The tacticities of the polymers are constant with conversion at constant values of ϵ .
4. Smooth changes in tacticities occur for p-chloro polymers prepared in mixtures of methylene chloride and toluene where the polymer remains in solution during the reaction.
5. The tacticities of the p-fluoro polymers remain insensitive to changes in solvent polarity under homogeneous conditions.
6. Isotactic sequences of average length greater than two are not formed for either the p-chloro or the p-fluoro polymer.

7. The smooth tacticity changes obtained for the p-chloro polymer appear to agree with the mechanism proposed by Kunitake and Aso.

8. Propagation occurs much faster than initiation for the p-chloro polymer.

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CHAPTER III

PROPAGATION STATISTICS

Introduction

Bernoulli and Markov Chains

Bernoullian and Markovian statistical models are commonly used to describe types of propagating polymer chains. Propagation mechanisms can be rationalized based on the fit of tacticity data to a statistical model.

A review of the two statistical treatments is given in Figures 9 and 10 taken from the book by Bovey [1]. The difference between the two models is the effect of previous events on subsequent monomer additions. In Bernoullian propagation, addition of monomer to yield a meso or a racemic sequence occurs regardless of the tacticity generated by the previous monomer unit. A Markov addition is one in which previous monomer additions have an influence on subsequent events. In first-order Markov processes, the probability of addition of a monomer unit leading to a racemic or meso placement depends on the tacticity generated by placement of the penultimate monomer unit of the chain end. A dependence on the ante-penultimate unit is defined as second-order Markovian addition. The mathematics involved become complicated as higher orders are considered. In this study only first-order Markov and Bernoullian statistics are considered.

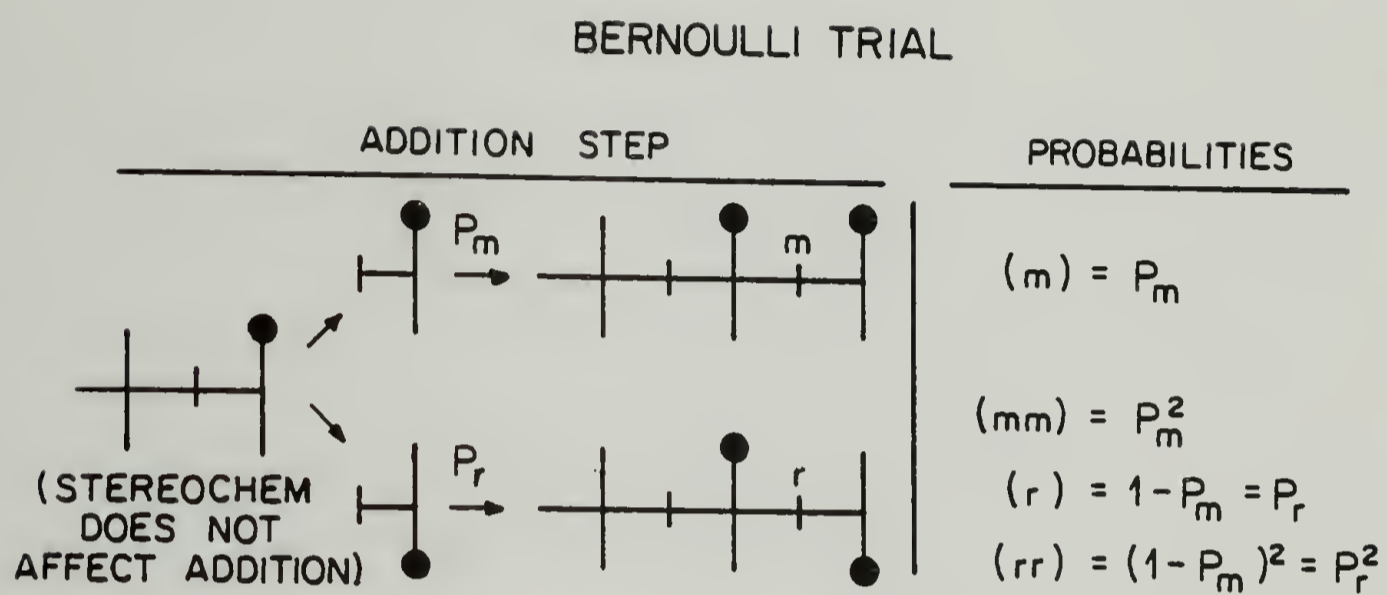


Figure 9. Bernoulli trial probabilities from [1].

FIRST ORDER MARKOV

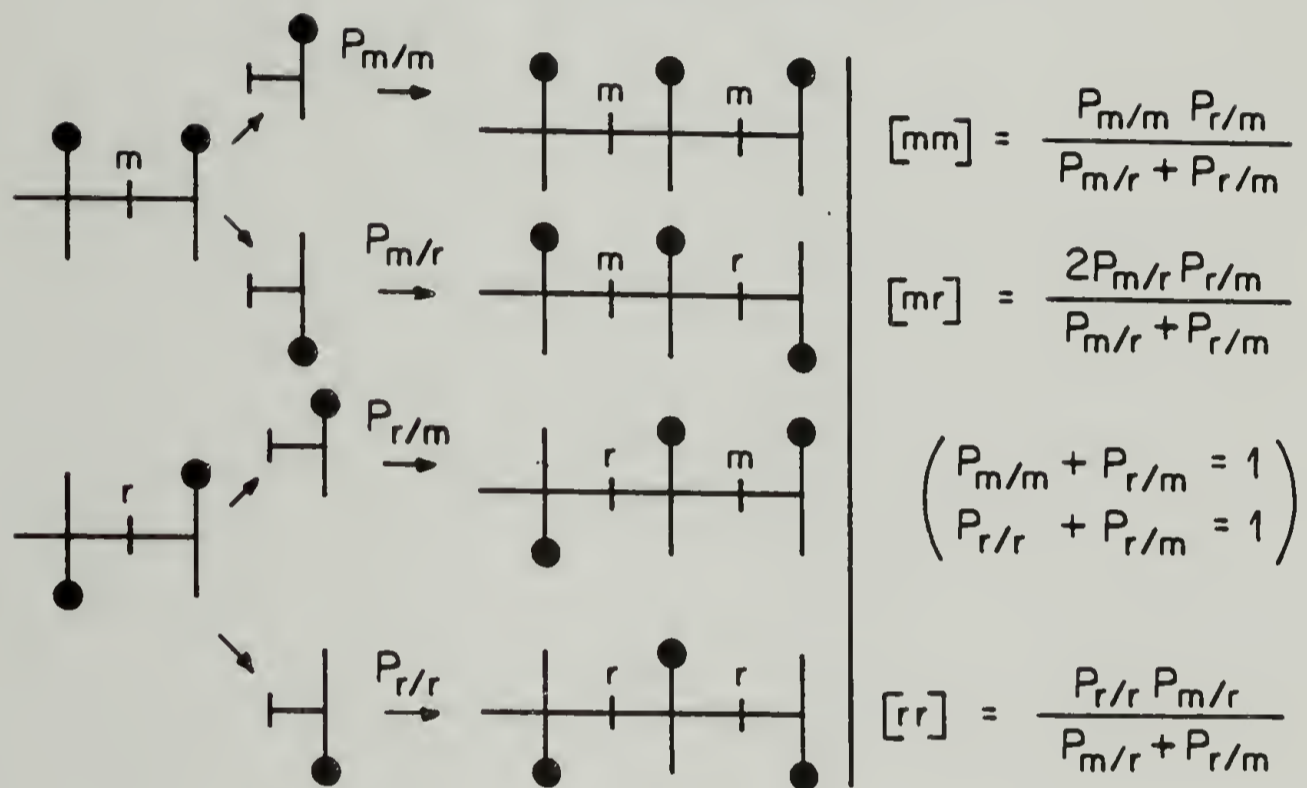


Figure 10. First-order Markov conditional probabilities from [1].

Statistics and Mechanism

The majority of polymers prepared by free radical mechanisms are Bernoullian in character and are highly heterotactic. For a mechanism to be described as Bernoullian, it must be evident that there are only two probabilities for the addition of a monomer unit. A Bernoullian fit can easily be tested using triad tacticity data and the equations of Figure 9.

First-order Markov statistics hold when it can be shown that the tacticity generated by addition of the penultimate monomer unit affects the geometry of the propagating center, thereby influencing addition of further monomer units. One well-known example of a first-order Markov chain is found in the cationic polymerization of alkyl vinyl ethers. The mechanism proposed by Cram and Kopecky [2] is based on a six-membered ring conformation attained by the carbocationic center due to interaction of the carbocation with the ether oxygen of the penultimate unit.

The testing of a first-order Markov fit requires tetrad or higher tacticity data. The tetrad data must correspond to that calculated by the equations of Figure 10. Sequence data higher than triads are difficult to obtain. ^{13}C -NMR has been used by Inoue [3] to assign pentad resonances for the p-carbon in the phenyl ring of poly(α -methylstyrene).

In the absence of tacticity sequence data higher than triads, several correlations may be used to predict the suitability of the

first-order Markov fit. The necessary parameters are defined by the following:

$$\Sigma_p = P_{m/r} + P_{r/m} \quad (3a)$$

$$\rho = \frac{2p_{(I)}p_{(S)}}{P_H} \quad (3b)$$

$$P_{m/r} = \frac{P_H}{2P_I + P_H} \quad (3c)$$

$$P_{r/m} = \frac{P_H}{2P_S + P_H} \quad (3d)$$

Σ_p is the sum of the conditional probabilities $P_{m/r}$ and $P_{r/m}$. For Bernoullian statistics, $\Sigma_p = 1$. The persistence length, ρ , defined by Coleman and Fox [4], is equal to $1/\Sigma_p$ for first-order Markov chains. $P_{m/r}$ is the probability of a chain containing a meso placement at the end adding monomer to obtain a racemic unit. Conversely, $P_{r/m}$ is the probability a meso unit being formed next to a racemic placement. Thus, triad data can be used to establish first-order Markov behavior.

Experimental

The polymers used in this study were either those synthesized by Jonte [5] or those described in Chapter II.

Proton NMR data were obtained as described in Chapter II.

Results and Discussion

Tables 12 and 13 show the calculated values of Σ_p and ρ for the p-chloro- and p-fluoro- α -methylstyrene polymers prepared by Jonte [5] in methylene chloride and n-hexane mixtures. The p-chloro polymer clearly shows non-Bernoullian character with $\Sigma_p \neq 1$ and first-order Markov behavior with $\Sigma_p = 1/\rho$. The p-fluoro polymer appears to fit both Bernoullian ($\Sigma_p = 1$) and first-order Markov ($\Sigma_p = 1/\rho$) statistics based on the triad NMR data available. However, comparison of the expected values of triad, tetrad, and higher sequences are identical for both Bernoullian and first-order Markov statistics when σ is small and the isotactic triad content is zero.

Tables 14 and 15 contain the calculated values of Σ_p and ρ for the polymers presented in Chapter II. Again the p-chloro polymer shows first-order Markov behavior, but only clearly below a value of ϵ of 9.9. Above $\epsilon = 9.9$, the p-chloro polymers could be described as either Bernoullian or first-order Markov according to the values of Σ_p and ρ . This dual behavior is also exhibited by the p-fluoro polymers. This is again a consequence of the small value of σ and the isotactic triad content of zero.

TABLE 12

Calculated values of first-order Markov correlation parameters for poly(p-chloro- α -methylstyrene) prepared in methylene chloride/n-hexane mixtures

REACTION ^a NUMBER	ϵ	TRIAD ^a TACTICITY			$P_{m/r}$	$P_{r/m}$	Σ_p	ρ	$1/\rho$	σ
		P_S	P_H	P_I						
30	14.8	.92	.07	.01	.78	.04	.82	1.23	.81	.045
54	14.5	.96	.03	.01	.60	.02	.62	1.62	.62	.025
55	12.5	.93	.05	.02	.56	.03	.59	1.72	.59	.045
64	12.2	.92	.07	.01	.78	.04	.82	1.23	.81	.045
56	12.2	.89	.09	.02	.69	.05	.74	1.35	.74	.065
65	12.1	.77	.15	.08	.48	.09	.57	1.75	.57	.155
53	11.9	.72	.22	.06	.65	.13	.78	1.28	.78	.170
58	11.9	.74	.17	.09	.48	.10	.58	1.70	.59	.175
66	10.6	.68	.23	.09	.56	.14	.70	1.42	.71	.205
59	8.9	.63	.28	.09	.61	.18	.79	1.26	.79	.230
52	8.4	.64	.27	.09	.60	.17	.77	1.29	.77	.225
67	7.9	.61	.31	.08	.66	.20	.86	1.16	.86	.235
57	2.8	.55	.35	.10	.64	.24	.88	1.14	.88	.275

a. Data from [5].

TABLE 13

Calculated values of first-order Markov correlation parameters
for poly(p-fluoro- α -methylstyrene) prepared in
methylene chloride/n-hexane mixtures

REACTION ^a NUMBER	ϵ	TRIAD ^a TACTICITY			$P_{m/r}$	$P_{r/m}$	Σ_p	ρ	$1/\rho$	σ
		P_S	P_H	P_I						
77	14.8	.92	.08	0	1.0	.04	1.04	.96	1.04	.040
78	14.7	.91	.09	0	1.0	.05	1.05	.96	1.04	.045
76	14.0	.90	.10	0	1.0	.05	1.05	.95	1.05	.050
79	13.2	.91	.10	0	1.0	.05	1.05	.96	1.04	.045
74	12.5	.90	.10	0	1.0	.05	1.05	.95	1.05	.050
75	12.2	.92	.08	0	1.0	.04	1.04	.96	1.04	.040
80	11.9	.92	.08	0	1.0	.04	1.04	.96	1.04	.040
81	10.6	.90	.10	0	1.0	.05	1.05	.95	1.05	.050
72	8.9	.90	.10	0	1.0	.05	1.05	.95	1.05	.050

a. Data from [5].

TABLE 14

Calculated values of first-order Markov correlation parameters for poly(p-chloro- α -methylstyrene) prepared in methylene chloride/toluene mixtures

REACTION NUMBER	ϵ	TRIAD TACTICITY			$P_{m/r}$	$P_{r/m}$	Σ_p	ρ	$1/\rho$	σ
		P_S	P_H	P_I						
56	14.8	.91	.09	0	1.0	.05	1.05	.96	1.05	.045
57	14.6	.89	.11	0	1.0	.06	1.06	.94	1.06	.055
58	12.7	.87	.13	0	1.0	.07	1.07	.94	1.06	.065
59	9.9	.85	.15	0	1.0	.08	1.08	.92	1.08	.075
63	4.2	.79	.18	.03	.75	.10	0.85	1.17	0.85	.120
63	3.2	.73	.23	.04	.74	.14	0.88	1.14	0.88	.155

TABLE 15

Calculated values of first-order Markov correlation parameters
for poly(p-fluoro- α -methylstyrene) prepared in
methylene chloride/toluene mixtures

REACTION NUMBER	ϵ	TRIAD TACTICITY			$P_{m/r}$	$P_{r/m}$	Σ_p	ρ	$1/\rho$	σ
		P_S	P_H	P_I						
65	14.8	.88	.12	0	1.0	.06	1.06	.94	1.06	.060
66	14.6	.90	.10	0	1.0	.05	1.05	.95	1.05	.050
67	12.7	.90	.10	0	1.0	.05	1.05	.95	1.05	.050
71	4.2	.93	.07	0	1.0	.04	1.04	.96	1.04	.035
73	3.2	.87	.13	0	1.0	.07	1.07	1.07	.94	.075

Having established that the p-chloro polymer can exhibit first-order Markov behavior, it is necessary to correlate first-order Markov statistics to a propagation mechanism. In the Kunitake mechanism, researchers have assumed Bernoullian statistics to hold. In fact, by the nature of the proposed mechanism, attack of the monomer on the propagating center is not uninfluenced by the polymer chain, as necessary for a Bernoullian process. The preceding stereotactic sequence does not influence the propagation directly by complexation of the carbocation as in the Cram model. However, limitation of the active center to a preferred conformation does fix the geometry at the active center and thus, the addition of monomer may behave as a first-order Markov process.

Conclusions

1. The p-chloro polymers appear to follow first-order Markov statistics based on triad data.
2. The statistics followed by the p-fluoro polymer cannot be distinguished.
3. The mechanism proposed by Kunitake and Aso does not fit the description for a first-order Markov process.

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CHAPTER IV

THE DETECTION OF MOISTURE IN THE POLYMERIZATION

Introduction

Initiation and Coinitiation

Lewis Acids can be used for cationic polymerization alone or in concert with a second species. Initiator-coinitiator systems where the initiating species is a stable carbocation are known, and examples abound in the literature [1-3]. Such systems, formed from a Lewis Acid and an organic halide, provide a well defined initiator and counteranion.

Less understood are those systems in which water is present either deliberately or residually. Debate has arisen over the exact necessity and role of water in polymerizations initiated by Lewis Acids, and many proposals can be found [4-6].

Stopping Experiments

Originally, "stopping experiments" were performed to determine the role of water in the initiation of cationic polymerization by Lewis Acids. In these experiments, dry, pure initiator is added to a rigorously dried monomer solution at controlled temperature under an inert atmosphere. If coinitiator is required, the reaction mixture remains quiescent, i.e., polymerization is "stopped". Conversely, the

occurrence of polymerization without added coinitiator indicated possible direct initiation by the Lewis Acid. Studies have been carried out by Kennedy [7], Branchu [8], and Dainton [9] on the polymerization of α -methylstyrene in various chlorinated solvents and with different initiators. For SnCl_4 and TiCl_4 in ethyl chloride and methylene chloride, respectively, no coinitiator was found to be necessary. All of the studies reported the use of accepted drying procedures for the reaction components. However, no quantitative information is given about the effectiveness of the drying agents used. Trace amounts of water may have been present. It is the intent of the work presented in this chapter to evaluate drying methods for use in this and future studies.

Determination of water content

With the use of initiator concentrations of the order of 10^{-3}M , detection of trace quantities of water in the polymerization system is of importance, and the water content may be too low to determine accurately by Karl Fischer analysis.

Burfield and coworkers [10-12] developed the use of tritiated water doping for the evaluation of the efficiencies of drying agents for organic solvents. Calcium hydride, CaH_2 , is the common desiccant used to dry methylene chloride. Sodium metal, although very powerful for drying aromatic solvents, is not recommended for halogenated solvents due the possibility of explosion.

There are two main advantages of the use of tritiated water as a tracer for the evaluation of drying methods. First, sensitivity to the part per billion level can be achieved with the appropriate activity of $^3\text{H}_2\text{O}$. Secondly, the assay is not affected by atmospheric moisture during sampling.

This technique is used to evaluate past drying methods used in this laboratory and to establish standard procedures for future studies. The present system, consisting of methylene chloride, p-chloro- α -methylstyrene, and tin tetrachloride, satisfies the criterion of absence of labile hydrogen. Doped solvent is also used in a polymerization.

Experimental

Purification of materials

Reagents. Methylene chloride, p-chloro- α -methylstyrene, and anhydrous tin tetrachloride were purified and predried as described in Chapter II. Water contents were determined by GC.

Doping agent. Tritiated water, $^3\text{H}_2\text{O}$, (from New England Nuclear, activity of 250 $\mu\text{C/g}$) was used as received and was handled according to the guidelines of the University of Massachusetts Department of Environmental Health and Safety.

Dessicants. Calcium hydride, in the form of a dry, fine powder (Aldrich, -40 mesh), was stored under nitrogen and used directly.

Sodium-potassium alloy was prepared by placing equal weights of sodium and potassium metal, both free from surface residue, in a dried, nitrogen-purged flask on a vacuum line and gently flaming the evacuated flask until a molten ball was formed.

3Å Molecular sieves were activated by heating at 270°C under vacuum for 24 hours. The sieves were stored and handled under a dry nitrogen atmosphere at all times.

Dessicant Studies

Sampling. The reagent to be doped was freshly distilled from the appropriate preliminary drying agent, then attached to and degassed on a high vacuum line manifold (mercury diffusion pump, 10^{-6} torr capability). The reagent was transferred to a second vessel on the vacuum line and doped with tritiated water which was added by syringe through a silicon rubber septum. The reagent was then sampled by syringe through the septum, and a scintillation count was obtained. The reagent was then transferred to the drying agent under study, stirred, and then transferred to a clean vessel for final sampling and scintillation count determination.

Scintillation counts. Scintillation counts were obtained on a Beckman 100S-LS scintillation counter. A measured amount of sample was mixed with 2ml of scintillation cocktail consisting of 1,4-bis(5-phenoyloxazol-2-yl)benzene (POPOP) and 2,5-diphenyloxazole (PPO). All counts were corrected with a blank solution of scintillation cocktail.

Polymerization

Polymerization was carried out in a vessel consisting of two sealed, glass 100ml round-bottomed flasks joined by a break-seal. Monomer and initiator solutions were prepared in separate sides of the vessel by means of vacuum line transfers and then sealed. The vessel was brought to -78°C , and the solutions were mixed after rupturing the break-seal. The polymerization was 0.50M in monomer and 6.1mM in initiator. The reaction was quenched with 5ml of chilled methanol.

Characterization

Molecular weight moments were obtained by GPC as described in Chapter II.

Results and Discussion

Dessicant studies

The results presented in Table 16 indicate that calcium hydride is a good preliminary dessicant. The amount of $^3\text{H}_2\text{O}$ was reduced from 673 ppm to 5.12 ppm. Further drying with either sodium-potassium alloy or 3Å molecular sieves gave similar results with the amount of residual $^3\text{H}_2\text{O}$ reduced to less than 1ppm. The values reported are the averages of three trials. These results are analogous to those obtained by Burfield and coworkers [12] for methylene chloride.

TABLE 16

Dessicant efficiencies for methylene chloride
as determined by doping with
tritiated water, $^3\text{H}_2\text{O}$

WATER CONTENT ^a BEFORE DOPING ppm	STARTING $^3\text{H}_2\text{O}$ LEVEL ppm	DESSICANT	RESIDUAL $^3\text{H}_2\text{O}$ CONTENT ppm
ca. 1000	673 ± 135^b	CaH_2	5.12 ± 15
		$\text{CaH}_2 + \text{Na-K}$	0.35 ± 0.05
		$\text{CaH}_2 + 3\text{A}$ Molecular Sieves	0.48 ± 0.40

a. Determined by GC

b. Errors are 95% confidence limit

As shown, both the sodium-potassium alloy and the molecular sieves are equally effective for drying methylene chloride. However, metals are not recommended for drying halogenated solvents, as mentioned previously. Molecular sieves, properly activated, have the following advantages:

1. Safety and ease of use.
2. Methylene chloride is easily distilled from the sieves under a dry atmosphere.
3. Water levels of less than 1ppm may be obtained.

Based on these points and the results in Table 16, molecular sieves are preferred for drying methylene chloride.

Polymerization

Methylene chloride which had been doped and dried by treatment with activated 3Å molecular sieves (0.4 ppm residual $^3\text{H}_2\text{O}$) was used for the polymerization of p-chloro- α -methylstyrene at -78°C with tin tetrachloride as initiator. The results are presented in Table 17. Polymerization did occur, but direct comparison with "stopping experiments" cannot be made because residual water was present. One can, however, compare the molecular weight of the polymer obtained with that expected based on the amount of initiator used. With an initiator level of 1.2 mole percent SnCl_4 with respect to monomer, a

TABLE 17

The use of tritiated water in the polymerization of p-chloro- α -methylstyrene in methylene chloride at -78°C with SnCl_4 as initiator

REACTION NUMBER	YIELD %	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	RESIDUAL $^3\text{H}_2\text{O}$ ppm
13	100	3,860,000	2,500,000	1.53	0.30

number average molecular weight, \bar{M}_n , of 13,000 is expected. The \bar{M}_n obtained is 2,500,000 which indicates that the number of chains initiated is much less than the number of initiator molecules. There are two explanations for this. The first possibility is that water cointiation is present. This can be checked by calculating the molecular weight expected based on the 0.40 ppm of $^3\text{H}_2\text{O}$ present. Assuming a first order dependence on water of the initiation reaction, a \bar{M}_n of 8.2×10^7 is expected. The obtained molecular weight of Reaction 13 falls between those molecular weights calculated by assuming initiation of one chain by every SnCl_4 alone and by cointiation with water. However, the amount of water present is most likely greater than 0.4 ppm since the amount of untritiated water is not reflected in the 0.4 ppm value. In this case the molecular weight expected for cointiation with water would be smaller than 8.2×10^7 .

The second possibility is that propagation is faster than initiation. Thus, the polymerization goes to completion before initiator is consumed. This can indeed occur in the polymerization of p-chloro- α -methylstyrene initiated by SnCl_4 as shown in Table 11 in Chapter II.

Conclusions

1. Activated 3A molecular sieves are the drying agent of choice for methylene chloride. The amount of residual $^3\text{H}_2\text{O}$ can be reduced to less than 1ppm.

2. The question of initiation versus cointiation cannot be resolved by use of "stopping experiments".

3. Propagation is much faster than initiation in these systems.

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C H A P T E R V
STUDIES OF THE POLYMERIZATION OF
p-METHOXY- α -METHYLSTYRENE

Introduction

The methoxy group is an electron donating species and, therefore, favorable to the development of a carbocation. Conjugation with the ether oxygen of the methoxy group imparts stability to the carbenium ion formed by p-methoxy- α -methylstyrene. Several polymers of methoxy substituted styrenes and α -methylstyrenes have been prepared by a cationic mechanism.

Temperature Effects

As noted in Chapter I, side reactions are common in cationic polymerization and prevent the attainment of a living species. One method of reducing side reactions, specifically chain transfer to monomer, is to increase the stability of the carbenium ion. Another is to vary the polymerization temperature in an attempt to "freeze out" chain transfer.

Guhaniyogi and Kennedy [1] identified the temperature necessary to eliminate chain transfer to monomer as -86°C for the polymerization of α -methylstyrene initiated by SnCl_4 . This

temperature was taken as the temperature at and below which the \bar{M}_n and \bar{M}_w/\bar{M}_n of the polymers obtained were constant.

Following the methods described by Kennedy, a series of polymerizations of p-methoxy- α -methylstyrene in methylene chloride initiated by SnCl_4 were carried out over a range of temperatures from 0°C to -95°C . The effect of temperature variation on the tacticities of the polymers was also determined.

Long-lived Behavior

The cumyl cation for the chloro, fluoro, and methoxy counterparts of the monomers used in this work have been observed by NMR in superacid solutions by Olah [2]. However, living or long-lived species have yet to be prepared under polymerization conditions. Attempts by Jonte [3] to prepare block copolymers of the p-fluoro and p-chloro polymers with alkyl vinyl ethers proved fruitless. The electron withdrawing chloro group and the weakly electron donating p-fluoro group are not expected to produce highly stable cations. The p-methoxy group, however, would form a much more stable cation and is a better candidate for monomer addition studies.

Based on the results of the temperature study on this monomer, conditions were found under which chain transfer to monomer was negligible. Sequential monomer addition studies with the p-methoxy, p-chloro, and p-fluoro monomers were carried out.

Experimental

Purification of Solvent

Methylene chloride was purified as described in Chapter II and was freshly distilled before use.

Synthesis and Purification of Monomer

p-Methoxy- α -methylstyrene was prepared by the method of Seymour [4] from the reaction of p-methoxyacetophenone with methylmagnesium iodide followed by dehydration. The monomer was distilled twice (b.p. 95°C, 1mm Hg), recrystallized from ethanol, and then dried in vacuo. Found: %C - 79.07; %H - 8.17; %O - 12.76; Theoretical: %C - 81.04; %H - 8.16; %O - 10.80. m.p. 33.5 - 34°C; water content 0.2 mole percent by Karl Fischer analysis.

Purification of initiator

A 0.043 M solution of SnCl_4 in methylene chloride was prepared as described in Chapter II.

Polymerization Reactions

All polymerizations were carried out in 100 ml round bottom flasks which had been heated under vacuum and filled with dry nitrogen. The flasks were equipped with teflon stir bars and aluminum-capped 11mm Wheaton necks with PTFE-backed silicon rubber

septa. Initiation was effected by introduction of the initiator solution by a gas tight, 1ml syringe, with stainless steel needle, inserted through the septum. Unless indicated otherwise, all initial monomer concentrations were 0.13 M, initiator was 1.3×10^{-3} M (0.1 mole percent with respect to monomer), and reaction times were 5 minutes.

Sequential monomer addition was achieved by adding an isothermal solution of the second monomer to the polymerization flask, containing unquenched poly(p-methoxy- α -methylstyrene), with a cannula and dry nitrogen pressure. Samples were taken before addition of a second monomer charge to determine molecular weights and yields. The polymerization reached at least 99% yield before the second monomer solution was added.

The reactions were quenched with 5 ml of chilled methanol, filtered, dissolved in methylene chloride, refiltered, reprecipitated in methanol, and then collected and dried in vacuo at 50°C to constant weight.

Polymer Characterization

Gel permeation chromatography. Molecular weight moments relative to polystyrene standards were determined on a Waters 201 gel permeation chromatograph as described in Chapter II.

Differential scanning calorimetry. Scans were obtained on a Perkin Elmer DSC-II at a heating rate of 20°C per minute.

Thermal gravimetric analysis. Scans were obtained on a Perkin Elmir TGS-2 Thermogravimetric Analyzer in the temperature range of 50°C to 500°C at a heating rate of 10°C per minute.

Nuclear magnetic resonance. Triad tacticities were determined on a Varian XL-300 300MHz ¹H-NMR spectrometer in 5% (w/v) chloroform-d solutions at 50°C with p-dioxane as internal standard. The relative areas of the integrations of the α-methyl proton resonances were used.

Results and Discussion

Reaction conditions

Initial attempts to vary the temperature of the polymerization gave the results in Table 18. The attainment of a reaction gel was most likely due to high concentrations of monomer. Variation of the initial monomer concentration yielded ungelled reaction mixtures which gelled upon warming as indicated in Table 19. The gelled mixtures were difficult to precipitate and to redissolve. Precipitation of the quenched polymer solution into methanol while the solution was still at low temperature gave polymer which was easily handled and readily soluble in methylene chloride and chloroform.

The difference between the polymers obtained as gels upon warming and those obtained by precipitating the quenched reaction mixture while cold was thought to be one of crystallinity. The results of DSC measurements for selected polymers, contained in Table 20, indicate

TABLE 18

Variation of temperature in the polymerization of
p-methoxy- α -methylstyrene in methylene chloride
initiated by SnCl_4

REACTION NUMBER	TEMPERATURE $^{\circ}\text{C}$	YIELD %	COMMENT
1	-40	69	All reactions resulted in a gel
2	-58	62	
3	-70	84	
4	-89	89	
5	-86	86	

$[\text{M}] = 0.27 \text{ M}$

TABLE 19

Variation of monomer and initiator concentrations for the polymerization of p-methoxy- α -methylstyrene in methylene chloride initiated by SnCl_4

REACTION NUMBER	MONOMER CONCENTRATION moles/l	YIELD %	COMMENT
7	0.18	96	All reactions remained free but gelled upon warming
8	0.13	96	
9	0.09	93	

T = -78°C

TABLE 20

Effect of precipitation method on the
melt behavior of polymers of
p-methoxy- α -methylstyrene

REACTION NUMBER	T ^a °C ^m	PRECIPITATION METHOD
8	201	Gel on warming
9	213	Gel on warming
15	166	Gel on warming
16	none	Precipitated cold
19	none	Precipitated cold
20	163	Gel on warming
21	none	Precipitated cold
22	none	Precipitated cold

a. Peak maximum; DSC II at 20°C/min heating rate

that the gelled polymers were perhaps crystalline, whereas the polymers precipitated cold were not. TGA, however, showed that the gelled polymers had varying weight losses at temperatures corresponding to the endotherms obtained by DSC. Therefore, the endotherms observed by DSC are most likely due to the loss of trapped solvent. The gelled polymers were annealed, and the DSC and TGA measurements were repeated. In most cases no endotherm was obtained by DSC and the TGA showed only one weight loss of 100% corresponding to polymer degradation. Figures 11 to 14 illustrate this behavior for one of the gelled polymers.

Figure 11 shows what at first appears to be a melting endotherm at 176°C. Figure 12, however, indicates a weight loss of approximately 20% at an onset temperature of 140°C. Thus it is most likely that the endotherm in Figure 11 is due to loss of trapped solvent. The DSC results shown in Figure 13 for the annealed polymer shows no transitions near 176°C and a very small transition at 212°C which is close to the values of T_m reported for poly(p-methoxy- α -methylstyrene) [3]. Figure 14 indicates only one weight loss of 100% at an onset temperature of 220°C for the annealed polymer. The small T_m peak shown in Figure 13 was most likely the result of annealing.

Using the technique of precipitating the quenched polymer solution while cold, the monomer concentration and reaction time were varied as shown in Tables 21 and 22, respectively. For Reactions 15 to 17, the polymerization solutions remained ungelled, and quenching

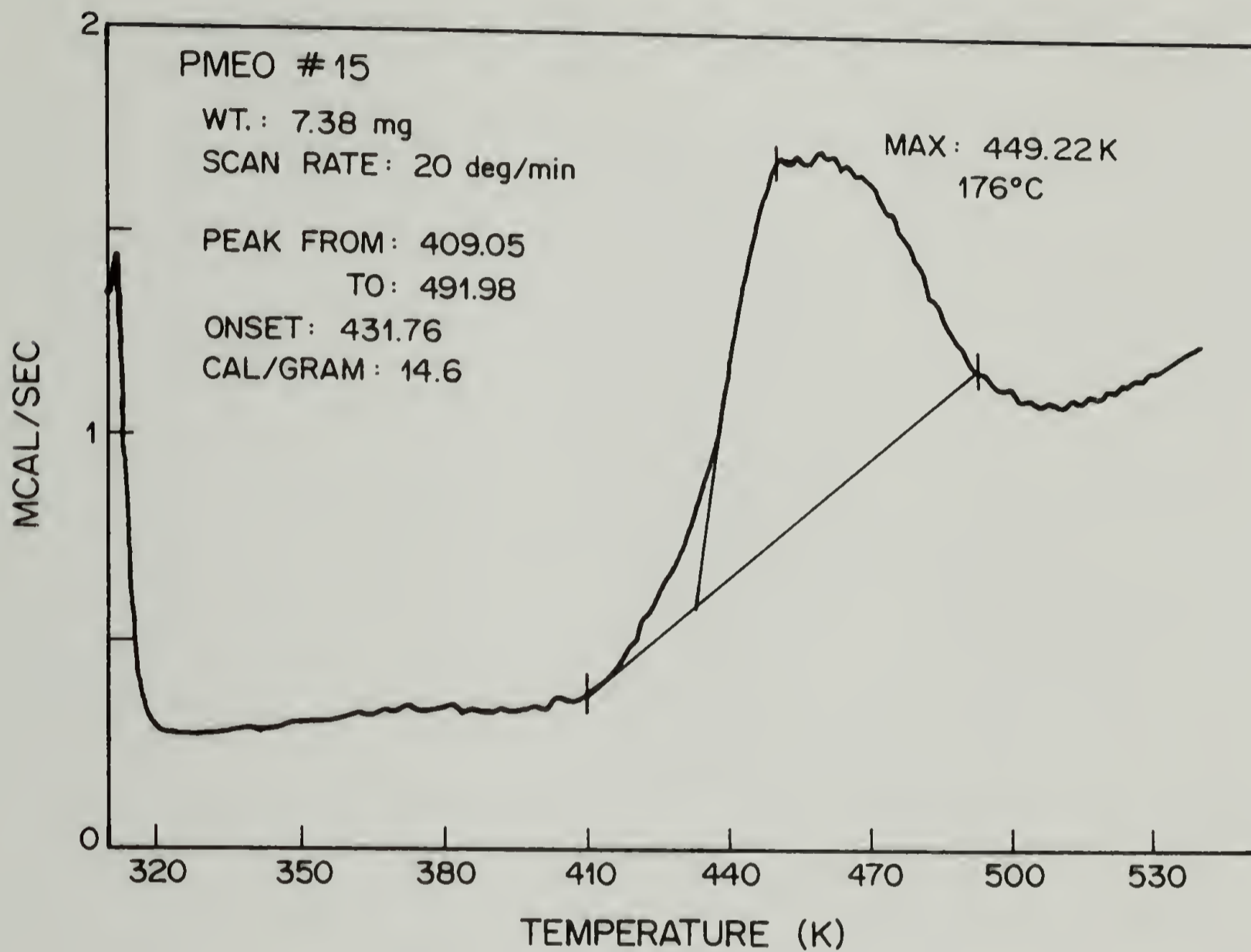


Figure 11. Differential Scanning Calorimetry (DSC) curve for poly(*p*-methoxy- α -methylstyrene) obtained as a gel, sample #15.

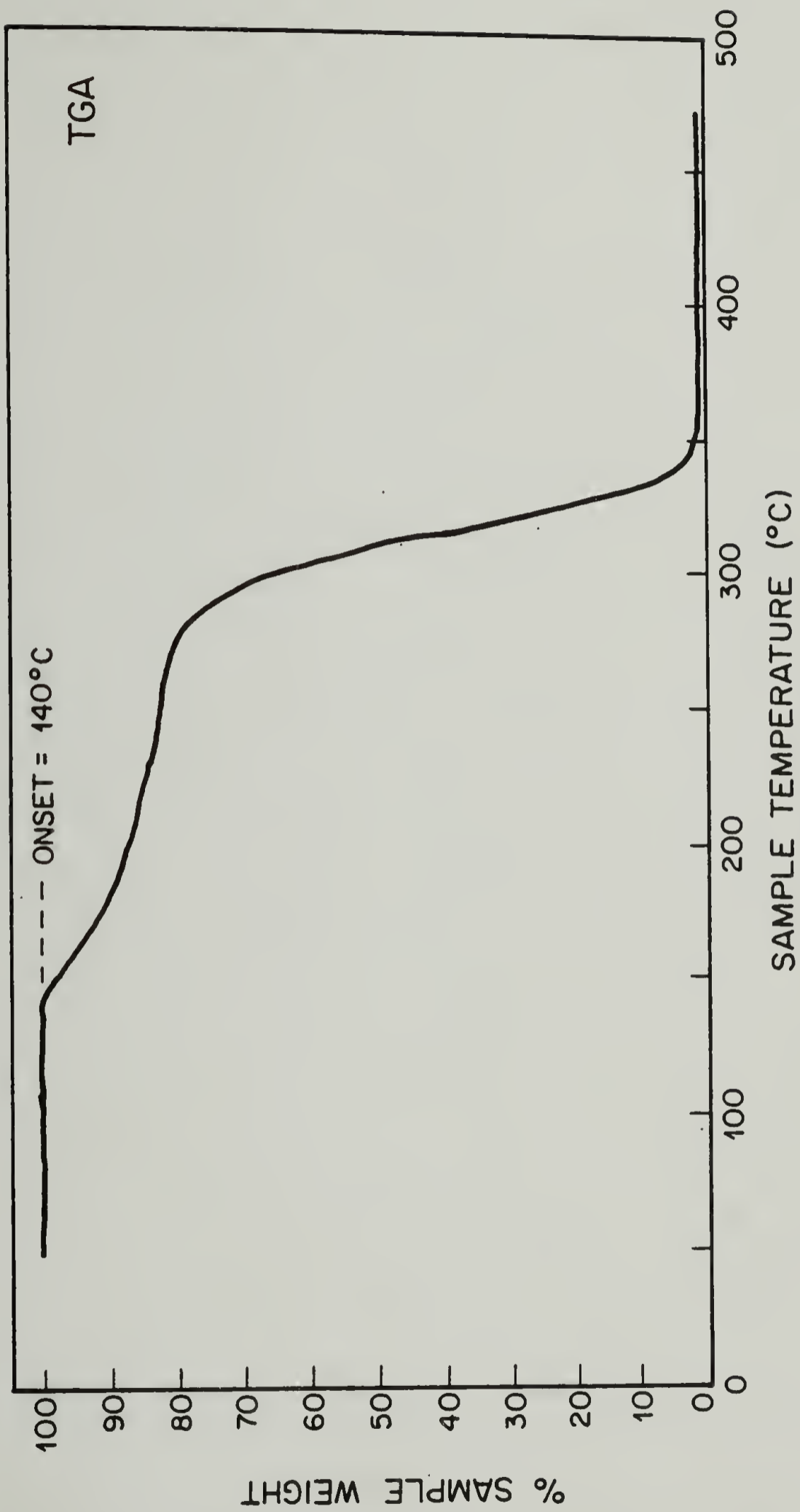


Figure 12. Thermal Gravimetric Analysis (TGA) for poly(p-methoxy- α -methylstyrene) obtained as a gel, sample #15.

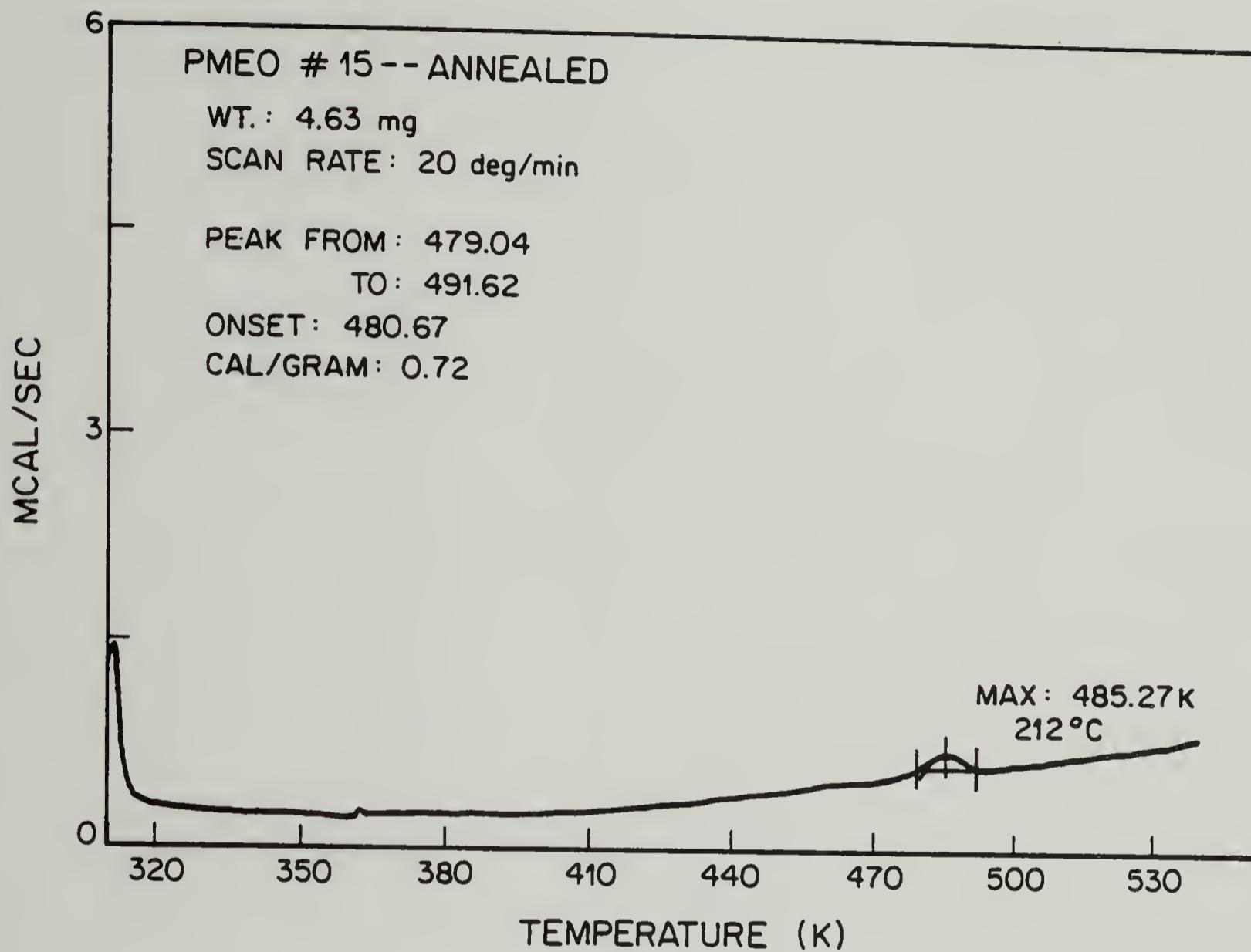


Figure 13. Differential Scanning Calorimetry (DSC) curve for poly(p-methoxy- α -methylstyrene) sample #15 after annealing.

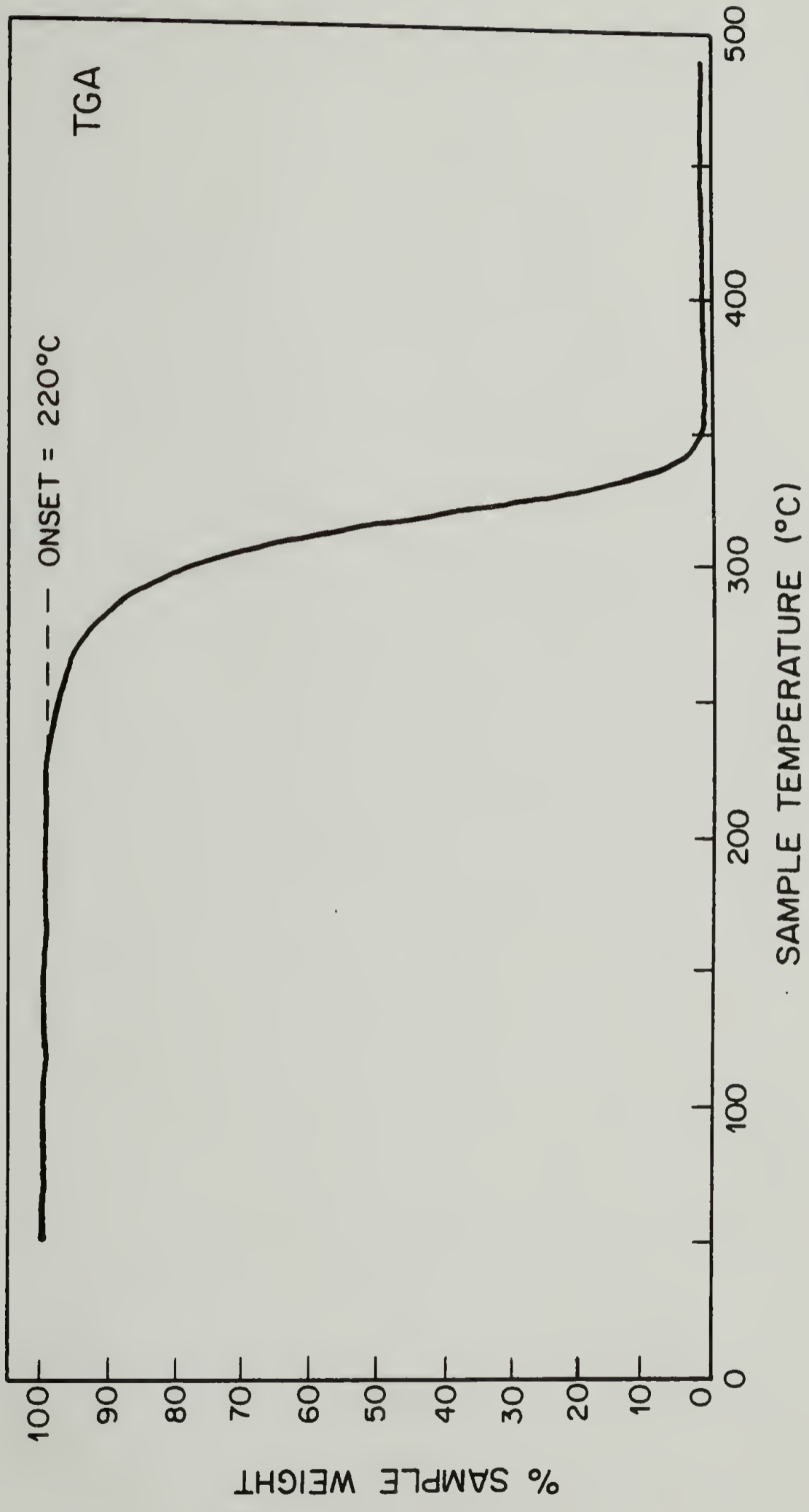


Figure 14. Thermal Gravimetric Analysis (TGA) for poly(p-methoxy- α -methylstyrene) sample #15 after annealing.

TABLE 21

Variation of monomer and initiator concentrations
for the polymerization of p-methoxy- α -methylstyrene
in methylene chloride initiated by SnCl_4

REACTION NUMBER	[M] moles/l	YIELD %	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
15	0.13	100	587,000	363,000	1.60
16	0.067	98	633,000	388,000	1.63
17	0.034	96	412,000	312,000	1.32

Ratio of initiator to monomer was constant at 0.10 mole percent
with respect to monomer. $T = -78^\circ\text{C}$.

TABLE 22

Variation of reaction time for the polymerization of p-methoxy- α -methylstyrene in methylene chloride initiated by SnCl_4

REACTION NUMBER	TIME (min)	YIELD %	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	COMMENT
23	0.13	15	100,000	86,700	1.16	Monomodal
24	1.0	84	637,000	416,000	1.53	Monomodal
25	2.5	89	969,000	537,000	1.81	Bimodal
26	5.0	99	618,000	474,000	1.30	Monomodal

$[M] = 0.13 \text{ M}$; $[I] = 1.35 \times 10^{-3} \text{ M}$, 0.10 mole% with respect to monomer

of the reactions was easily achieved. It should be noted that the molecular weight moments, particularly \bar{M}_n , are similar for all of the polymers obtained. This result is expected since the ratio of monomer to initiator was kept constant for this study.

The results of Reactions 23 to 26 show that the polymerization goes to completion in 5 minutes. Figure 15 shows that the rate of polymerization appears to decrease after 1 minute. This decrease in rate may be attributed to increasing difficulty of diffusion of the monomer through the polymer solution as the polymer chain grows.

Based on these results, a monomer concentration of 0.13 M and a reaction time of 5 minutes were sufficient to obtain high yields of polymer and ungelled reaction media.

Table 23 contains the results for variation of the initiator concentration. A linear dependence of molecular weight on initiator concentration is one of the criteria for a living or long-lived system. As seen in Figure 16, the dependence appears to be linear. However, using the monomer and initiator concentrations of Reaction 23, a \overline{DP}_N of 1000 can be calculated. This corresponds to a \bar{M}_N of 148,000 for the p-methoxy polymer. This calculated \bar{M}_n is quite different from the \bar{M}_N of 959,000 reported in Table 23. The polymerization appears to involve extremely fast propagation relative to initiation, similar to the situation described for the polymerization of the p-chloro monomer in Chapter II.

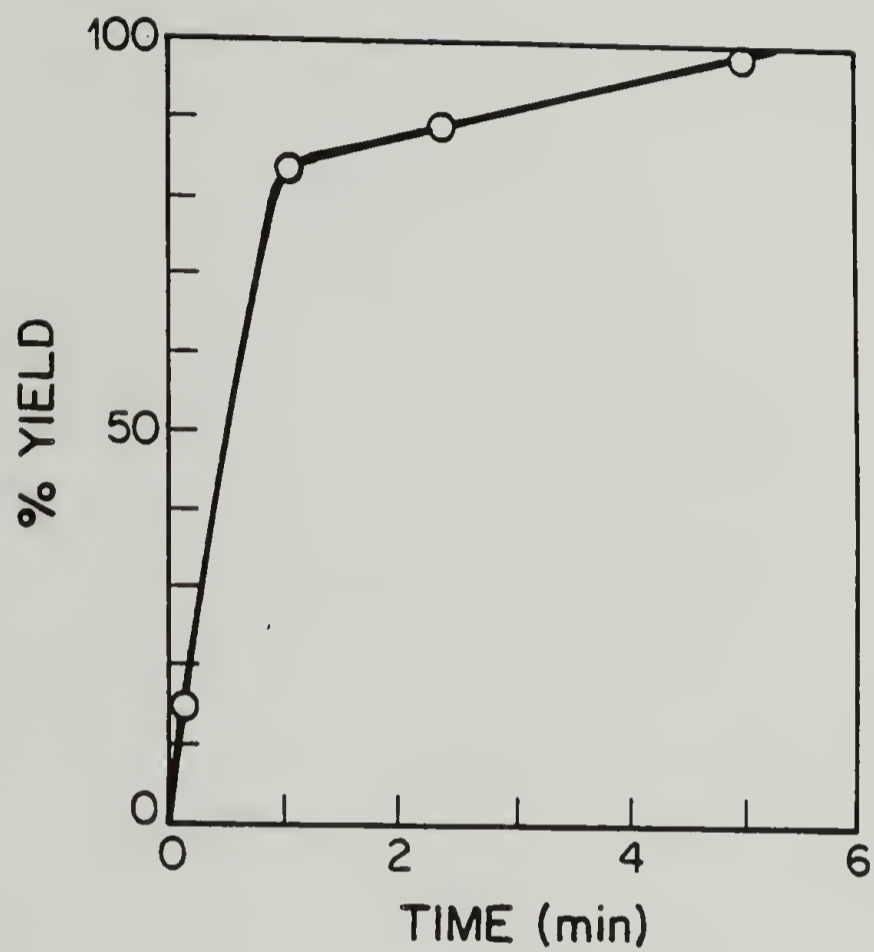


Figure 15. Yield of poly(p-methoxy- α -methylstyrene) as a function of time.

TABLE 23

Variation of initiator concentration for the polymerization
of p-methoxy- α -methylstyrene in methylene chloride
initiated by SnCl_4

REACTION NUMBER	$[\text{SnCl}_4]$ moles/l	YIELD %	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
21	1.3×10^{-4}	59	2,330,000	959,000	2.40
19	6.5×10^{-4}	100	478,000	327,000	1.46
22	9.8×10^{-4}	97	284,000	223,000	1.27

$[\text{M}] = 0.13 \text{ M}; T = -78^\circ\text{C}.$

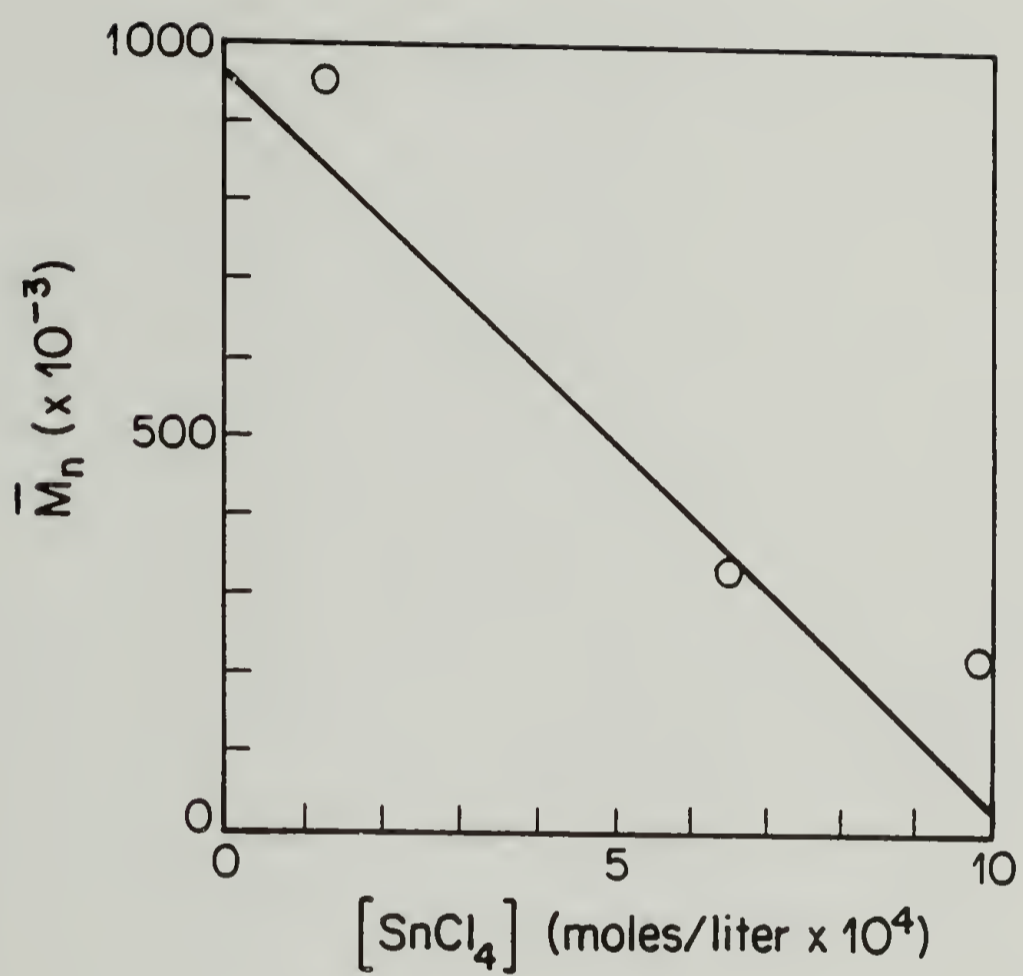


Figure 16. Effect of initiator concentration on the number average molecular weight of poly(p-methoxy- α -methylstyrene).

Temperature Variation

Molecular Weight. The effect of varying the polymerization temperature on molecular weight and yield is shown in Figures 17 and 18, respectively. No high polymer was obtained for polymerization temperatures above -30°C . According to Figure 17, four regions can be defined: 0°C to -30°C , -30°C to -50°C , -50°C to -75°C , and -75°C to -95°C . The boundaries of the four regions represent temperatures at which control of molecular weight changes from one mode to another.

The activation energy differences between propagation and chain transfer, and thus the activation energy for the degree of polymerization, $E_{\overline{DP}_N}$, for the temperature regions of -30°C to -50°C and -50°C to -75°C can be estimated from the slopes of the lines for those regions in Figure 17. If termination is not considered, $E_{\overline{DP}_N}$ can be determined by application of the following equations:

$$\overline{DP}_N = \frac{R_p}{R_{ct}} = \frac{k_p [M] [M^+]}{k_{ct} [M] [M^+]} \quad (4a)$$

$$k_i = A_i \exp \frac{-E_i}{RT} \quad (4b)$$

$$\overline{DP}_N = \frac{\overline{M}_N}{MW_{\text{monomer}}} \quad (4c)$$

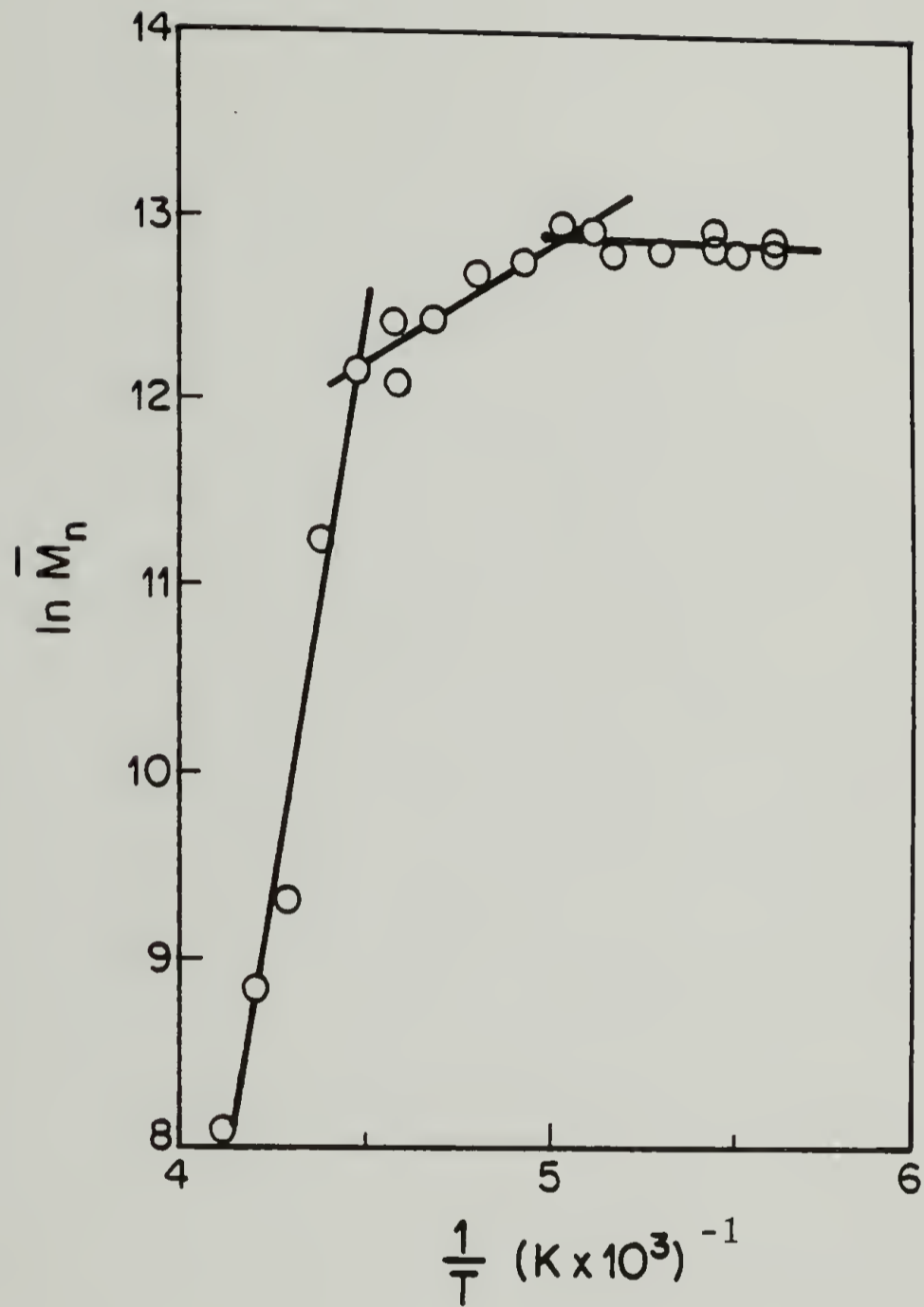


Figure 17. Effect of temperature on the number average molecular weight of poly(p-methoxy- α -methylstyrene).

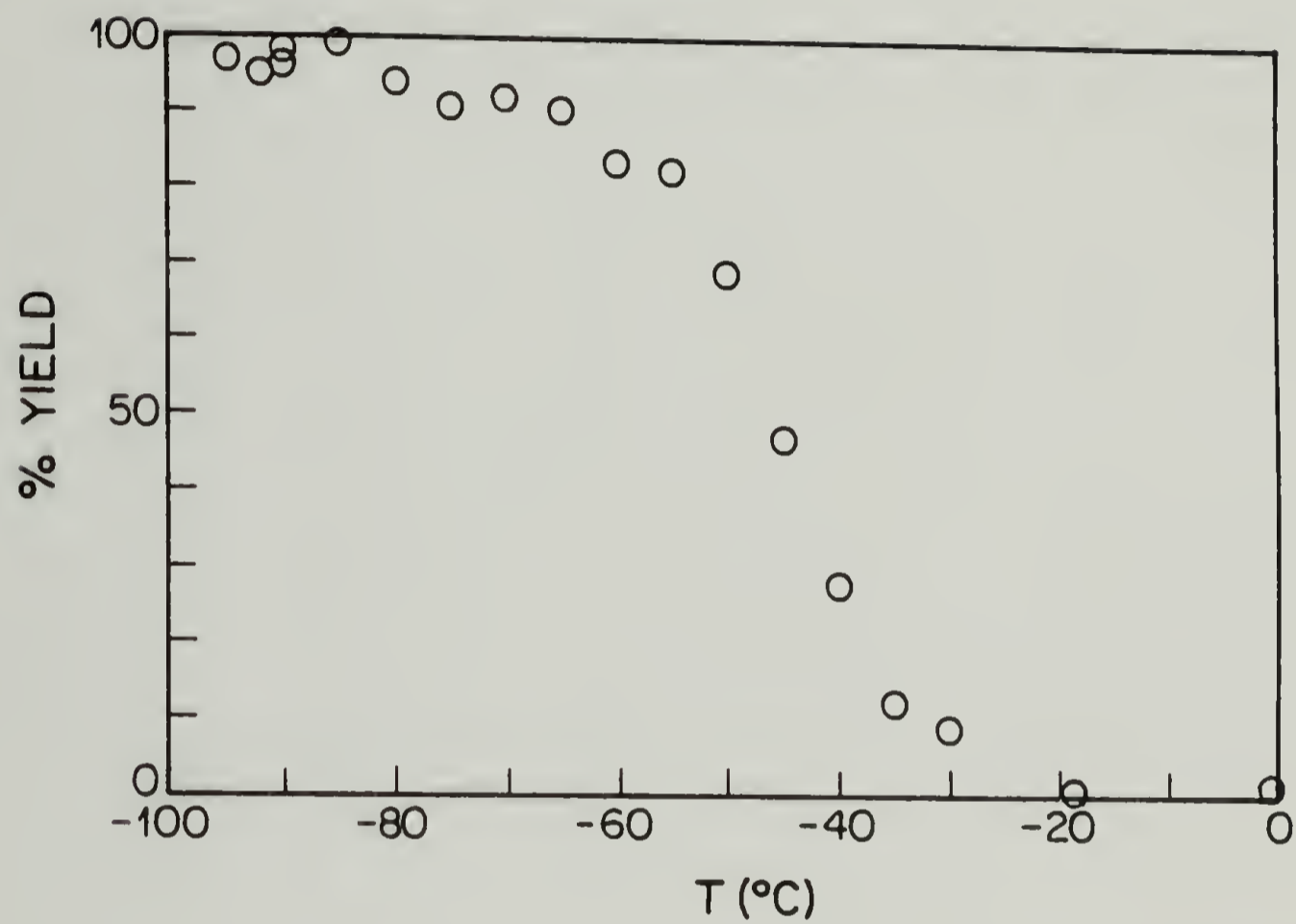


Figure 18. Yield of poly(p-methoxy- α -methylstyrene) as a function of temperature.

$$\ln \bar{M}_N = \ln MW_{\text{monomer}} \frac{A_p}{A_{ct}} + \frac{E_{ct} - E_p}{R} \frac{1}{T} \quad (4d)$$

$$E_{\overline{DP}_N} = E_p - E_{ct} \quad (4e)$$

Where R_p = rate of propagation

R_{ct} = rate of chain transfer to monomer

R = gas law constant

E_{ct} = activation energy for chain transfer to monomer

E_p = activation energy for propagation

For the temperature range of -30°C to -50°C , the slope of the line is 9.46 K which corresponds to $E_{\overline{DP}_N} = -1.88 \times 10^{-2}$ kcal/mole or -7.86 kJ/mole. For the region between -50°C to -75°C , the slope of 1.61 K leads to $E_{\overline{DP}_N} = -3.20 \times 10^{-3}$ kcal/mole or -1.34×10^{-2} kJ/mole. This change in activation energy could signify a change in the molecular termination from one form of chain transfer to another or from chain transfer to termination. The effect of temperature on the solvation state of the propagating carbenium ion may also contribute to the change in activation energy as discussed in the following section on tacticity.

The final region from -75°C to -95°C is of the most interest since the molecular weights of the polymers obtained in this temperature range are invariant. Such constancy of molecular weight

with temperature may be due to the absence of chain transfer to monomer. The extent of chain transfer to monomer can be determined by the Mayo Equation [5] as depicted in Figure 19. A plot of $(\overline{DP}_N)^{-1}$ versus $(M)_0^{-1}$ at constant temperature yields two general cases as shown in Figure 20. When chain transfer is absent, the chain transfer coefficient, C_M , is zero as indicated by the intercept of zero for line A of Figure 20. A finite intercept, as represented by line B, indicates the presence of chain transfer to monomer.

The effect of varying the monomer concentration for the present system at -85°C is shown in Table 24 and Figure 21. The degree of polymerization varies linearly with monomer concentration as expected. The presence of a finite intercept indicates chain transfer to monomer. According to Figure 21, the value of C_M is 2.27×10^{-4} , or propagation is approximately 4000 times as fast as chain transfer. The ratio of the rate constant for termination to the rate constant for propagation is 3.12×10^{-5} as obtained from the slope of the line in Figure 21. Propagation is 32,000 times as fast as termination.

The existence of chain transfer to monomer at -85°C is surprising since the slope of the line for the -75°C to -95°C region in Figure 17 is essentially zero. Figure 18 shows that the yield of the polymers obtained in this region is high. Reinvestigation of the -75°C to -95°C region using shorter polymerization times to obtain smaller yields may result in a line with a small, positive slope.

$$\frac{1}{\overline{DP}_N} = \frac{k_t}{k_p} \times \frac{1}{(M)_0} + C_M$$

WHERE: \overline{DP}_N = NUMBER AVERAGE DEGREE OF POLYMERIZATION
 k_t = TERMINATION RATE CONSTANT
 k_p = PROPAGATION RATE CONSTANT
 $(M)_0$ = INITIAL MONOMER CONCENTRATION
 C_M = CHAIN TRANSFER COEFFICIENT FOR CT TO MONOMER

Figure 19. The Mayo Equation

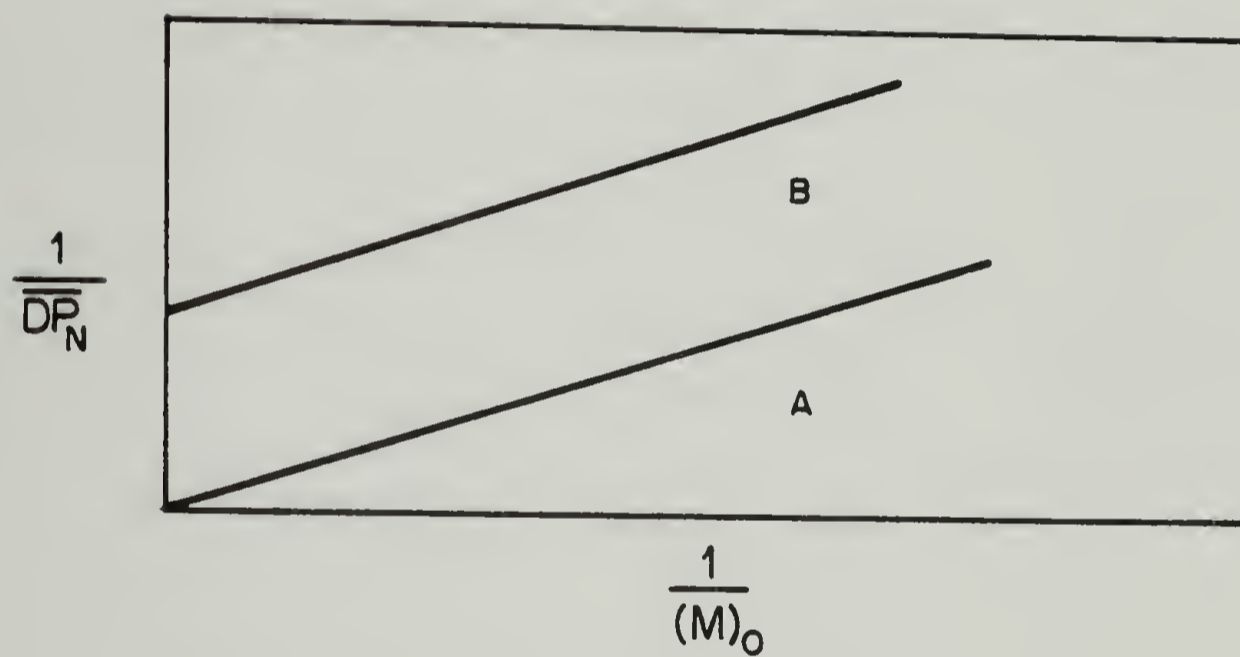


Figure 20. Idealized plot of the Mayo Equation.

TABLE 24

Variation of monomer concentration for the polymerization of *p*-methoxy- α -methylstyrene in methylene chloride initiated by SnCl₄

REACTION NUMBER	[M] moles/l	YIELD %	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	\bar{DP}_n
100	0.19	95	704,000	356,000	1.95	2,401
99	0.13	97	559,000	333,000	1.68	2,245
101	0.06	97	307,000	201,000	1.53	1,354
102	0.03	95	183,000	117,000	1.57	786

T = -78°C; $\bar{DP}_N = \bar{M}_n/\text{monomer molecular weight}$; [SnCl₄] = 1.3 x 10⁻³M

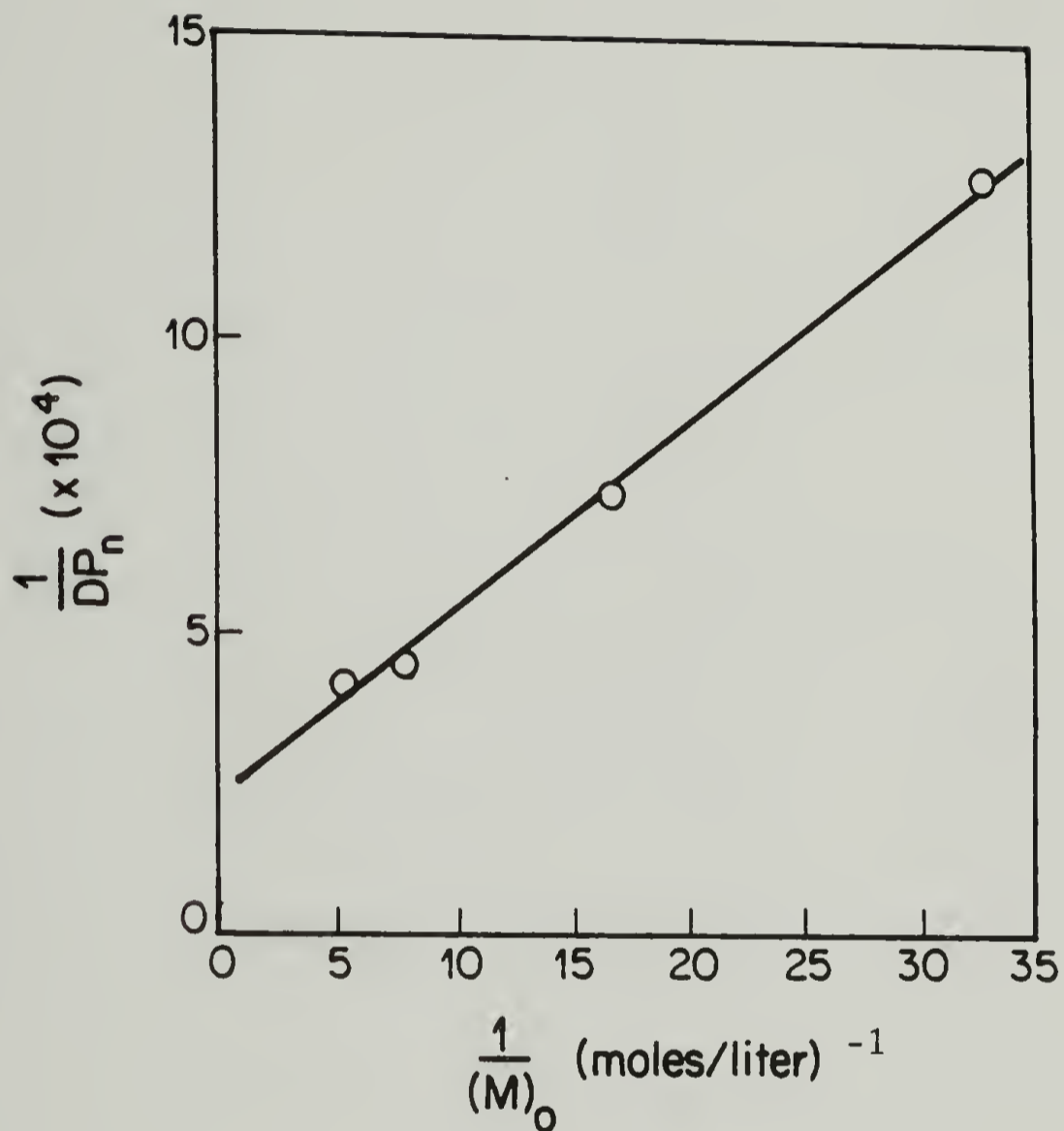


Figure 21. Plot of the Mayo Equation for the polymerization of p-methoxy- α -methylstyrene at -85 C.

TABLE 25

Effect of polymerization temperature on the tacticities of poly(p-methoxy- α -methylstyrene) prepared in methylene chloride

REACTION NUMBER	TEMPERATURE °C	TRIAD TACTICITY			σ^a
		P _S	P _H	P _I	
95	-30	.70	.30	0	.150
91	-35	.62	.38	0	.190
81	-40	.75	.25	0	.125
92	-45	.74	.26	0	.130
93	-50	.86	.14	0	.070
94	-55	.87	.13	0	.065
96	-55	.89	.11	0	.055
83	-60	.89	.11	0	.055
87	-65	.93	.07	0	.035
84	-70	.97	.03	0	.015
82	-75	.94	.06	0	.030
88	-80	.94	.06	0	.030
85	-85	.91	.09	0	.045
89	-90	.91	.09	0	.045
86	-92	.95	.05	0	.025
90	-95	.93	.07	0	.035

of the polymers. The lack of isotactic triads for the polymers as prepared in polar methylene chloride is analogous to the results obtained for the p-chloro and p-fluoro polymers prepared under similar conditions. The steric bulk of the p-methoxyphenyl group most likely prevents the occurrence of long sequences of isotactic units. Based on the results for variation of solvent polarity for the p-fluoro polymer, large variations in tacticities with solvent polarity for the p-methoxy polymer are not expected. The p-methoxy group, with a σ^+ value of -0.27 [7], should stabilize the carbenium ion formed from the p-methoxy monomer rendering it less sensitive to changes in the environment.

The average sequence lengths, as calculated by the equations of Chapter II, are listed in Table 26. The isotactic sequence, with a value of 1, is constant with temperature. The syndiotactic sequence length increased with decreasing temperature. The correlation parameters, as calculated from the equations of Chapter III, are presented in Table 27. All of the polymerizations appear to be first-order Markov processes as indicated by the values of Σ_p and $1/\rho$.

The first-order Markov behavior exhibited by the p-methoxy polymers and the presence of the ether oxygen of the methoxy group could indicate that propagation proceeds by the mechanism proposed by Cram and Kopecky [8] for alkoxy vinyl ethers. However, that mechanism predicts the formation of highly isotactic polymers. The mechanism also requires the formation of a six-membered ring, between the

TABLE 26

Tacticity sequence lengths in polymers obtained from the cationic polymerization of *p*-methoxy- α -methylstyrene in methylene chloride

REACTION NUMBER	TEMPERATURE °C	POLYMER TACTICITIES				CALCULATED SEQUENCE LENGTHS	
		SYNDIOTACTIC ^a P(S)	SYNDIOTACTIC ^b P _S	ISOTACTIC ^a P(I)	ISOTACTIC ^b P _I	ISOTACTIC $\mu(I)$	SYNDIOTACTIC $\mu(S)$
95	-30	.85	.70	.15	0	1	6
91	-35	.81	.62	.19	0	1	4
81	-40	.88	.75	.12	0	1	7
92	-45	.87	.74	.13	0	1	7
93	-50	.93	.86	.07	0	1	13
94	-55	.94	.87	.06	0	1	16
96	-55	.94	.89	.06	0	1	16
83	-60	.94	.89	.06	0	1	16
87	-65	.96	.93	.04	0	1	24
84	-70	.98	.97	.02	0	1	49
82	-75	.97	.94	.03	0	1	32
88	-80	.87	.94	.03	0	1	32
85	-85	.96	.91	.04	0	1	24
89	-90	.96	.91	.04	0	1	24
86	-92	.98	.95	.02	0	1	49
90	-95	.96	.93	.04	0	1	24

TABLE 27

Calculated values of first-order Markov correlation parameters for poly(p-methoxy- α -methylstyrene) prepared in methylene chloride

REACTION NUMBER	TEMPERATURE °C	TRIAD TACTICITY					Σ_p	ρ	1/ ρ	σ
		P_S	P_H	P_I	$P_{m/r}$	$P_{r/m}$				
95	-30	.70	.30	0	1	.18	1.18	.85	1.18	.150
91	-35	.62	.38	0	1	.23	1.23	.81	1.23	.190
81	-40	.75	.25	0	1	.14	1.14	.88	1.14	.125
92	-45	.74	.26	0	1	.15	1.15	.87	1.15	.130
93	-50	.86	.14	0	1	.08	1.08	.93	1.08	.070
94	-55	.87	.13	0	1	.07	1.07	.94	1.06	.065
96	-55	.89	.11	0	1	.06	1.06	.94	1.06	.055
83	-60	.89	.11	0	1	.06	1.06	.94	1.06	.055
87	-65	.93	.07	0	1	.04	1.04	.96	1.04	.035
84	-70	.97	.03	0	1	.02	1.02	.98	1.02	.015
82	-75	.94	.06	0	1	.03	1.03	.97	1.03	.030
88	-80	.94	.06	0	1	.03	1.03	.97	1.03	.030
85	-85	.91	.09	0	1	.05	1.05	.95	1.05	.045
89	-90	.91	.09	0	1	.05	1.05	.95	1.05	.045
86	-92	.95	.05	0	1	.02	1.02	.98	1.02	.025
90	-95	.93	.07	0	1	.04	1.04	.96	1.04	.035

carbenium ion and adjacent ether oxygen, which is difficult to form for the propagating center of p-methoxy- α -methylstyrene. Kunitake proposed [9] that the deviation from sp^2 hybridization resulting from formation of the six-membered ring is unfavorable to stabilization of the carbenium ion by the pendant ether oxygen.

Sequential Monomer Additions

Sequential additions of the monomers used in this study to unquenched polymers of p-methoxy- α -methylstyrene were carried out at -85°C , a temperature well within the region of constant molecular weight as defined in Figure 17. The major requirement of a long-lived polymer is the ability to add its own monomer after 100% conversion is reached. As seen from Table 28, sequential addition of the p-methoxy monomer resulted in a slight increase in the molecular weight of the polymer. However, the polymer obtained after the addition of the second monomer charge had a bimodal molecular weight distribution as shown in Figure 22. This can be explained by considering the initiation of the polymerization. As stated previously, not all of the initiator is consumed in the initiation reaction. When additional monomer is added after the first polymerization is complete, the unconsumed initiator and the long-lived carbenium ions, if they exist, compete for the monomer. Thus, new polymer chains are initiated, and a bimodal molecular weight distribution is observed.

TABLE 28

Sequential addition of monomers to the unquenched polymerization of p-methoxy- α -methylstyrene in methylene chloride

REACTION NUMBER	ADDED MONOMER	CONCENTRATION OF ADDED MONOMER moles/l	RESULT OF ADDED MONOMER
75	p-methoxy	0.13	Increased MW; Bimodal
113	p-chloro	0.13	p-Methoxy homopolymer
114	p-chloro	0.13	p-Methoxy homopolymer
115	p-fluoro	0.14	p-Methoxy homopolymer

$[p\text{-MeO}]_{\text{initial}} = 0.13 \text{ M}$; $[\text{SnCl}_4] = 1.35 \text{ mM}$; $T = -85^\circ\text{C}$

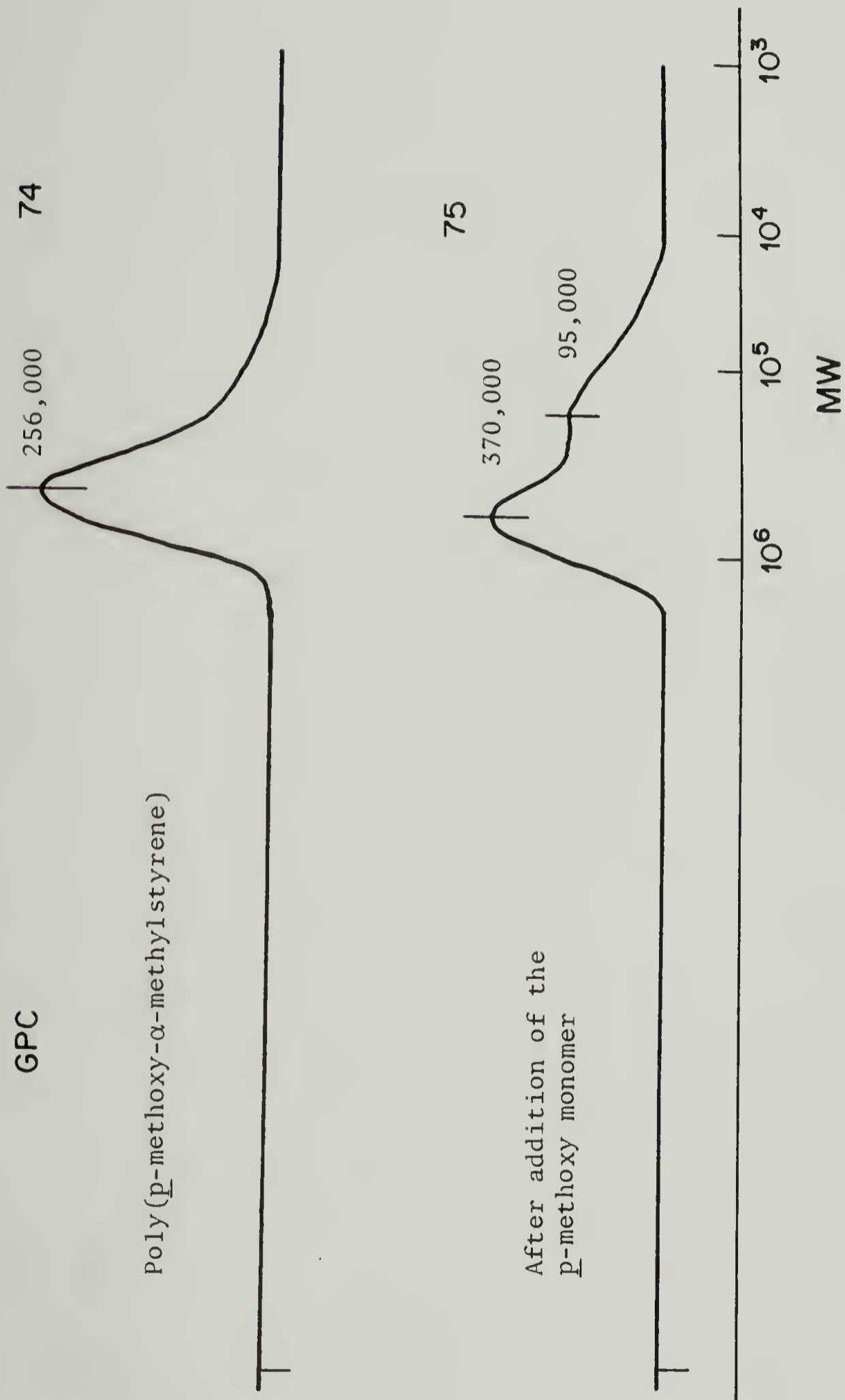


Figure. 22. GPC for the sequential addition of the p-methoxy monomer.

Figures 23 and 24 show the GPC results for addition of the p-chloro and p-fluoro monomers, respectively. Addition of the p-chloro monomer resulted in a slight increase in molecular weight. Elemental analysis for the polymer indicated the absence of any chloride. Nearly 100% of the p-chloro monomer was recovered from the reaction mixture.

Similarly, the p-fluoro monomer failed to produce an increase in the molecular weight of the polymer. No fluoride was detected by elemental analysis of the polymer, and 95% of the p-fluoro monomer was recovered from the reaction mixture. These results were expected. If the propagating center of the p-methoxy polymer were indeed long-lived, addition of a p-chloro or p-fluoro monomer to produce a less stable carbenium ion is unlikely.

Conclusions

1. Chain transfer to monomer is present at -85°C for the polymerization of p-methoxy- α -methylstyrene in methylene chloride with SnCl_4 initiator.
2. The value of C_M at -85°C is 2.27×10^{-4} .
3. The ratio of the rate constant for termination to the rate constant for propagation at -85°C is 3.21×10^{-5} .

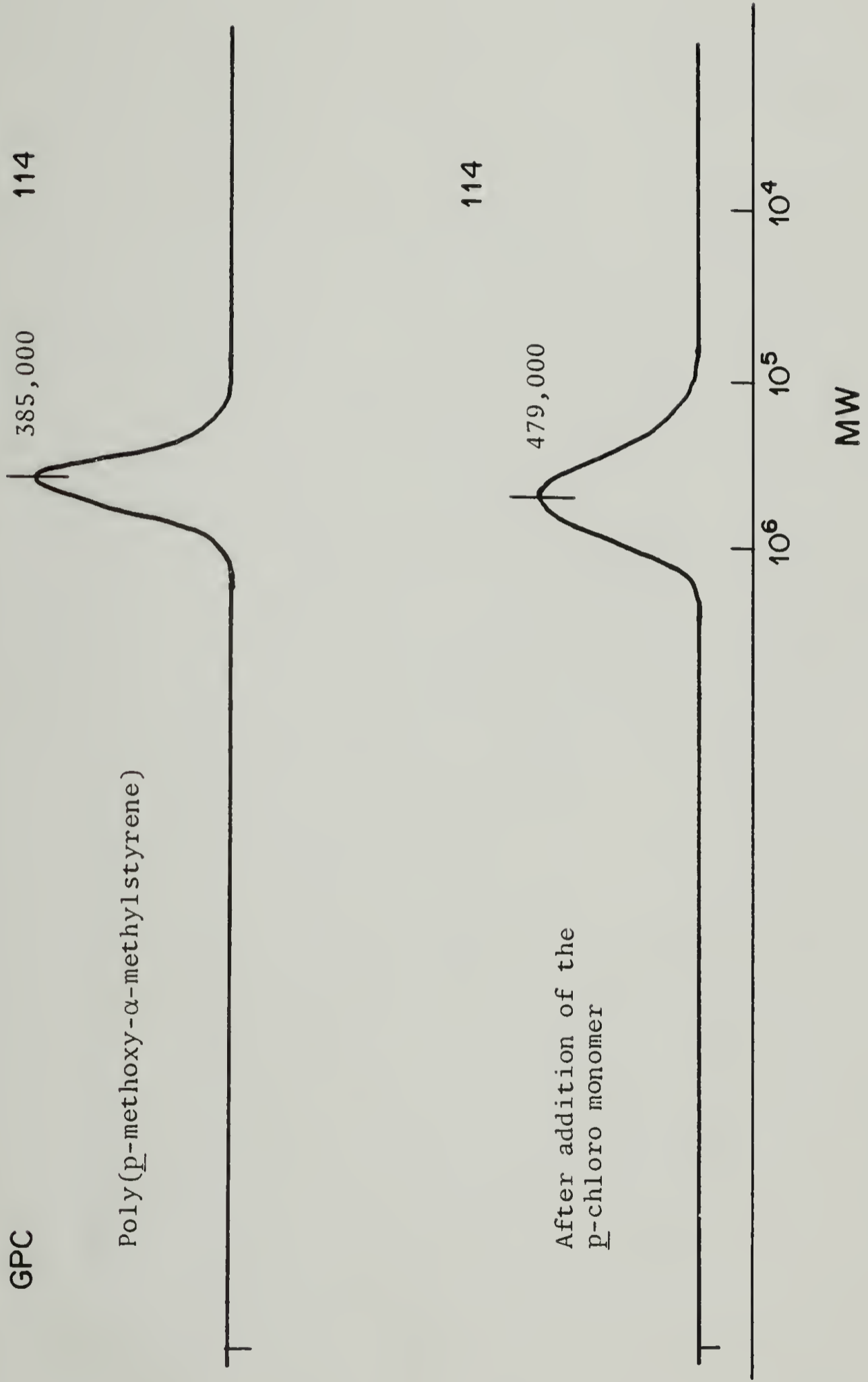


Figure 23. GPC for the sequential addition of the p-chloro monomer.

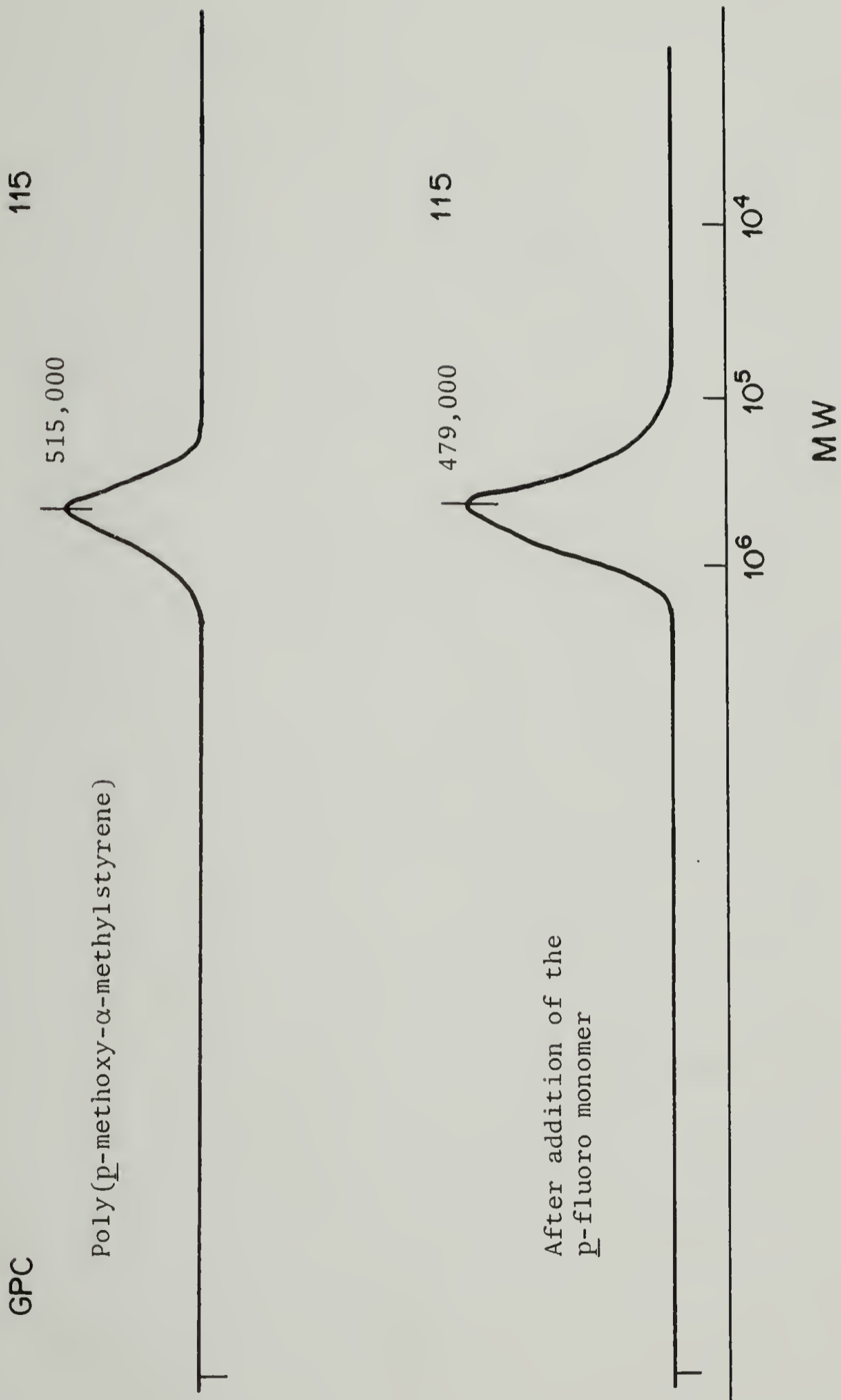


Figure 24. GPC for the sequential addition of the p-fluoro monomer.

4. Poly(p-methoxy- α -methylstyrene) is predominantly syndiotactic as determined by triad tacticities obtained by $^1\text{H-NMR}$.
5. Increasing the temperature of polymerization increases the amount of heterotactic triads in poly(p-methoxy- α -methylstyrene).
6. No isotactic triads were detected.
7. p-Methoxy- α -methylstyrene does not add its own monomer under the conditions used in this study.
8. p-Chloro- and p-fluoro- α -methylstyrene do not add to unquenched poly(p-methoxy- α -methylstyrene).

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C H A P T E R V I

SUMMARY AND RECOMMENDATIONS

The major goals of this work were to determine the nature of the reactions that produced the results of the previous study and to characterize the behavior of the polymerization of the monomers studied. These goals have been met, and new avenues for investigation have arisen. A review of the results of this work is given here followed by recommendations for future work.

Solvent Polarity and Reaction Homogeneity

In Chapter II, precipitation was found to be the cause of abrupt changes in the molecular weights and yields of the p-chloro and p-fluoro polymers and in the tacticity of the p-chloro polymer. As determined by $^1\text{H-NMR}$, the tacticities of both polymers were unchanged with conversion at a constant value of solvent dielectric constant, ϵ .

Variation of the solvent polarity under homogeneous conditions resulted in smooth changes in tacticity for the p-chloro polymer. However, the relative amounts of syndiotactic, heterotactic, and isotactic triads were quite different from the amounts obtained in heterogeneous media at comparable calculated dielectric constant. An isotactic triad content greater than 5% could only be obtained in heterogeneous media.

The tacticity of the p-fluoro polymer remained insensitive to variation of solvent polarity. This behavior supports the postulate that the p-fluoro group, with a negative σ^+ value, stabilizes the propagating carbocation. The p-chloro group destabilizes the carbenium ion by electron withdrawal rendering it sensitive to environmental changes.

Propagation Statistics

The p-chloro polymer followed first-order Markov propagation statistics. A first-order Markov process could not be reconciled to the Kunitake mechanism, despite smooth the tacticity changes with variation of the solvent polarity and high syndiotactic contents at high dielectric constants obtained for the p-chloro polymer.

The statistics followed by the p-fluoro polymer could not be unambiguously assigned. The use of higher order tacticity data such as tetrads or pentads would not be of use. Calculated values of higher order sequences are identical for first-order Markov and Bernoullian statistics based on the triad data obtained for the polymers.

Moisture Detection

The use of tritiated water was found to be a valuable tool in determining the effectiveness of drying procedures. 3Å molecular sieves were determined to be powerful for drying methylene chloride.

Water was found to be impossible to remove entirely from the polymerization system, thereby rendering "stopping experiments" inadequate for determining the role of water in initiation.

Polymerization of p-Methoxy- α -methylstyrene

The conditions necessary to obtain ungelled, easily quenched polymerization media were determined. The number average molecular weights of the polymers varied linearly with varying monomer or initiator concentrations, but did not equal the number average molecular weights calculated based upon the ratio of monomer to initiator concentrations.

The temperature range in which the number average molecular weights were unaffected by temperature variation was determined by use of an Arrhenius plot and the activation energies for the degree of polymerization were calculated. The Mayo Equation was used to evaluate the extent of chain transfer to monomer in this temperature range. Propagation occurred 4000 times as fast as chain transfer to monomer and 32,000 times as fast as termination. The changes in polymer tacticity with temperature followed the same trends as the number average molecular weights. All polymers were predominantly syndiotactic, with increasing syndiotacticity at lower temperatures.

Even though long-lived p-methoxystyrenes have been prepared by initiation with iodine by other investigators, the poly(p-methoxy- α -methylstyrenes) produced in this work were not long-lived.

Recommendation for Future Work

The solvent studies should be expanded to include the p-methoxy and other monomers. The effect of temperature on the tacticities of the p-chloro and p-fluoro polymer prepared in solutions of various polarity should be determined. The extent of chain transfer to monomer for the polymerizations of the p-chloro and p-fluoro monomers should be determined. Knowledge of the propagation rates for the polymerizations would help in determining the identity of the propagating species.

^{13}C -NMR may be used to determine tetrad and higher tacticity data to confirm the first-order Markov behavior of the p-chloro and p-methoxy polymers.

The use of radioactive tracers should be expanded in these polymerizations. If pure, long-lived systems can be developed, labeled reagents can be used to quench the polymerization reaction and to obtain an estimate of active center concentration. A labeled, well-defined, and stable carbocationic initiator can also be used for the same purpose.

Solvent-initiator systems other than methylene chloride-tin tetrachloride should be investigated for use in the polymerization of p-methoxy- α -methylstyrene. The region between -75°C and -95°C should be restudied for temperature effects on molecular weights using shorter polymerization times. Polymerization below -95°C with a nucleophilic counteranion may result in long-lived polymers.

Sequential monomer addition studies should be carried out with well-defined initiators such as t-butyl hexachloroantimonate and comonomers that generate carbenium ions of equal or greater stability than that of p-methoxy- α -methylstyrene.

APPENDIX

The following computer program, written in Fortran IV, was used to calculate molecular weight moments from experimental GPC curves. Line 530 contains the linear calibration curve for a polystyrene standard calibration. The program was written by J. Michael Jonte in 1979 and revised by Daniella J. Fisher in 1982. Lines 891 to 893 contain a calibration curve for the high molecular weight region. It must be noted that the sensitivity of the μ -styrigel columns in the one million molecular weight region decreases, and thus a second calibration is needed for this region.

Computer Program for Calculating
Molecular Weight Moments from
GPC Curves

```

100  PROGRAM GPC(INPUT,OUTPUT)
110C  A PROGRAM TO COMPUTE WEIGHT AND NUMBER AVERAGE MOLECULAR
      WEIGHTS AS WELL AS THE RATIO OF MW TO MN FROM GPC DATA.
120C  THE CALIBRATION DATA FROM A PLOT OF STANDARD SAMPLES IS ENTERED
      VIA A DATA STATEMENT.  THE FLOW RATE, SAMPLE NUMBER, ELUTION
130C  TIMES AND CORRESPONDING PEAK HEIGHTS ARE READ IN.  THE PROGRAM
      CONVERTS THE FLOW AND ELUTION TIMES TO ELUTION VOLUMES
140C  AND THESE RESULTANT ELUTION VOLUMES TO MOLECULAR WEIGHTS
      USING THE EQUATION OF THE LINEAR PORTION OF A CALIBRATION
150C  GRAPH.  MW AND MN ARE CALCULATED BY SUMMING THE APPROPRIATE
      TERMS FOR EACH MOMENT.  THE MWD IS CALCULATED BY DIVISION
160C  OF MW BY MN.  THE RESULTS ARE THEN PRESENTED IN TABULAR FORM.
170C
180C  INPUT NOTES
190C  THE DATA SHOULD BE ARANGED IN THE FOLLOWING MANNER:
200C  ELUTION TIME DATA:  THE FIRST ENTRY SHOULD CONTAIN THE SAMPLE
      NUMBER AND THE NUMBER OF DATA POINTS FOR THAT SAMPLE, AND
210C  THE FLOW RATE CONTAINING A DECIMAL (SEPARATE EACH ENTRY BY
      A COMMA).
220C  THE ELUTION TIMES AND CORRESPONDING PEAK HEIGHTS ARE PLACED
      NEXT.  THEY SHOULD BE ENTERED AS PAIRS, AND MUST CONTAIN
230C  DECIMAL POINTS AND BE SEPARATED BY COMMAS.  (EXAMPLE:
      10.0,1.1,11.0,2.3, AND SO ON)
240C
250C  VARIABLE NAMES -- ALPHETICAL
255C
260C  BSTD ----- Y- INTERCEPT OF CALIBRATION CURVE
270C  ELTIME ----- ELUTION TIME
280C  ELVOL  ----- ELUTION VOLUME
290C  FLRT  ----- FLOW RATE
300C  LGMW  ----- LOG OF MOLECULAR WEIGHT FROM CALIBRATION CURVE
310C  MI    ----- MOLECULAR WEIGHT OF A FRACTION OF THE POLYMER
320C  MN    ----- NUMBER AVERAGE MOLECULAR WEIGHT
330C  MSTD  ----- SLOPE OF CALIBRATION CURVE
340C  MW    ----- WEIGHT AVERAGE MOLECULAR WEIGHT
350C  MWD   ----- RATIO OF MW TO MN
360C  NI    ----- NUMBER OF MOLECULES OF MOLECULAR WEIGHT MI
370C  NIMI  ----- PRODUCT OF NI AND MI (PROPORTIONAL TO PEAK HEIGHT)
380C  NIMISQD ----- PRODUCT OF NI AND THE SQUARE OF MI
390C  NPTS  ----- NUMBER OF DATA POINTS FOR ONE SAMPLE
400C  PKHT  ----- PEAK HEIGHT
410C  SMPLNO ----- SAMPLE NUMBER
420C  SUMNI  ----- SUM OF ALL NI
430C  SUMNIMI ----- SUM OF ALL NIMI
440C  SUMSQD ----- SUM OF ALL NIMISQD

```

```
450C
460C THIS PROGRAM WRITTEN BY J. MICHAEL JONTE, MAY 1979
465C REVISED BY DANIELLA J. FISHER, MAY 1982
470  INTEGER SMPLNO
480  REAL MN, MW, MWD, MSTD, LGMW(100), MI, NI, NIMI, NIMISQD
490  DIMENSION ELTIME(100), PKHT(100), ELVOL(100)
500C
510C SET VALUES FOR SLOPE AND Y-INTERCEPT OF STANDARD CALIBRATION
      CURVE
520C
530  DATA MSTD/-.1483/,BSTD/10.44/
540C
550C PRINT HEADING
560C
570  PRINT 2
580  2 FORMAT (1H,10X, 65HGPC MOLECULAR WEIGHTS AND DISTRIBUTIONS
      FROM WATERS MO
585+  DEL 201 GPC      //)
590C
600C READ SAMPLE NUMBER, NUMBER OF DATA POINTS, AND FLOW RATE
610C
611  4 PRINT 1
612  1 FORMAT(1X, 90 HENTER SAMPLE NUMBER, NUMBER OF DATA POINTS
      AND FLOWRATE, TO
613+  END PROGRAM, ENTER 9999,0,0.0)
620  5 READ*, SMPLNO, NPTS, FLRT
630C
640C CHECK FOR END OF DATA
650C
660  IF(SMPLNO .EQ. 9999)60,10
670C
680C READ ELUTION TIMES AND PEAK HEIGHTS
690C
691  10 PRINT 3
692  3 FORMAT(1X, 37 HENTER ELUTION TIMES AND PEAK HEIGHTS)
700  READ*, (ELTIME(K), PKHT(K), K=1, NPTS)
710C
720C INITIALIZE THE SUMMING VARIABLES
730C
740  SUMNI = 0.0
750  SUMNIMI = 0.0
760C
780C CALCULATE ELUTION VOLUMES FROM ELUTION TIMES AND FLOW RATE
790C
800  DO 20 N=1, NPTS
810  ELVOL(N)=FLRT*ELTIME(N)
820  20 CONTINUE
830C
840C CALCULATE THE MOLECULAR WEIGHTS FOR THE CORRESPONDING ELUTION
```

```

      VOLUMES USING THE CALIBRATION CURVE PARAMETERS AND
850C  SUM THE TERMS OF THE MOMENTS
860C
861C  LINES 891,892,893 ARE USED WHEN ONE CALIBRATION CURVE IS NOT
      VALID FOR THE ENTIRE MW RANGE OF THE COLUMNS
862C
870   DO 30 J=1, NPTS
880   LGMW(J) = MSTD * ELVOL(J) + BSTD
890   MI = 10.0 ** LGMW(J)
891   IF (MI .LE. 10**5.55) GO TO 90
892   LGMW(J) = -0.2288*ELVOL(J) + 12.26
893   MI = 10.0 ** LGMW(J)
900   90 NIMI = PKHT(J)
910   NI = NIMI * MI
920   NIMISQD = NIMI * MI
930   SUMNIMI = SUMNIMI + NI
940   SUMNI = SUMNI + NI
950   SUMSQD = SUMSQD + NIMISQD
960   30 CONTINUE
970C
980C  CALCULATE THE MOLECULAR WEIGHT MOMENTS
990C
1000  MN = SUMNIMI/SUMNI
1010  MW = SUMSQD/SUMNIMI
1020  MWD = MW/MN
1030C
1040C  PRINT HEADINGS
1050C
1060  PRINT 40, SMPLNO
1070  40 FORMAT(///32X,24H***** SAMPLE NUMBER, I8, 11H *****//
1075+  10X, 12 HELUTION TIME, 5X, 11H PEAK HEIGHT /)
1080  PRINT 50, (ELTIME(L), PKHT(L), L=1, NPTS)
1090  50 FORMAT(13X, F5.1, 13X, F5.1/)
1095  PRINT 70, FLRT
1096  70 FORMAT (13X, 12H FLOWRATE = , F4.2)
1100  PRINT 55, MN, MW, MWD
1110  55 FORMAT(//10X, 38H NUMBER AVERAGE MOLECULAR WEIGHT(MN)
      = , F8.0//10X,
1115+  39H WEIGHT AVERAGE MOLECULAR WEIGHT(MW) = , F8.0//10X,
1120+  17H MW TO MN RATIO = , F4.2/////))
1130C
1140C  REPEAT PROCESS FOR NEW SAMPLE
1150C
1160  GO TO 4
1170  60 CONTINUE
1180  STOP
1190  END

```