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Stereoregular poly-[alpha]-methylstyrenes.

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STEREOREGULAR POLY- α -METHYLSTYRENES

A Dissertation Presented

By

Judith Elliott Sutherland

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

DOCTOR OF PHILOSOPHY

March 1972

Major Subject: Polymer Science and Engineering

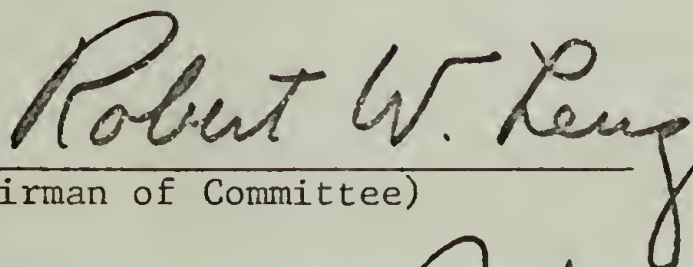
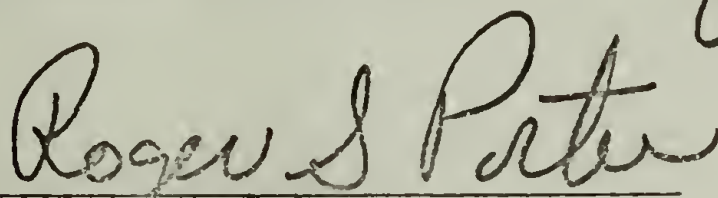
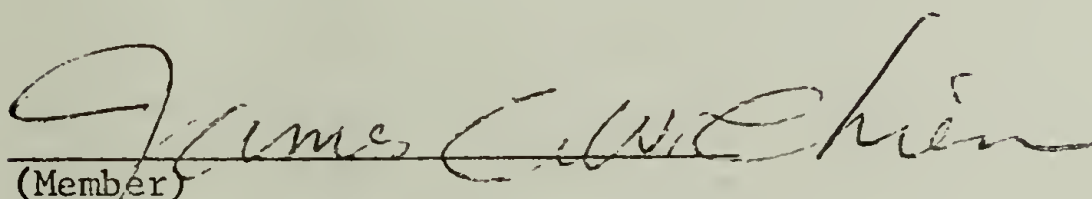
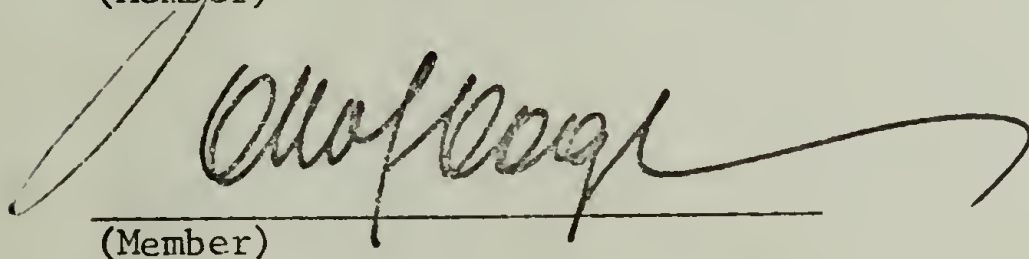
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Approved as to style and content by:


(Chairman of Committee)
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(Member)
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March 1972

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I N T R O D U C T I O N

Poly- α , \underline{p} -dimethylstyrene, which was one of the first vinyl monomers reported to yield a crystalline polymer, was polymerized in a cationic system initiated with BF_3OEt_2 .¹ In 1958 Thomas and Friedlander² polymerized α , \underline{p} -dimethylstyrene, α -methylstyrene, and styrene using BF_3 , BF_3OEt_2 , BCl_3OEt_2 , and SnCl_4 and compared the degree of crystallinity that could be induced in these three polymers under identical conditions of preparation. Crystallinity could be developed in the polymers of α , \underline{p} -dimethylstyrene, but only borderline crystallinity (as indicated by x-ray diffraction patterns) could be induced in α -methylstyrene polymers, and no crystallinity could be observed in styrene polymers. The purpose of the present study, therefore, has been to examine the cationic polymerization reactions of α -methylstyrene and substituted α -methylstyrene monomers in order to determine the differences in the structure of the polymers or in the polymerization mechanism which affect the formation of crystallinity.

Structural Requirements for Crystallinity. Polymer molecules can pack in a regular manner with their chain axes parallel to one another to form solid materials which have three-dimensional regularity that is characteristic of crystallinity found in small molecules. In order to do so, the polymer chain must have a high degree of configurational regularity and be able to assume the conformational regularity required as they pack into the crystal structure. Configurational regularity is determined by the molecular structure and the chemical composition of the monomeric units, the modes of addition of each successive unit, and

the stereoregular placement of the substituent groups. Conformational regularity refers to the geometrical arrangement of the atoms with respect to rotation about single bonds. The conformation which a polymer chain adopts depends upon the bond lengths and angles, the Van der Waals radii, the necessity of staggered bonds, and the planarity of certain groups, i.e. carbonyl groups. Vinyl polymers with isotactic configurations usually assume a helical conformation thus minimizing steric interferences between successive pendant groups, while syndiotactic polymers assume planar zigzag chain conformations. It is necessary that the conformation required, in order for the polymer to pack into the regular order of the crystal structure, must be both thermodynamically and kinetically accessible.

Structural Requirements for Crystallinity. Stereoregularity refers to the configuration of the repeating units in the polymer chain and requires the orderly arrangement of the substituents about the main chain carbon atoms which have two different substituents. In this type

of vinyl monomer unit, $-\text{CH}_2-\overset{\text{X}}{\underset{\text{Y}}{\text{C}}}-$, there are three possible placements

of the substituents of this carbon atom in a triad sequence: isotactic, syndiotactic and heterotactic. An isotactic polymer is one composed predominantly of isotactic triads in which all the substituents on the backbone carbon atom will have the same steric order. A syndiotactic polymer is one composed predominantly of syndiotactic triads in which the substituents on the carbon atom alternate regularly in the steric configuration, and the atactic polymer is one in which the placements

occur randomly so that a large proportion of the triad is heterotactic. Representations are given in Figure 1 where a is a triad with isotactic placement, b is the triad with the syndiotactic placement, and c is the triad with heterotactic placement. In this representation, the backbone carbon atoms are in the plane of the paper and the substituents are represented as being above and below the plane by the solid and broken lines, respectively.

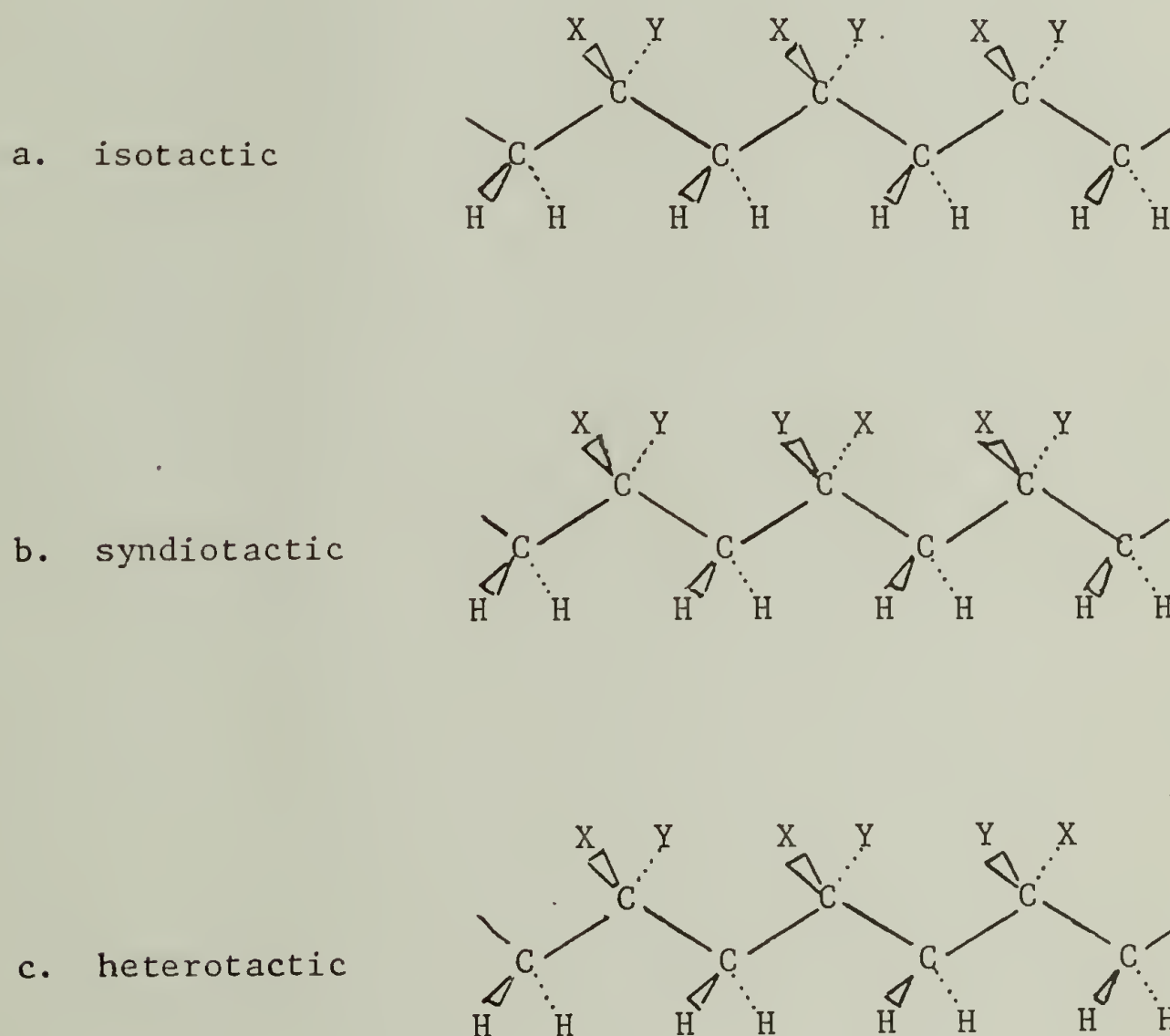


Figure 1. Representation of the configuration in isotactic, syndiotactic, and heterotactic triads.

The substituents on the center carbon atom and the methylene protons in each of the triad sequences have a different molecular environment which can be detected by nuclear magnetic resonance spectroscopy and be used to characterize the microstructure of the polymer. With atactic poly- α -methylstyrene in which one of the substituents is a methyl group and the other is a phenyl, the resonance for the α -methyl protons has been resolved to show a distinct peak for each of the three triad sequences in the region of 9 - 10 τ . Figure 2 is a typical spectrum of an atactic polymer. Three different assignments^{4,5,6} have been proposed for these peaks, and conflicting analysis of the stereoregularity has been reported on the basis of these different assignments. These have been summarized in Table I with the evidence upon which the assignments were made. The assignments of the peaks to each of the three possible triads are given in the order of their increasing field strength, where i, h, and s represent isotactic, heterotactic and syndiotactic triads, respectively.

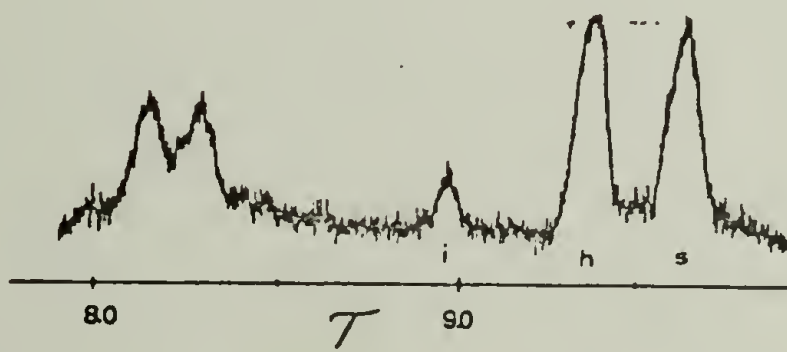


Figure 2. NMR spectra of poly- α -methylstyrene in solution in C_6H_5Cl obtained at 100 MHz and 140°C.³

TABLE I

Summary of the Assignments of the Peaks in the
 α -Methyl Region of Poly- α -Methylstyrene

<u>Order of Assignment with Increasing Field Strength in the Region of 9-10τ</u>	<u>Basis for Assignment</u>	<u>Reference</u>
i, h, s	Model Studies and Similarity to Poly(Methyl-Methacrylate)	4
s, h, i	Considered Crystallinity in Sample as Evidence of Isotactic Configuration	5
h, i, s	Analysis of Methylene Region Using NMR Parameters	6

The protons of the methylene carbon in the backbone chain of poly- α -methylstyrene are equivalent in syndiotactic sequences and non-equivalent in isotactic sequences. If the NMR spectra are well resolved, the methylene resonance absorption appears as a singlet for the equivalent protons and as an AB quartet for the non-equivalent protons.

In 1968 Fujii, Worsfold, and Bywater⁷ reported that deuteration of a methylene proton did not simplify the methylene signals in the NMR spectra of anionically-prepared poly- β -d₁- α -methylstyrene and indicated that the protons in the isotactic placement (meso-methylene protons) were equivalent. Ramey and Statton³ re-examined the methylene region using the spectra from both 100 and 220 MHz instruments. They made new assignments upon the basis of the triad-tetrad relationship which now support the original Brownstein assignment (number 1 in Table I). In 1971 Cantow and his coworkers⁸ analyzed the proton spectra in the phenyl

region of deuterated samples of poly- α -methylstyrene, poly-3,4,5-trideutero- α -methylstyrene and poly-4-deutero- α -methylstyrene (reproduced in Figure 3). He showed that the ortho and meta protons also split into three peaks. Analysis of the microstructure of a deuterated polymer using the ortho-phenyl protons shows good agreement with the analysis of the same polymer using α -methyl protons based on the first assignment in Table I.

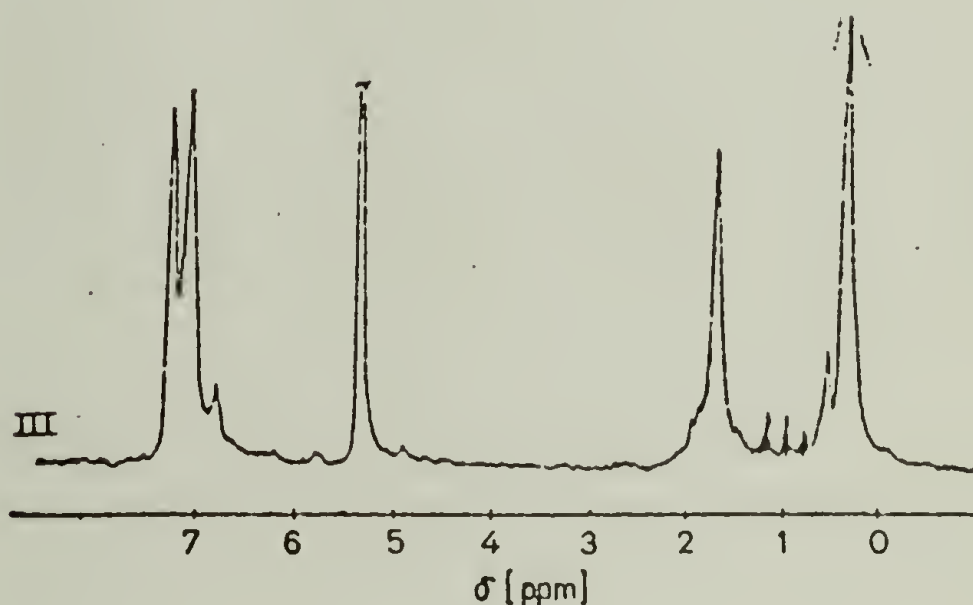


Figure 3. NMR spectra of poly-4-deutero- α -methylstyrene polymerized in a cationic system.

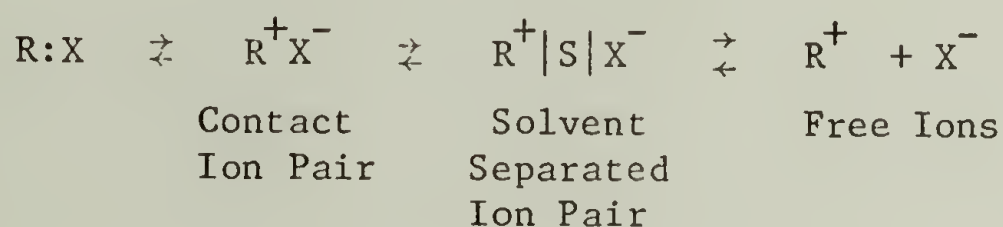
The ring current chemical shift contribution for the protons of the α -methyl substituent of poly- α -methylstyrene based upon the values calculated by Johnson and Bovey⁹ for a hydrogen nucleus at any position

relative to the benzene ring are +0.096, -1.107 and -2.310 ppm for the isotactic, heterotactic and syndiotactic configurations, respectively. The positive value for the isotactic configuration indicates an increase in the apparent field for the protons which causes the resonance peak to occur at a lower applied field strength. The negative values indicate a corresponding reduction in the apparent field and a higher applied field for resonance to occur. The assignment of the three peaks on the basis of the ring currents then would be isotactic, heterotactic and syndiotactic triads with increasing field strength which is in agreement with that proposed by Brownstein, Bywater, and Worsfold. The peaks for the isotactic, heterotactic and syndiotactic triads occur at $\tau = 9.21, 9.76$ and 10.66 , respectively.

Stereoregulation. To prepare vinyl polymers with the high degree of stereoregularity needed for crystallization requires a specific driving force or a mechanism to influence the placement of the incoming monomer unit during the polymerization reaction. A mechanism for influencing the placement of monomer unit is by controlling the relative orientation of the monomer during the addition step. In the stereospecific polymerization initiated by ionic species, this control of orientation requires that the counterion remain associated with the active growing chain end. In the polymerizations in which the propagating end is either a carbanion or a carbonium ion, this influence depends upon the structure of the ion pair.

Both Plesch¹⁰ and Szwarc¹¹ have reviewed the literature concerning the concept and structure of ion pairs and solvated ion pairs

and have summarized the spectral and kinetic evidence supporting their existence. The degree of the separation of the opposite charges of ion pairs depends upon the interaction with the solvent. A contact ion pair is defined as is any pair of oppositely charged ions within a critical distance of each other in which there is no interaction with the solvent between the ions (although the ion pair may be surrounded by a solvent shell). A solvent separated ion pair is one in which the oppositely charged ions are separated by one or more solvent molecules, and free ions are those in which a number of solvent molecules separate the charges so that they behave as essentially independent ions. It has been shown kinetically that these species of ion pairs participate in the solvolysis reaction of alkyl halides in acetic acid¹². Each has its own characteristic rate constant and its own products.



This concept has been used in describing the structure of the possible ionic species present in both cationic and anionic polymerizations. However, the real possibility of the formation of triple ions and higher ionic aggregates must be considered in reactions carried out in non-polar solvents and must be taken into account in speculating about the various structures.

The extent of dissociation of the ions will be influenced by the polarity of the solvent and the ability of the solvent (or monomer,

polymer, or excess initiator) to solvate the ion pair. In very polar solvents the carbonium ions may exist as free ions, but in non-polar solvents there will be an equilibrium concentration of the ion pairs and solvent-separated ion pairs (and other aggregates). Each of these may participate in the chain propagation reaction, and each will have its own characteristic rate constant and stereochemistry. Decreasing the temperature will generally increase the dissociation of the ion pair by increasing solvation and hence will change the magnitude of the rate constants and will shift the equilibrium concentration changing the relative concentration of the several species.

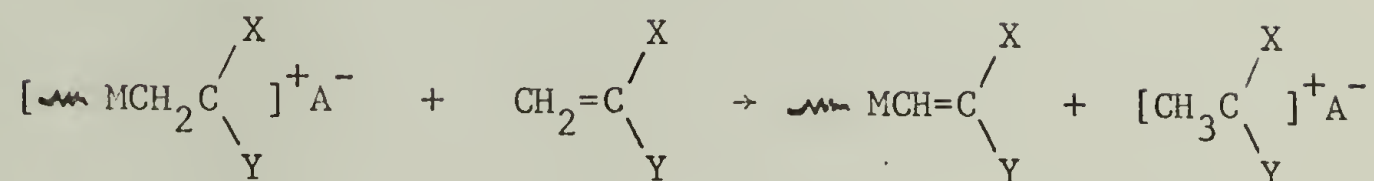
The mechanism, the rate of polymerization, and possible stereoregulation depend upon the exact nature of this interaction. The effectiveness of the stereoregulation by this ionic species depends upon three factors: (1) the extent of the dissociation of the ion pairs, (2) pre-coordination of the incoming monomer unit by the counterion, and (3) the steric and polar contribution of the substituents on the monomer and end group.

Cationic Polymerization. Cationic polymerization reactions of vinyl monomers are chain-growth polymerization reactions in which the active propagating end is a carbonium ion. This propagation reaction will frequently be accompanied by a number of side reactions involving carbonium ions. The molecular weight and yields will be affected by the chain transfer reactions of the various components in the reaction mixture. Examples of these reactions are the following:

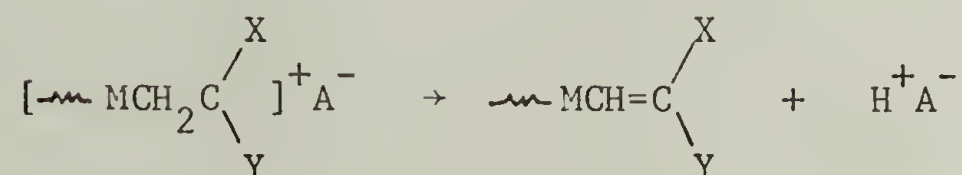
1. Hydride ion extraction from the solvent:



2. Transfer of a proton to monomer:

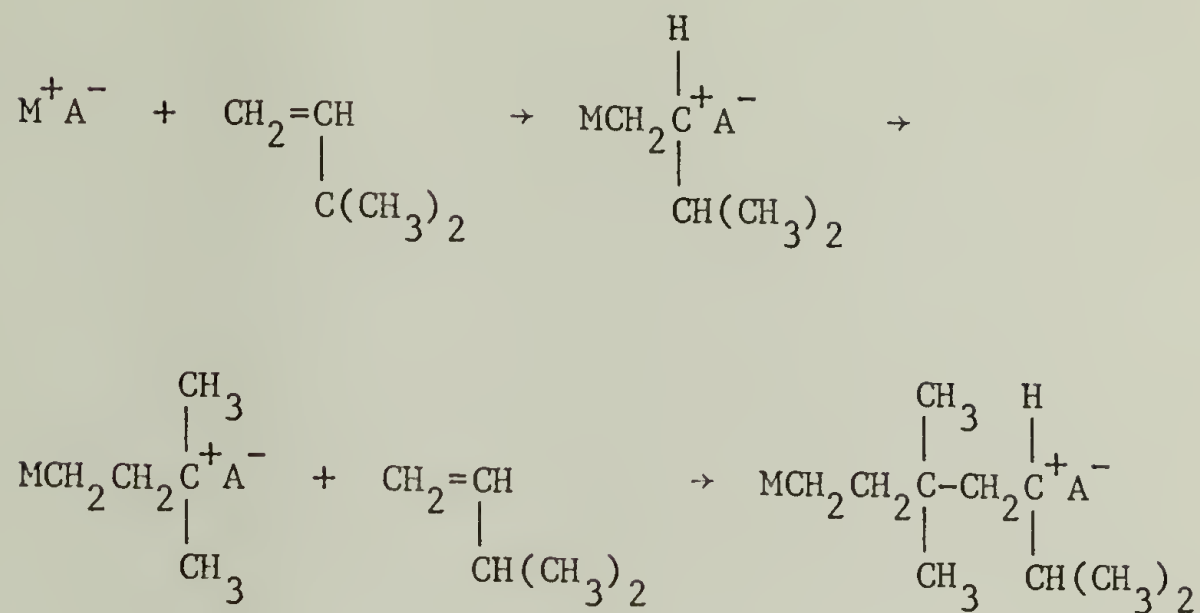


3. Transfer of a proton to the counterion:

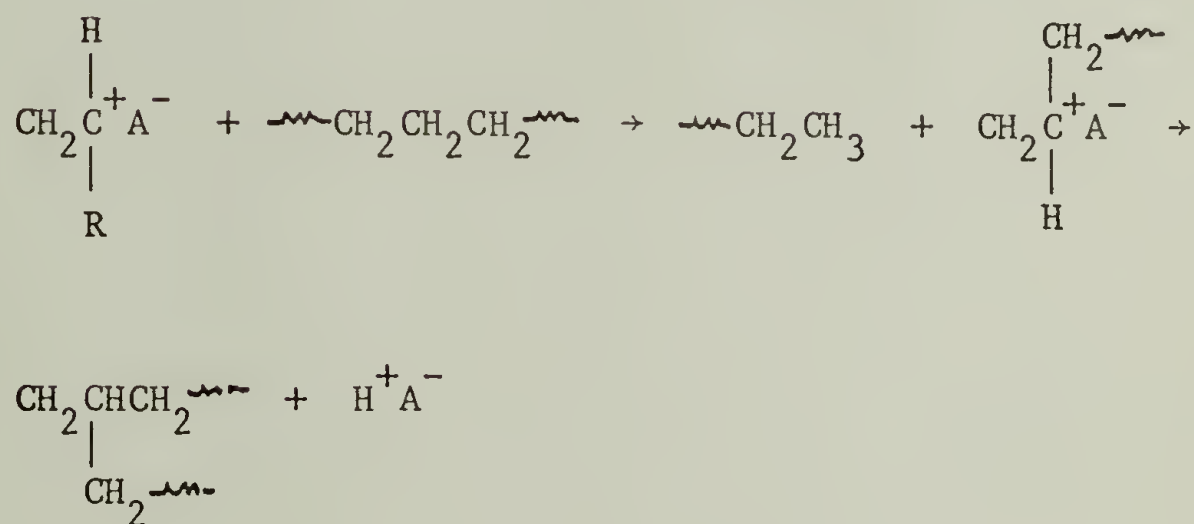


Still other carbonium ion reactions will determine the structure of the polymers formed; their occurrence will depend upon the stability of the carbonium ion. Carbonium ion stabilities are determined by inductive effects and resonance stabilization by the substituent groups. If the structure of the carbonium ion formed is initially a primary or secondary carbonium ion, then the probability of rearrangement to a secondary or tertiary ion, respectively, is very great and the polymers will either be branched or the repeating unit will not be structurally equivalent to the structure of the monomer. These reactions are represented by the following examples:

1. Intramolecular rearrangement to form a different repeating unit:



2. Hydride extraction from the polymer backbone to form branches:



The bulkiness of the substituents can shield the backbone carbons and sterically hinder reactions which result in branching. This shielding effect is found in the polymerization of isobutene and the α -methylstyrene monomers.

Cationic polymerization reactions of vinyl monomers can be initiated by any reaction which will generate a sufficiently reactive

carbonium ion that in turn can propagate to give larger carbonium ions. The types of compounds which have been used include protonic acids, Lewis acids with co-catalysts, and organic cations as well as carbonium ions formed with ionizing radiation. The effectiveness of the initiator in forming high molecular weight polymers depends upon the particular monomer, the solvent, and the temperature.

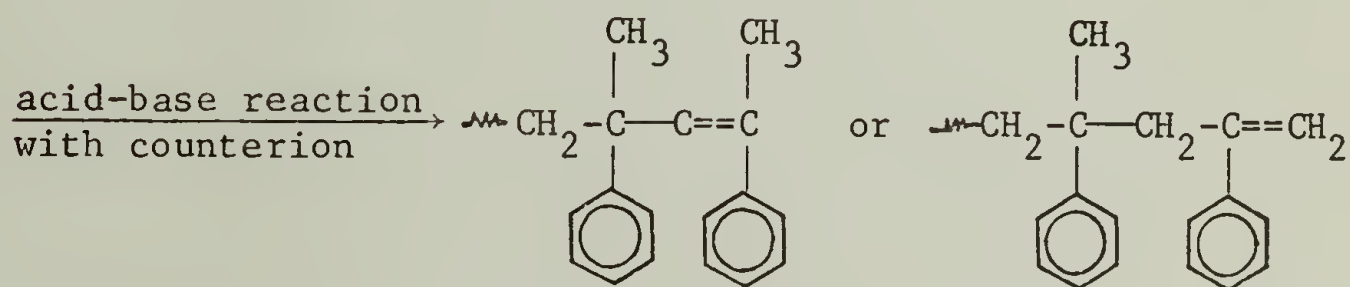
Polymerization Mechanism. The mechanism of several cationic polymerizations of α -methylstyrene has been investigated by kinetic experiments and by analysis of the microstructure of the polymers formed. Attempts have been made to correlate changes in the rate, in the degree of polymerization and in the tacticity of the polymer with variations in the polymerization system.

There is strong kinetic evidence showing that anhydrous Lewis acids do not initiate polymerization but in the presence of a co-catalyst¹³, such as trace amounts of acid, water, or alkyl halide, rapid initiation can occur. It is generally agreed that initiation with protonic acids and Lewis acid cocatalyst complexes occurs by the addition of a proton to the olefinic group of the monomer¹⁰.

When triphenylmethyl salts are used as initiators, the organic cation adds directly to the monomer¹⁴. The rate constant for the initiation reaction of α -methylstyrene was measured for this initiator by following the consumption of the triphenylmethyl cation by UV absorption; at 30°C the rate constant had a value of 2.85 liters/mole/min in methylene chloride. A comparison of the rate of initiation of styrene and α -methylstyrene with triphenylmethyl stannic pentachloride showed that α -methylstyrene is initiated at a rate thirty times faster than that for

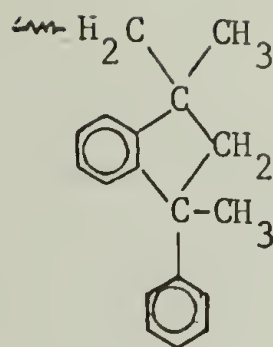
unsubstituted styrene. This increased rate was explained by the increased stability of the carbonium ion because of the inductive effect of α -methyl substituent.

The mechanism generally proposed for the termination reaction in the polymerization of α -methylstyrene is based upon kinetic studies of acid-catalyzed dimerization of this monomer¹⁰ by assuming that the mechanism of termination in polymerization is independent of the degree of polymerization of the propagating polymer and that the chain ends will have structure similar to those found in the dimers. In that case, termination of the polymer chain is accompanied by elimination of the proton from the growing end, either with the assist of or ultimate capture by the counter-anion to reform the initiating species. The dimerization studies showed that two possible structures could be formed from this reaction - one was an unsaturated end:



and the other was a saturated indanyl structure.

self-alkylation →

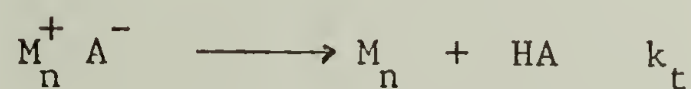


These reactions were dependent upon the catalyst and temperature. At the low temperatures (well below 0°C) required for the preparation of high molecular weight products, the rate of indanyl formation is probably so slow that the chain end should be principally the unsaturated olefinic group. Analysis of low molecular weight poly- α -methylstyrene prepared at 0°C showed that the terminal structure was an unsaturated end group¹⁵.

For the polymerization of α -methylstyrene there are generally two reactions which compete with propagation¹⁰; these are chain transfer reactions which terminate the polymer chain and depropagation. By determining the equilibrium monomer concentration for α -methylstyrene in an anionic polymerization in which there is no chain transfer or termination reaction, Bywater and Worsfold¹⁶ showed that at room temperature the rate of depropagation is not competitive with the rate of polymerization until the monomer concentration is less than 0.025 moles/l. Similarly, in cationic polymerization it may be the rate of chain transfer that limits the molecular weight at room temperature and not the rate of depropagation.

In general for cationic polymerization reactions the degree of polymerization increases with decreasing temperature¹⁷. The reason for this change is that with decreasing temperature the rate of transfer falls off more rapidly than the rate of propagation because of the higher activation energy for transfer. For example, the activation energy for transfer has been found to be 4.5 kcal/mole greater than the activation energy for propagation in the polymerization reaction of α -methylstyrene with SnCl_4 in ethyl chloride.

Most of the kinetic studies on this monomer have been carried out in the temperature range which yields only dimers or low molecular weight polymers. The correlation of the monomer concentration with degree of polymerization and polymerization rate depends upon whether low or high molecular weight products are formed. The following polymerization reaction scheme has been proposed:



HA is an unspecified acid complex which generates a carbonium ion; M_0 is the monomer; $\text{M}_n^+ \text{A}^-$ is the active growing end and M_n is the terminated polymer. Both the polymerization reactions initiated with SnCl_4 in ethyl chloride^{13,18} and $\text{BF}_3/\text{H}_2\text{O}$ ¹⁵ in ethylene dichloride supported this general mechanism. In the latter system there was no kinetic evidence to indicate chain transfer to monomer¹⁵.

The heat of polymerization¹⁶ for α -methylstyrene is 8.15 kcal/mole. This low value is indicative of the steric strain that hinders the propagation reaction.

NMR Analysis. The microstructure of samples of poly- α -methylstyrene prepared in different polymerization systems has been determined by NMR spectra analysis. For comparison purposes, all the results have been interpreted on the basis of the assignments for the resonance peaks of the α -methyl protons proposed by Brownstein, Bywater and Worsfold.

Polymers prepared in low temperature (-78 to -30°C) cationic systems, initiated with Lewis acid complexes or organic cations in solvent in which the polymer was soluble, generally contain 80-90% syndiotactic triads and are the most stereoregular. The same initiators used in solvent in which the polymer was not soluble give more atactic polymers with triad contents of 35-75% syndiotactic triads, 20-45% heterotactic triads, and 1-13% isotactic triads. The atactic polymer is comparable to that of the α -methylstyrene polymers prepared in anionic and Ziegler-Natta polymerization systems.

Table II tabulates the results of three investigations showing the effect of varying the Lewis acid on the stereoregularity of poly- α -methylstyrene. The results of each of the investigations show that the variation in the syndiotactic content of the different polymers was not greater than 2 or 3%. In each investigation the tacticity was independent of the type of Lewis acid used. There are large differences in the triad analyses for samples presumably prepared in comparable systems. However, the variations in the temperature and the solvent in the preparation of the NMR spectra could account for a major portion of the differences.

because the resolution of the NMR spectra of poly- α -methylstyrene and the chemical shifts of the groups relative to each other vary with the solvent⁶.

TABLE II

Effect of the Variation of Lewis Acids on the Stereoregularity of Poly- α -Methylstyrenes^a

<u>Initiator</u>	Fraction of Triads			<u>Reference</u>
	<u>i</u>	<u>h</u>	<u>s</u>	
TiCl ₄	.00	.19	.81	4
BF ₃	.00	.11	.89	4
SnCl ₄	.00	.15	.85	4
AlCl ₃	.00	.15	.85	4
TiCl ₄	.04	.14	.78	19 ^b
BF ₃ OEt ₂	.00	.17	.83	19 ^b
SnCl ₄ / Cl ₃ CCOH	.00	.18	.82	19 ^b
BF ₃ OEt ₂	.00	.00	1.00	20
SnCl ₄	.00	.03	.97	20
TiCl ₄	.00	.00	1.00	20
AlCl ₃	.00	.00	1.00	20

^a Polymerizations carried out in toluene at -78°C. Co-catalyst is assumed to be trace amounts of water unless specified.

^b For comparison purposes, assignment of resonance peaks in NMR spectra interpreted according to Brownstein, Bywater and Worsfold.

Table III tabulates the triad analysis of samples of poly- α -methylstyrenes prepared in a series of solvents with different polarities or abilities to dissolve the growing polymer chain. There are no great differences in the triad contents of polymers prepared in toluene and methylene chloride which have dielectric constants of 2.37 and 8.86, respectively. In this case, therefore, the tacticity appears to be independent of the solvent. The polymers prepared in methylcyclohexane with a dielectric constant of 2.02, all have decreased fractions of syndiotactic triads, but the polymers are not soluble in this solvent and precipitate during polymerization. Ohsumi¹⁹ and Kunitake²⁰ who did this work suggested that the tacticity is dependent on either the solvation of the polymer or the physical state of the reaction system.

Table IV summarizes the results showing the effect of polymerization temperature on the microstructure of poly- α -methylstyrene. In all of the systems examined, decreasing the temperature increased the syndiotactic content of the polymer.

TABLE III

Effect of the Variation of the Solvent on the
Stereoregularity of Poly- α -Methylstyrenes

<u>Initiator</u>	<u>Solvent</u>	Temperature °C	Fraction of Triads			<u>Reference</u>
			<u>i</u>	<u>h</u>	<u>s</u>	
BF ₃ OEt ₂	Toluene	-78	.00	.17	.83	19 ^a
	Methylene Chloride	-78	.00	.16	.84	19 ^a
	Toluene	-78	.00	.00	1.00	20
	Methylcyclohexane	-78	.12	.34	.54	20
TiCl ₄	Toluene	-78	.00	.00	1.00	20
	Methylcyclohexane	-78	.12	.38	.50	20
SnCl ₄ /Cl ₃ CCOH	Toluene	-78	.00	.18	.82	19 ^a
	Methylene Chloride	-78	.00	.16	.84	19 ^a
SnCl ₄	Toluene	-78	.00	.03	.97	20
	Methylcyclohexane	-78	.22	.43	.35	20

^aFor comparison purposes, assignment of resonance peaks in NMR spectra interpreted according to Brownstein, Bywater and Worsfold.

TABLE IV

Effect of the Variation of the Temperature on the
Stereoregularity of Poly- α -Methylstyrenes

<u>Initiator</u>	<u>Solvent</u>	Temperature <u>°C</u>	Fraction of Triads			<u>Reference</u>
			<u>i</u>	<u>h</u>	<u>s</u>	
AlEtCl ₂	Toluene/Hexane	0	.05	.15	.80	5 ^a
		-30	.06	.13	.81	5 ^a
		-78	.00	.08	.92	5 ^a
BF ₃ OEt ₂	Toluene/Hexane	0	.01	.16	.83	5 ^a
		-60	.00	.14	.86	5 ^a
		-78	.00	.13	.87	5 ^a
BF ₃ OEt ₂	Toluene	-30	.01	.12	.87	20
		-75	.00	.00	1.00	20
BF ₃ OEt ₂	Methylcyclohexane	-30	.12	.34	.54	20
		-75	.08	.19	.73	20

^aFor comparison purposes, assignment of resonance peaks in NMR spectra interpreted according to Brownstein, Bywater and Worsfold.

An attempt to correlate the microstructure of poly- α -methylstyrene to the structure of the counter-anion in a polymerization initiated with triphenylmethyl salts and Lewis acids was reported by Matsuguma and Kunitake¹⁶. The data were reported in terms of Bovey's σ value which is the probability of generating an isotactic diad. The σ value was found to be independent of the initiator in the polar solvent (methylene chloride/acetonitrile) but increased with decreasing polarity of the solvent. In an 8:3 mixture of the methylcyclohexane and methylene chloride, the σ value for the counter-anion increased in the following order:



which parallels the order of the increasing size of the counter-anion, with the exception of SnCl_5^- .

These authors proposed a model for the stereospecific propagation which requires the following conditions:

1. the carbonium ion has sp_2 hybridization,
2. the active species is an ion pair,
3. the polymer chain end is in the most stable conformation,
4. the direction of attack by the incoming monomer is regulated by the tightness of the ion pair.

They assumed that the larger anion and the non-polar solvents enhanced the tightness of the ion pair and increased the stereocontrol. With the counterions from the Lewis acids, they proposed that the interaction of the counter-anions with the carbonium ions was weaker and

less effective in influencing the orientation of the incoming monomer. In this case the monomer placement was determined by steric requirements and syndiotactic placement occurred.

Crystallinity. Several workers have examined poly- α -methylstyrene polymers to determine whether the more stereoregular samples could be induced to crystallize. Both Hersberger and his coworkers¹⁷ and Bywater and coworkers⁴ reported that all of the polymers were amorphous.

Okamura²¹ reported that an unstretched film of a high molecular weight sample of poly- α -methylstyrene prepared in n-hexane/chloroform using BF_3OEt_2 gave an x-ray diffraction pattern which was sharper than the pattern reported by Hersberger showing four rings with d-spacing at 8.74, 5.02, 3.75, and 3.08 Å. When the film was stretched to ten times the original length, however, the pattern became diffuse. They attribute this behavior to molecular entanglement and the stereospecific structure of the polymer.

In 1963 Sakurada and his coworkers⁵ reported that α -methylstyrene polymerized with a Ziegler-Natta catalyst gave a polymer in which crystallinity could be induced by a heat annealing procedure under special conditions. According to the NMR high resolution spectra, this polymer was less stereoregular than other samples prepared in the same study. It was reported to have 72% syndiotactic triads^a, 24% heterotactic triads, and 4% isotactic triads. Polymers initiated with BF_3OEt_2 in the same study were 87% syndiotactic and those initiated with AlEtCl_2 were 92% and were not reported to be crystalline.

^aAssignment of resonance peaks in NMR spectra interpreted according to Brownstein, Bywater and Worsfold.

E X P E R I M E N T A L

Chemicals

Monomers:

Sources:

α -Methylstyrene	Eastman Organic Chemicals
α , <u>p</u> -Dimethylstyrene	Pfaltz and Bauer
	K and K Laboratories
	Prepared in This Study*
<u>p</u> -Isopropyl- α -Methyl- Styrene	Aldrich Chemical Company
α ,2,4-Trimethylstyrene	Prepared in This Study*

Initiators:

Boron Trifluoride	Matheson Gas Products
Boron Trifluoride Etherate	Eastman Organic Chemicals

Solvents:

For Polymerizations:

Toluene	Reagent Grade from Stock
Chloroform	Reagent Grade from Stock
<u>n</u> -Hexane	Reagent Grade from Stock
Methanol	Reagent Grade from Stock

For Characterization: Infrared

Carbon Disulfide	Fisher Scientific Company
Chloroform	Matheson, Coleman, and Bell
Benzene	Matheson, Coleman, and Bell

For Characterization: Annealing Studies

<u>n</u> -Heptane	Matheson, Coleman, and Bell
Butanone-2	Pfaltz and Bauer
Heptanone-2	Eastern Chemical Corporation
Octanone-2	Matheson, Coleman, and Bell
Xylene	Columbia Organic Chemical Company
Toluene	Fisher Scientific Company

For Characterization: NMR

Hexachloro-1,3-Butadiene	Eastman Organic Chemicals
Diphenyl Ether	Fisher Scientific Company
Deuteriochloroform	Diaprep, Incorporated

* Prepared according to the direction of Knaeps and Van der Eycken²²

For Characterization: Solution Studies

Carbon Disulfide	Fisher Scientific Company
Methylene Chloride	Mallencrodt
Trifluoroacetic Acid	Eastman Organic Chemicals
1,1,1-Trichloroethane	Eastman Organic Chemicals
Carbon Tetrachloride	Matheson, Coleman, and Bell
Benzene	Matheson, Coleman, and Bell
Chlorobenzene	
Xylene	Columbia Organic Chemical Company
1,1,2,2-Tetrachloroethane	J. T. Baker Chemical Company
2-Dichlorobenzene	Eastman Organic Chemicals
Decahydronaphthalene	Eastman Organic Chemicals
Dimethyl Sulfoxide	Fisher Scientific Company
1,2,4-Trichlorobenzene	Eastman Organic Chemicals
Hexachloro-1,3-Butadiene	Eastman Organic Chemicals
α -Chloronaphthalene	Fisher Scientific Company
Diphenyl Ether	Fisher Scientific Company
Acetone	Matheson, Coleman, and Bell
<u>m</u> -Cresol	K and K Laboratories
Acrylonitrile	Matheson, Coleman, and Bell
Mesitylene	Eastman Organic Chemicals
Styrene	Aldrich Chemical Company
Cumene	Chemical Sample Company
1,2,3,4-Tetrahydronaphthalene	Eastman Organic Chemicals
4,4-Thiobis-6- <u>Tert</u> -Butyl- <u>m</u> -Cresol	(A. Weisman)

Drying Agents:

Calcium Hydride	K and K Laboratories
Linde Molecular Sieve-3A	Union Carbide
Calcium Chloride-Anhydrous	J. T. Baker Chemical Company
Sodium Sulfate-Anhydrous	J. T. Baker Chemical Company
Phosphorous Pentoxide	Fisher Scientific Company

Monomer Synthesis:

Bromomethane	Matheson Gas Product
Diethyl Ether	Mallencrodt
Magnesium Turnings	J. T. Baker Chemical Company

Treatment of Glassware. A drying column for solvent consisted of a large column 3.5 cm in diameter and 50 cm in length with a 1 liter storage flask at the top and a leur tapered ground glass joint for a

syringe needle for the delivery of dry solvent at the bottom. It was equipped with a medium porosity glass frit and a Teflon stockcock and was filled with Linde Molecular Sieve 3A which had been activated by heating to 400°C under a stream of nitrogen for two hours. The contents of the column were protected from the atmosphere by a nitrogen blanket over the reservoir.

A drying column for the monomer was a smaller version of the solvent drying column (1.2 cm in diameter and 32 cm in length) without the reservoir. The column was closed to the atmosphere by a serum cap and a slow stream of nitrogen was admitted during the transfer of the monomer to the reaction flask. A layer of fresh calcium hydride covered the frit to a depth of one inch.

Purification of Monomers. The monomers were purified by washing with three portions of a 10% aqueous solution of sodium hydroxide followed by three portions of distilled water (or until neutral to indicator paper). Preliminary drying was over anhydrous sodium sulfate. The monomer was stored over calcium hydride until evolution of hydrogen ceased. Just prior to use, the monomer was transferred to a drying column for the monomer and added directly to the reaction system or a dried flask for temporary storage. The analysis of the monomers by gas chromatography are given in Table V.

Initially, after the inhibitor was removed as described above, the monomers were distilled under vacuum. The procedure was discontinued because of dimerization in the still flask and the formation of trace amounts of polymer in the collection flask when chilled to -78°C.

TABLE V

Analysis of Monomers by Gas Chromatography

<u>Monomer</u>	<u>Source</u>	<u>% Purity</u>
α -Methylstyrene	Eastman Organic Chemical	99.8
α , p -Dimethylstyrene	Pfaltz and Bauer	99.8
	K and K Laboratories	99.2
	Prepared in This Study	99.9
p -Isopropyl- α -Methylstyrene	Aldrich Chemical Company	99.1
α ,2,4-Trimethylstyrene	Prepared in This Study	99.9

10% Carbowax M-20 on Chrom-W support

Purification of Solvents. Toluene: Toluene was distilled and a center cut (60%) was subsequently refluxed over metallic sodium for forty eight hours. It was distilled into a dry-serum-capped brown bottle. If the solvent were to be stored for longer than three weeks, it was transferred to a drying column containing activated molecular sieve (3A). The solvent was delivered from this column into the reaction flask as needed.

Hexane: n -Hexane was purified according to the directions for preparing spectroquality solvent²³. It was stirred with two portions of fuming sulfuric acid, washed with a 5% aqueous solution of sodium hydroxide and water until neutral to indicator paper. The solvent was refluxed over metallic potassium for forty eight hours and distilled into a dry-serum-capped bottle. It was transferred to a drying tower for storage and was delivered into the reaction flask as needed.

Chloroform: The chloroform was refluxed over phosphorous pentoxide for twenty four hours and distilled directly into the reaction flask. It was not stored longer than twenty four hours.

The solvents were checked for water by gas chromatography and none was detected.

Purification of Initiators. Boron trifluoride etherate was dried over calcium hydride and vacuum distilled into a flask closed with a serum cap. It was not stored longer than ten days.

Boronfluoride was used without further purification.

Polymerization Procedure. All glassware used for polymerization reactions was dried in a 140°C oven for at least four hours and cooled in a dessicator. Larger pieces were cooled in a stream of nitrogen. The reaction system was assembled, closed to the atmosphere with serum caps, and flamed while being purged with nitrogen. Transfers were made with dry-nitrogen filled syringes.

Solution Polymerization Initiated with BF_3OEt_2 . The polymerization initiated with BF_3OEt_2 was carried out in a 100 ml three-neck flask equipped with a stirrer with a Teflon blade, a nitrogen inlet and a pressure release trap containing n-butyl phthalate. In a typical preparation 27 ml of dry toluene and 3.3 ml of α -methylstyrene (0.0254 moles) were added directly to the reaction flask. The mixture was well stirred, cooled to -78°C in an isopropanol-carbon dioxide bath, and 0.1 ml of BF_3OEt_2 (0.79^m moles) was added. After four hours, the reaction was terminated by pouring into rapidly stirring methanol. A white product precipitated and was collected by filtration. The polymer was washed with several portions of methanol. The excess methanol was

removed and without further drying the polymer was dissolved in chloroform and reprecipitated in methanol. It was dried in a vacuum oven at 60°C for twenty four hours. This reaction gave a yield of 2.2 g (73%) of poly- α -methylstyrene with a number average molecular weight of 220,000 (in toluene at 37°C). The analyses were: C, 91.49%; H, 8.54%. (Calculated for $[\text{C}_9\text{H}_{10}]_n$: C, 91.47%; H, 8.53%.)

Polymerization Initiated with BF_3 . In the polymerization initiated with BF_3 , the same reaction set-up and procedure were followed as described for the initiation with BF_3OEt_2 . The stirrer was replaced with a magnetic stirring bar and the BF_3 was injected for 10 seconds into the reaction flask which was equipped with a pressure release trap. The gas above the reaction mixture was at atmospheric pressure.

Polymerization of α ,p-dimethylstyrene. In the polymerization with p-substituted monomers the polymer precipitated during the reaction. The reaction mixture rapidly became a very stiff gel and stirring was discontinued. Because the polymers were insoluble at room temperature, they were extracted with methanol for twenty four hours in a soxhlet in place of reprecipitation. This was followed by an extraction for 4 to 6 hours with butanone-2 and another twenty four hour extraction with methanol.

To decrease the molecular weight of the polymers, several variations in the procedures were tried in an attempt to prepare soluble polymers of α ,p-dimethylstyrene. In one case the initiator was added directly to the solvent and a 10% solution of the monomer in the same solvent was added dropwise with stirring. In a second variation, a 10%

solution of the BF_3OEt_2 initiator was added dropwise to a monomer-solvent mixture.

In a third experiment, the BF_3 was injected above the solvent for ten seconds while nitrogen was being swept through the reaction flask. The nitrogen sweep was continued while the flask was chilled to -78°C . The monomer which was diluted with the solvent to form a 30% solution was chilled to -78°C and injected slowly. The BF_3 above the solution initiated polymerization as the monomer solution left the needle. A long-orange-stalactite-like needle was formed. When unreacted monomer reached the solvent in the flask, an orange color developed.

In another modification, a 50% solution of α,\underline{p} -dimethylstyrene was added to a dry test tube closed with a serum cap. The polymerization was initiated by injecting BF_3 for ten seconds while at room temperature and the reaction mixture was plunged into an isopropanol/carbon dioxide bath. No color developed and no polymer was detected in a sample withdrawn from the reaction flask after twenty four hours. The remaining reaction mixture was returned to the -78°C bath and reinitiated. An orange-colored film formed at the surface of the monomer-solvent mixture immediately. Over a period of ten days the orange color and stiff gel slowly extended into the main bulk of the mixture until the whole mixture became a stiff gel. If the tube were allowed to warm, the color would begin to disappear. When rechilled to -78°C , the color returned. The polymer formed in the system was not soluble.

Copolymer Composition. Homopolymers of poly- α -methylstyrene have been shown to depolymerize upon thermal degradation to yield 95% monomer²⁴. It is assumed that the substituted α -methylstyrenes will also depolymerize and that the individual monomers can be detected by gas chromatography. Therefore, the samples of the copolymers were subjected to thermal degradation in a nitrogen atmosphere in a Pyrex tube and the volatile products were condensed in a U-tube chilled to -78°C . The condensate was rinsed from the U-tube with methylene chloride. A sample of this solution was analyzed by gas chromatography on a column of 10% Carbowax on a Chromosorb W substrate at 125°C . The relative areas for the peaks in the chromatogram for each monomer present in the condensate is a measure of each monomer in the copolymer.

To check the response of the gas chromatograph, samples of the monomer and mixtures of the monomer pairs were examined. The retention time on the column for the three monomers are:

α -methylstyrene	2.5 min
α , p -dimethylstyrene	4.0 min
p -isopropyl- α -methylstyrene	7.0 min

Table VI gives the monomer pairs, the mole ratio of each preparation, and the ratio of the area under the peaks for each analysis.

TABLE VI

Comparison of the Mole % Ratio in Each Monomer Pair
with the Ratio of Area Under Each Peak in the
Gas Chromatograms

<u>Monomer Pair</u>	<u>Mole % Ratio</u>	<u>Ratios of Area Under the Peaks</u>
p-H/p-Me	1.12	1.14
		1.12
p-H/p-isopropyl	1.50	1.51
		1.54
p-Me/p-isopropyl	1.32	1.33
		1.31

p-H: α -methylstyrene; p-Me: α ,p-dimethylstyrene;
p-isopropyl: p-isopropyl- α -methylstyrene

This result shows that each monomer can be detected in the gas chromatograph without interference due to the presence of the second monomer.

In a typical experiment, a sample of the copolymer of α ,p-dimethylstyrene with α -methylstyrene, C-3 (22 mole % α -methylstyrene), was thermally degraded at 315°C. After thirty minutes 97% of the sample had volatilized. The volatile products were condensed in the U-tube. One milliliter of methylene chloride was used to rinse the products from the U-tube. A 10 μ l sample was analyzed on the gas chromatograph and gave two peaks, one occurring after 2.5 minutes and the other after 4 minutes. The first peak was due to the α -methylstyrene component and the second peak was due to the α ,p-dimethylstyrene component. The α -methylstyrene content of this copolymer was 22%. Figure 4 gives a trace of this analysis.

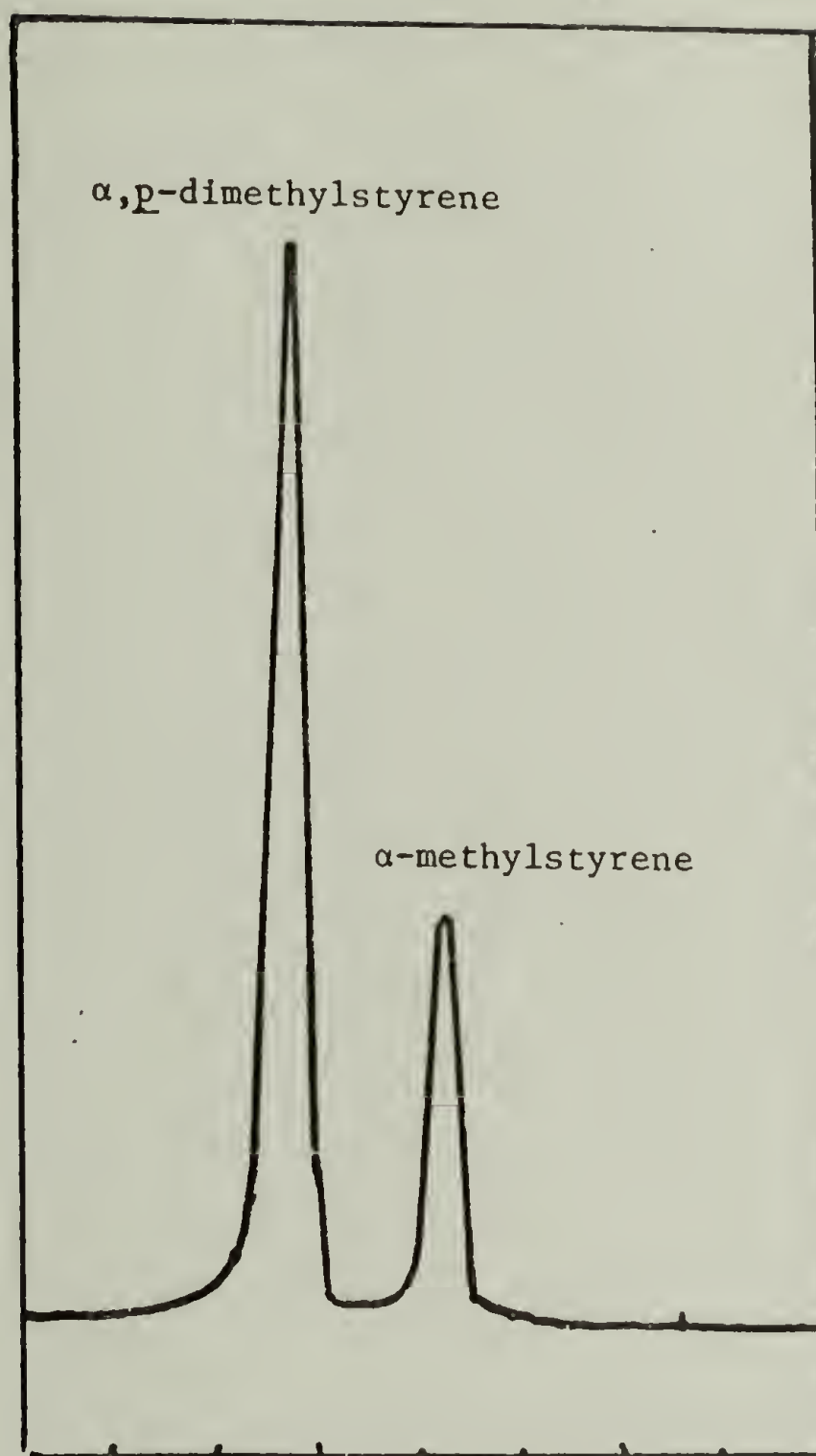


Figure 4. Gas chromatogram of analysis of the products from thermal degradation of the copolymer of α ,p-dimethylstyrene and α -methylstyrene.

Characterization. All polymer samples were characterized for structure and composition by infrared spectroscopy, nuclear magnetic spectroscopy, elemental analysis, molecular weights, crystallinity, and thermal analysis.

Infrared spectroscopy: Infrared absorption spectra were obtained on a Perkin Elmer Grating Spectrophotometer Model 257. Samples of poly- α -methylstyrene were examined as thin films cast from chloroform onto sodium chloride plates and as solutions in carbon disulfide. The spectra of the p-substituted polymers and copolymers were obtained from either pressed films or KBr discs.

Elemental Analysis: Elemental analyses and molecular weight determinations were provided by the Microanalytical Laboratory. The elemental analysis for carbon and hydrogen were run on a Coleman Carbon Hydrogen Analyzer.

Molecular Weights: Molecular weights were measured on either the Hewlett Packard Vapor Osmometer Model 301A in chloroform at 37°C or benzene at 50°C or the Hewlett Packard Membrane Osmometer, Model 501, in toluene at 37°C or chloroform at 25°C.

Viscosities: Viscosities were measured in a Ubbelohde viscometer at $30.00 \pm 0.03^\circ\text{C}$. Viscosity average molecular weights were calculated using the relationship derived from light scattering measurements by Sirianni²⁵.

$$[\eta] = 1.08 \times 10^{-4} M^{0.71}$$

Crystallinity: Two methods were used for the qualitative detection of crystallinity in the polymers: (1) X-ray diffraction using a General Electric Diffractometer Model XRD-5 and (2) observation under the polarizing microscope. The x-ray diffraction spectra were prepared using nickel-filtered $\text{CuK}\alpha$ radiation (35Kv, 20 ma). The forward reflections were recorded from a flat surface of powder specimens.

Glass Transition: The glass transition, T_g , were also determined on the Differential Scanning Calorimeter at heating rates of $20^\circ\text{C}/\text{min}$. The value of the T_g reported for the various polymers was taken from the midpoint of the slope of the line between the initial base line and the line after the transition. The T_g was the average of two to four runs for at least two samples of each preparation. These values were confirmed by observing the disappearance of strain birefringence in films on the Mettler Hot Stage mounted on a polarizing microscope.

Thermogravimetric Analysis: Thermogravimetric analysis was obtained using a DuPont Thermal Analyzer to measure the thermal stability of the polymers. The samples were heated at $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

Film Preparation: Films were molded between heavy aluminum foil on a Pasadena Hydraulics, Inc. press. The α -methylstyrene polymers were preheated to 210 – 215°C for five minutes and then pressed at 11,000 psi for ten minutes. The films were air cooled. The poly(α , p -dimethylstyrene) samples were molded at 190°C at 2500 psi for three minutes.

Dynamic Mechanical Measurements: The dynamic mechanical measurements were made on the Vibron Dynamic Viscoelastometer.

Gas Chromatography: The purity of the monomer and the solvent was checked on a Varian Aerograph Gas Chromatograph. The columns that were used were 10% Carbowax M-20 on a Chromosorb W substrate. The detector was a thermal conductivity bridge, and the carrier gas was helium. For monomer analyses, the column temperature was set for 80-230°C and was programmed at 10°C/min.

Nuclear Magnetic Resonance Spectroscopy: Nuclear magnetic resonance spectra were obtained on a Varian A-60 and A-100 instruments. The spectra of the poly- α -methylstyrene samples were prepared in hexachloro-1,3-butadiene at 120°C. The spectrum of the poly- α , p -dimethylstyrene sample was prepared in diphenyl ether at 175°C. The microstructure of each polymer was determined by measuring the relative area under the peaks for the α -methyl protons by the cut and weigh method.

Melting: The crystalline melting temperature was determined on a Perkin Elmer Differential Scanning Calorimeter Model DSC 1-B. The calibration of the instrument was checked before each use by recording the melting endotherm of a tin sample. The instrument was adjusted so that the onset of this endotherm occurred at 505°K. The range of the melting endotherm as well as the peak have been recorded for each crystalline sample. These values were checked by observing the disappearance of the birefringence on a hot stage Mettler mounted on a polarizing microscope.

R E S U L T S A N D D I S C U S S I O N

In the beginning of this study, the assumption was made that the stereoregularity and the rate of crystallization were the two parameters influencing the formation of crystallinity in the poly- α , p -dimethylstyrene. It was my intention to prepare this polymer and correlate the variations in the polymerization reaction and to re-examine the cationic polymerization of α -methylstyrene and determine the differences which lead to the formation of amorphous polymers.

The cationic system, BF_3OEt_2 in toluene at -75°C had been reported to form crystalline poly- α , p -dimethylstyrene by Thomas and Friedlander². Okamura²¹ had reported the preparation of crystalline poly- α -methylstyrene in a mixture of n -hexane and chloroform initiated with BF_3OEt_2 . Therefore, the cationic polymerizations of these two monomers, α -methylstyrene and α , p -dimethylstyrene, were re-examined in reactions initiated with BF_3 and BF_3OEt_2 in toluene, n -hexane and in a mixed solvent (n -hexane/chloroform 7:3) at -78°C , and the properties and microstructure of the polymers were characterized. The study was extended to two other ring substituted α -methylstyrene monomers: p -isopropyl- α -methylstyrene and α ,2,4-trimethylstyrene.

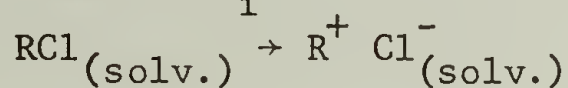
Structure of the Monomers. α -Methylstyrene is a vinyl monomer with two bulky substituents on the α -carbon; viz., a methyl and a phenyl group which can exert inductive and resonance effects, respectively, to stabilize a carbonium ion in a cationic polymerization. Both the stability of the carbonium ion and the bulkiness of the substituents have a direct influence on the nature of the competitive chain transfer

reactions, the ceiling temperature and reversibility as well as influencing the structure of the ion pair end group in cationic polymerization. Any changes in the stability of the carbonium ion should be detected either in the properties of the polymers - the molecular weight and molecular weight distribution or the microstructure.

p-Substitution of an alkyl group increases the stability of the incipient carbonium ion by releasing electrons to the electron-deficient carbon to disperse the partial positive charge which in turn decreases the energy of activation in the transition state. There is evidence for this in small compound chemistry. Successive substitution of a p-methyl group in triarylmethylchloride has been reported to lower the free energy of ionization showing that the carbonium ion had become more stable.

TABLE VII¹⁰

Values of ΔG_i° for the Reaction:



<u>RC1</u>	ΔG_i° <u>Tetrachloroethane</u>
$(\text{C}_6\text{H}_5)_3\text{CCl}$	5.8
$(\text{p-MeC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CCl}$	5.0
$(\text{p-MeC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CCl}$	4.5
$(\text{p-MeC}_6\text{H}_4)_3\text{CCl}$	3.6

In a ^{13}C NMR study²⁶ of a series of styrenes, substitution of a methyl or alkyl group in the p-position was shown to increase the shielding at the β -carbon suggesting an increase in the conjugative interaction of the ring with the vinyl group which is an indication of an increase in the electron density at that position and, therefore, presumably an increase in the ability to stabilize the carbonium ion at the α position. The effect of this increased stabilization can be seen in comparing the propagation rate constant in cationic polymerization of styrene with p-methylstyrene²⁷. The p-methylstyrene monomer reacts twenty-five times faster than styrene in a cationic polymerization.

Substitution in the p-position should not significantly affect the steric requirements but substitution in the o-position would. In the same ^{13}C NMR study, the authors, on the basis of chemical shift data, proposed that the o-methyl substituent introduces steric hindrance to conjugation of the vinyl group with the benzene ring. The presence of this substituent causes the vinyl group to be slightly twisted out of the plane of the benzene ring and effective interaction is decreased. However, if the o-substituent is a methoxy group in place of a methyl group, the degree of steric hindrance is less. A model of the o-methoxy substituted polymer shows that the angle which the carbon-oxygen-carbon bonds form places the bulk of this substituent out of plane of interference with the α -methyl group.

Properties of the Initiators. Boron trifluoride²⁸ is a non-polar, colorless gas at the temperature of these polymerizations. It has a melting point of -127.1°C and a boiling point at -99.9°C . It is

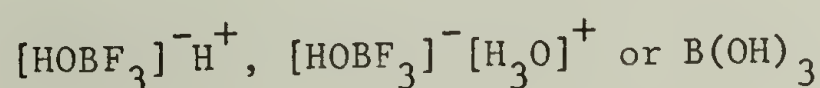
a trigonal, planar molecule with sp_2 hybridization. The boron-fluorine bond is 1.30 Å, the fluorine-boron-fluorine angle is 120° and the distance between fluorine atoms is 2.25 Å. This compound is a strong Lewis acid. Because of the length of the boron-fluorine bond, it has been postulated that the bonding has partial double bond character. This partial double bond character accounts for the order of reactivity found in the series of boron halides:



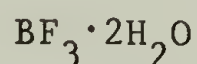
which is the reverse order that one would expect on the basis of the electronegativity of the halide. Boron trifluoride exists as a monomeric compound but complexes easily with electron donor compounds such as ethers, esters, and other Lewis bases to form stable complexes.

Boron trifluoride is added to the polymerization reaction as a gas. It is soluble in toluene and chloroform but essentially insoluble in n-hexane.

Most authorities agree that a cocatalyst is required for initiation of polymerization with BF_3 . There are several possibilities: a complex with a monomer unit to give the tetrahedral structure similar to BF_3OEt_2 ; a complex with adventitious trace impurities such as water or acid; or a stable intermediate complex from reaction with water. Boron trifluoride combines with water to form complexes with either one, two or three moles of water to give:



The crystal structure²⁹ of at least one of these complexes has been determined - the boron trifluoride dihydrate:



Boron halides react with water to yield boric acid and hydrogen halides. With BF_3 , many of the intermediates are stable species and the reaction does not go to completion. Dihydroxyfluoroboric acid, $[(\text{HO})_2\text{BF}_2]\text{H}$, was obtained by Nieuwland³⁰ from the reaction of 1 mole of BF_3 with 2 moles of H_2O from a distillation at 25 mm of Hg.

Boron trifluoride etherate is a 1:1 complex of boron trifluoride and diethyl ether. The bonding in the boron trifluoride is changed from sp_2 to sp_3 hybridization to form a tetrahedral structure with an increase in the boron-fluorine bond length from 1.30 Å to 1.43 Å. The boron-oxygen bond is 1.50 Å. The bonding in the ether is unchanged (at least in the case of dimethyl ether). This coordination compound is a polar, colorless liquid at room temperature which is stable and can be distilled. It has a dipole moment of 4.92 D, a melting point of -60.4°C and a boiling point of 125.7°C . Boron trifluoride etherate is added to the polymerization mixture as a liquid but all reaction temperatures used in this study were below the melting point of the initiator so crystallization often occurred.

Properties of the Solvents. Toluene has a slight but definite polarity with a dielectric constant of 2.4 and a dipole moment of 0.37 D. n-Hexane is a non-polar solvent with a dielectric constant of 1.99 at -50°C . Both solvents have a melting point of -95°C .

Chloroform is a polar solvent with a dielectric constant of 6.76 at -60°C and a dipole moment of 1.87 D. Its melting point is -61.7°C . When used as a co-solvent in polymerization reactions carried out at -78°C , a hexane-chloroform-monomer mixture is a viscous solution.

The solvent has a dual role in these polymerization reactions: as a diluent for the reactants and the products and as a possible agent for solvating the ions or ion pairs. Since initiation with BF_3 requires a co-catalyst, essentially the active species is being generated in situ in these polymerizations. Therefore, the interaction with the solvent may directly influence the mechanism of the reaction, the structure of the active species, and the rate of formation.

Polymerization of α -Methylstyrene. Table VIII gives the data and observations for the polymerization reactions in the polymerization of α -methylstyrene with BF_3 and BF_3OEt_2 in toluene, n-hexane and the mixed solvent, n-hexane/chloroform. Table IX tabulates the data for the elemental analysis, the number average molecular weights (\overline{M}_n), the viscosity average molecular weights (\overline{M}_v) and the percent yield. No color was observed in the polymerizations initiated with BF_3OEt_2 in toluene or the mixed solvent (n-hexane/chloroform) or with BF_3 in toluene. The polymerizations initiated with BF_3 in the mixed solvent and in n-hexane had a characteristic orange color. The orange color appeared at the instant of initiation and remained until the reaction was terminated by the addition of methanol. In the polymerization with the monomer frozen at -78°C , color developed immediately on the addition of both initiators, yellow for BF_3OEt_2 and orange for BF_3 .

TABLE VIII

A Summary of the Polymerization Reactions of
 α -Methylstyrene in the Cationic System at -78°C

<u>Sample No.</u>	<u>Solvent</u>	<u>Monomer Conc. Vol %</u>	<u>Mole Ratio [M]/[I]</u>	<u>Reac- tion Time Hrs.</u>	<u>Color</u>	<u>State</u>
BF_3OEt_2						
A-6	Toluene	11	32	4	None	sol
B-12	Toluene	10	46	12	None	sol
A-23	Hexane	9	13	6	None	--
A-66 ^c	Hexane	9	15	21	Yellow	ppt
A-54	Mixed ^a	10	88	7	None	sol
B-14	Mixed ^b	7	67	17	None	ppt
C-13	Bulk	100	6	96	Yellow	--
BF_3						
A-9	Toluene	11	5	23	None	sol
A-22	Hexane	9	4	16	Orange	ppt
A-64	Hexane	9	4	21	Orange	ppt
A-55	Mixed ^a	8	4	5	Orange	sol ^d
C-11	Bulk	100	13	96	Orange	--

^aMixed: Hexane/chloroform: 7:3 (vol/vol)

^bMixed: Hexane/chloroform: 86/14 (vol/vol)

^cReaction reinitiated

^dA mixture of polymer in solution and precipitated polymer. Pre-
 cipitated fraction was a trace to less than 2% of the total yield.

TABLE IX

Analytical Data for Poly- α -Methylstyrene

Sample No.	Solvent	%C ^a	%H ^a	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_v/\overline{M}_n$	Yield %
BF ₃ OEt ₂							
A-6	Toluene	91.49	8.54	220	540	2.4	73
B-12	Toluene	91.47	8.31	140			87
		91.32	8.52				
A-23	Hexane						sl
A-66	Hexane						19
A-54	Mixed ^b	91.19	8.30	48	295	6.1	39
		91.24	8.34				
B-14	Mixed ^c	91.49	8.26	205			51
		91.68	8.26				
C-13	Bulk			.78			89
BF ₃							
A-9	Toluene	90.48	8.74	425	480	1.1	100
A-22	Hexane	90.69	8.51	4.07	20	5.0	46
A-64	Hexane	90.85	8.26	1.10			55
A-55	Mixed ^b	91.30	8.60	<30	449	~14	100
		91.24	8.55				
C-11	Bulk			1.27			86

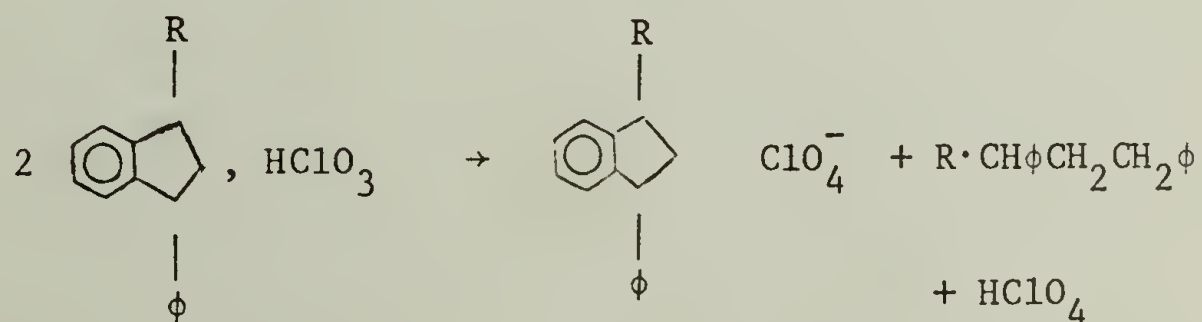
^aCalculated for [C₉H₁₀]_n: C, 91.47%; H, 8.53%

^bMixed: Hexane/chloroform: 7:3 (vol/vol)

^cMixed: Hexane/chloroform: 86:14 (vol/vol)

No attempt was made to identify the source of the color. The possible sources of this color would be the cation in the propagating chain, the indanyl ion in the chain termination reaction or a Friedel-Craft reaction with the BF_3 and the benzene ring which is found in ring alkylation reactions. The free carbonium ion is not likely in the polymerization of α -methylstyrene in hexane nor is the indanyl ion likely at the temperature (-78°C) of this reaction. Therefore, it is concluded that the color is due to a Friedel-Craft reaction with the aromatic ring and BF_3 .

The absence of color in the polymerizations initiated with BF_3OEt_2 suggests that the propagation is by ion pairs or covalent end groups. The covalent end group has been proposed by Plesch³¹ to account for one of several reaction mechanisms that have been observed in the polymerization of styrene in methylene chloride or ethylene dichloride with perchloric acid. This particular reaction requires a four mole excess of monomer, is insensitive to water but sensitive to the addition of common ion, a perchlorate salt. Plesch concluded that the active species was a non-ionic intermediate. Originally he proposed that this intermediate was a linear perchlorate ester of polystyrene. More recent evidence suggests that indane compounds may be involved³¹.



All of the polymerization reactions carried out in toluene were apparently homogeneous. In the mixed solvent, the nature of the polymerization reaction depended upon the ratio of the hexane to chloroform. In the more hexane rich media, the polymerizations were heterogeneous. Those samples of poly- α -methylstyrene which were prepared in n-hexane precipitated during the polymerization. These polymers had lower molecular weights and were obtained in lower yields. Boron trifluoride etherate is insoluble in n-hexane at -78°C and only limited initiation occurred in this system. When the initiation was repeated two more times, the polymer yield was increased to 19%. Polymer precipitated as soon as the initiator was added. A yellow color developed after the third addition of initiator.

Polymers prepared in toluene had a number average molecular weight greater than 140,000. The $\overline{M}_v/\overline{M}_n$ ratio, which is a qualitative measure of the distribution, is between 1 and 2.4. The polymers prepared in the mixed solvent (hexane/chloroform 7:3) had a $\overline{M}_v/\overline{M}_n$ ratio of 5 to 14 indicating that the samples had large fractions of very low molecular weight species. The presence of a low molecular weight fraction suggests the existence of dimers to oligomers.

Poly- α -methylstyrene samples prepared with both initiators were white granular powders which were soluble in the common organic solvents such as toluene, benzene, and chloroform at room temperature. The infrared absorption spectra, the nuclear magnetic resonance spectra and the elemental analyses confirm that each of the samples is a linear vinyl polymer.

The infrared adsorption spectrum of poly- α -methylstyrene (Figure 5) shows the major bands for mono-substituted benzene with bands at 760 and 690 cm^{-1} and a strong band for the methyl substituent at 1470 cm^{-1} . In the very low molecular weight polymers no branching by alkylation of the benzene ring was detected. No differences in structure were detected in the infrared spectra of the polymers prepared in varying reaction conditions.

The thermogravimetric analysis for this polymer is given in Figure 6. Poly- α -methylstyrene is thermally unstable. When a sample of the polymer is heated at a rate of 10°C/min, the onset of rapid degradation occurs at 280°C; however, this is preceded by a much slower rate of degradation that is first observed near 150°C.

Crystallinity was not detected in any of the samples of poly- α -methylstyrene prepared in this study by x-ray diffraction or by thermal analysis on the DSC. The x-ray diffraction spectra of powders showed only the two amorphous halos characteristic of amorphous polystyrene diffraction spectra. The maxima of these two halos occurred at 16 and 10° 2 θ .

High resolution nuclear magnetic spectra of all samples of poly- α -methylstyrene prepared in this study reproduce those in the literature for polymers prepared in cationic systems. Figures 7 and 8 give spectra of polymers prepared in a good solvent and a non-solvent for the growing polymer chain. In Figure 7 the portion of the spectra assigned to the α -methyl protons is resolved into two peaks, while the resonance peak of the methylene protons is a single peak with a shoulder. In Figure 8 the sample is more heterotactic and the α -methyl protons

are divided into three peaks for the isotactic, heterotactic and syndiotactic triads. The fourth peak observed in this region may be assigned to a chain end. The chemical shifts relative to dioxane for the resonance peaks are given in Table X.

TABLE X

Chemical Shifts of Protons in the NMR Spectra
of Poly- α -Methylstyrene

<u>Protons</u>	Chemical Shift, ppm ^a	
	<u>Figure 7</u>	<u>Figure 8</u>
Aromatic	-3.50	-3.52
	-3.36	-3.36
Methylene	+1.99	+1.40
		+1.96
α -Methyl		
Isotactic	--	+2.54
Heterotactic	+3.05	+3.00
Syndiotactic	+3.27	+3.26
Chain End	--	

^aRelative to dioxane, 100 MHz spectra

The analysis of the microstructure of the polymers are given in Table XI where the fractional concentration of the triads are tabulated as i, h or s for the isotactic, heterotactic and syndiotactic triads. The glass transition temperature, T_g , and the calculated glass transition temperature at infinite molecular weight, $T_g(\infty)$, are included.

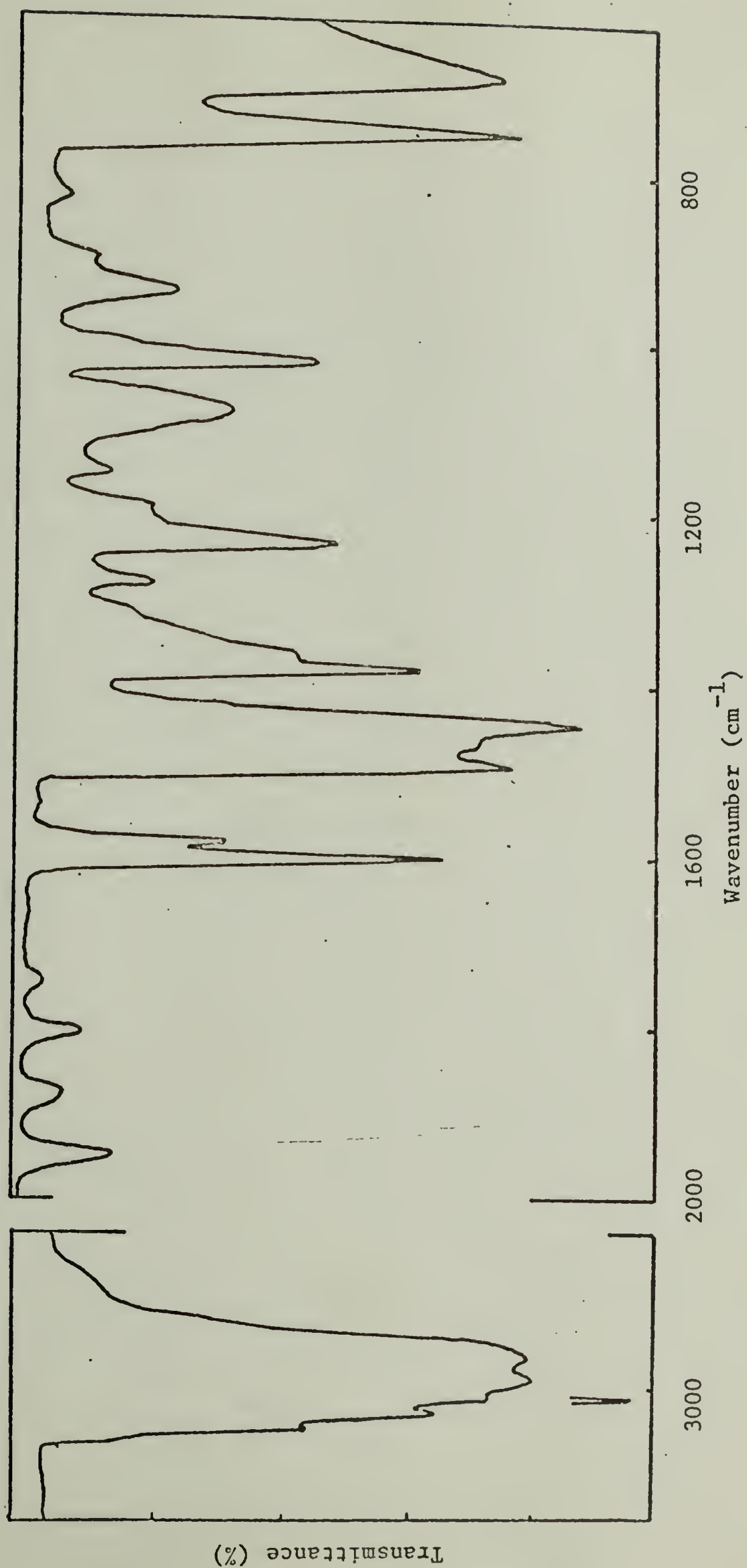


Figure 5. Infrared absorption spectra of poly- α -methylstyrene

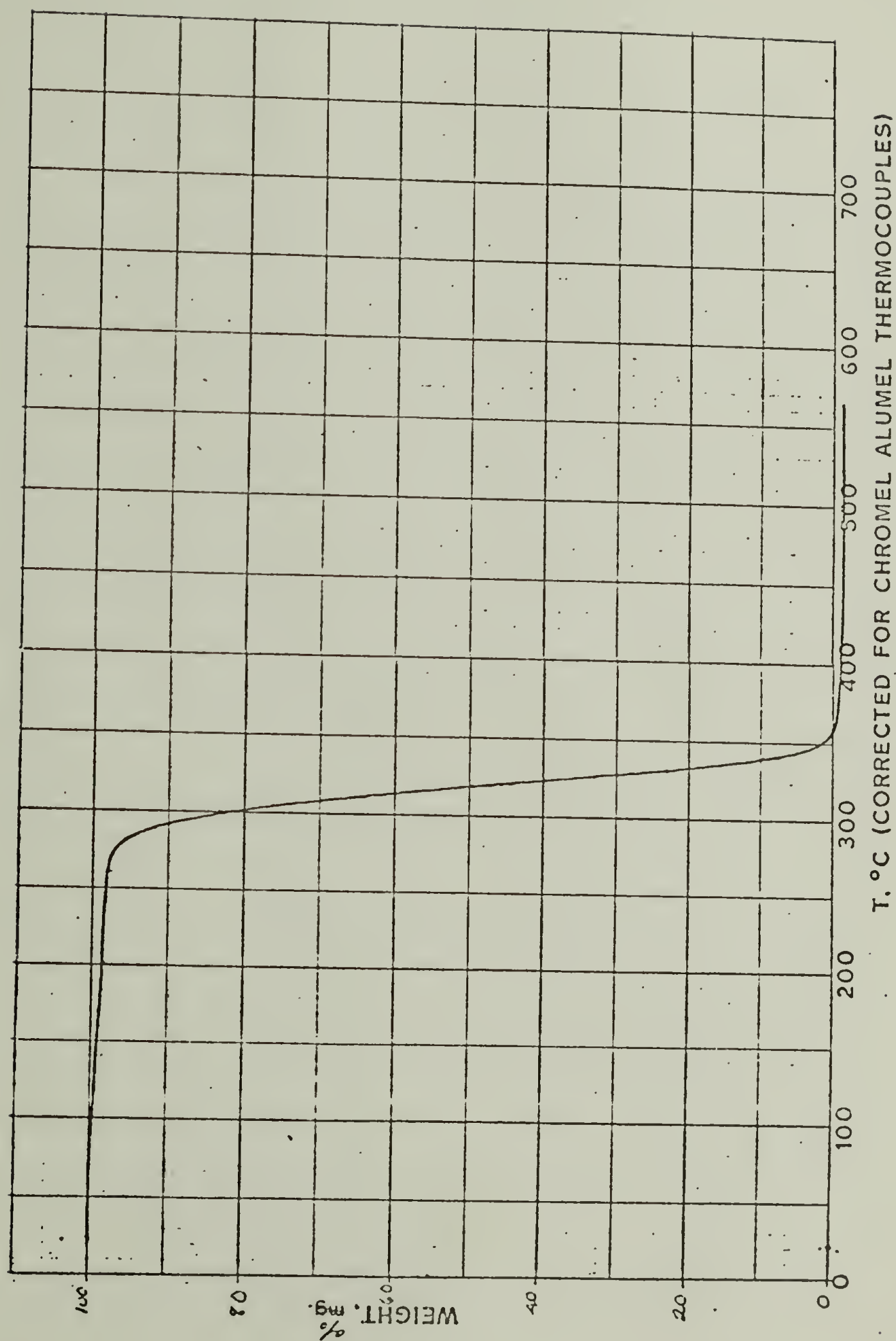


Figure 6. A TGA thermal curve of poly- α -methylstyrene at a heating rate of 10°C/min in a nitrogen atmosphere.

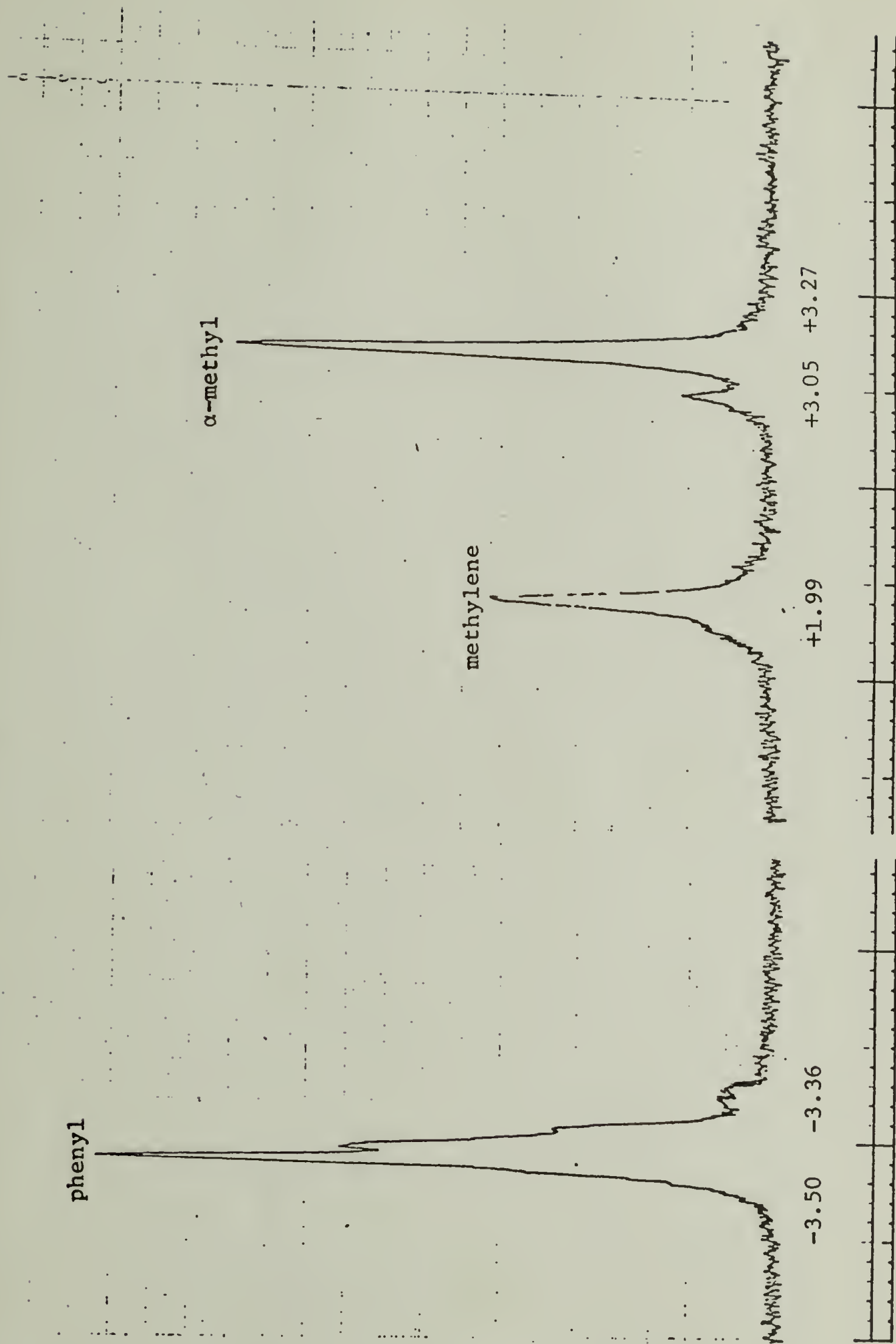


Figure 7. NMR spectra of poly-α-methylstyrene prepared in toluene/ BF_3OEt_2 . Sample was in solution in hexachloro-1,3-butadiene at 100 MHz and 120°C.

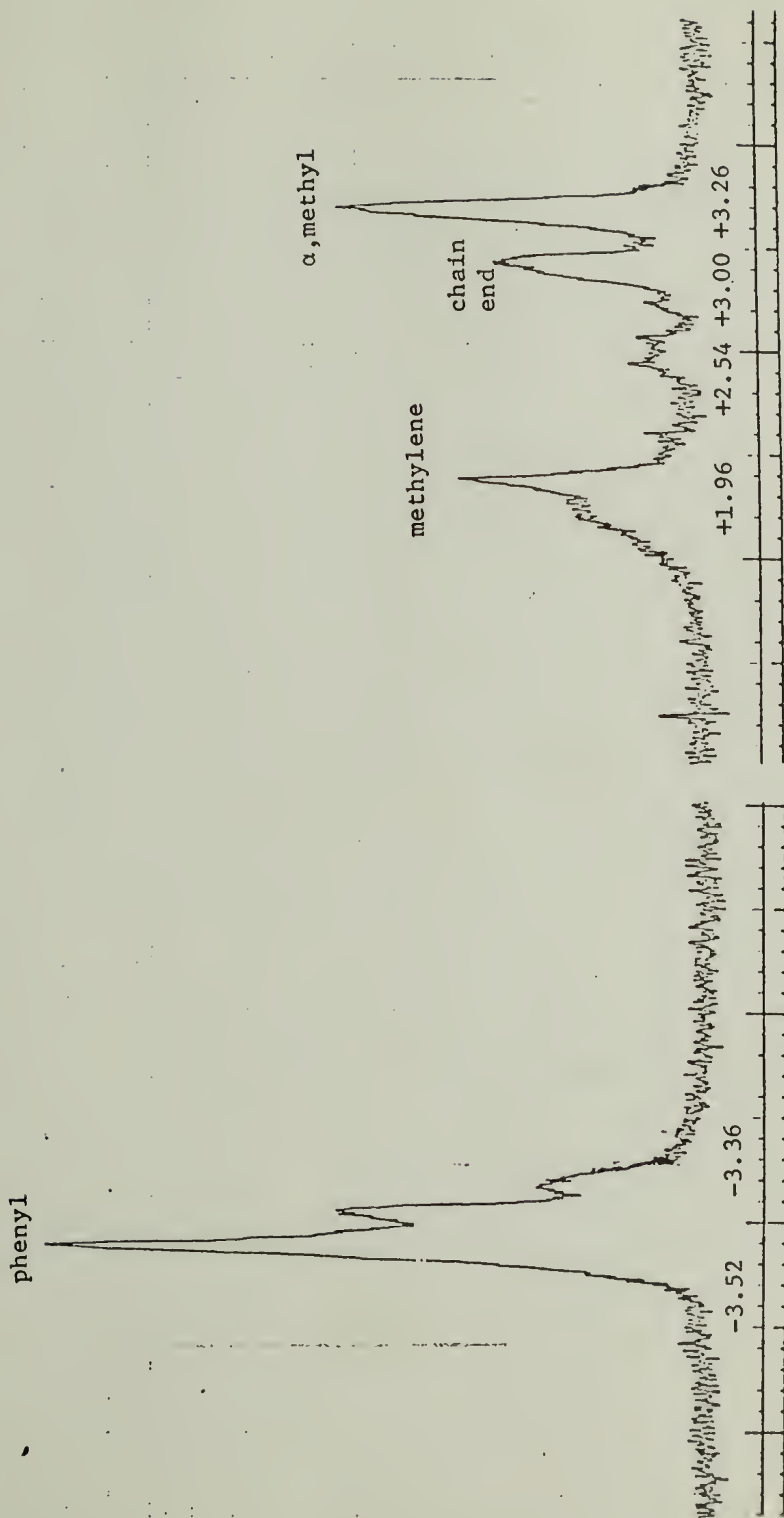


Figure 8. NMR spectra of poly- α -methylstyrene prepared in hexane/ BF_3 . Sample was in solution in hexachloro-1,3-butadiene at 100 MHz and 120°C.

TABLE XI

Characterization of Poly- α -Methylstyrene by
Glass Transition and Triad Analysis^a

<u>Sample</u>	<u>Solvent</u>	<u>T_g</u> <u>°C</u>	<u>T_g(∞)</u> <u>°C</u>	Triad Analysis		
				<u>i</u>	<u>h</u>	<u>s</u>
BF ₃ OEt ₂						
B-12T	Toluene	181				
B-12M		187	190			
B-12A		179				
A-6		187	188	0	0.11	0.89
A-54	Mixed ^b	184	191	0	0.19	0.81
A-23	Hexane	173				
A-66		115				
BF ₃						
A-9	Toluene	188	189	0	0.12	0.88
A-55	Mixed ^b	175	187	0	0.16	0.84
A-22	Hexane	152		0.11	0.32	0.57

^aTriad Analysis from NMR spectra prepared on a Varian A 100 at 120°C in hexachloro-1,3-butadiene

^bMixed Solvent: n-hexane/chloroform

The value of $T_g(\infty)$ is calculated using Cowie's relationship for the dependency of the T_g on molecular weight: $T_g = T_g(\infty) - 3.6 \times 10^5 M_n^{-1.32}$. This relationship holds for both syndiotactic and atactic polymers for the range of the molecular weight data included in the study. It does

not hold for polymers with a \overline{M}_n less than 5,000. Figure 9 is a representative trace of the glass transition observed on the Differential Scanning Calorimeter.

Samples of polymers which were prepared in a good solvent, toluene, had the highest concentration of syndiotactic triads: 88-89%. The fraction of syndiotactic triads in the polymers prepared in the mixed solvent was 81-84%. However, the differences in the glass transition of these polymers recorded in Table XI are due to molecular weight differences rather than tacticity. The fraction of syndiotactic triads is reduced approximately 30% for the polymers prepared in the non-solvent, n-hexane. Since Cowie's relationship for the dependency of T_g on molecular weight does not hold for polymers with a \overline{M}_n less than 5,000, it is not possible to separate the effect of tacticity and molecular weight on the glass transition of these polymers prepared in n-hexane. It should be noted that the polymers prepared in the mixed solvent had large M_v/M_n ratios which suggests that the increase in the isotactic diad fractions may be related to the low molecular weight tail in these polymers.

Films which were prepared by casting from a toluene solution were subjected to various procedures of heating and solvent swelling to induce crystallinity. The films were not stable above the glass transition temperature, and degradation was always observed in annealing experiments in which the samples were held for any period of time above this temperature. Birefringence associated with crystallinity could not be detected under the polarizing microscope in the solvent-cast films or the films molded at 190°C. No crystallinity was induced in

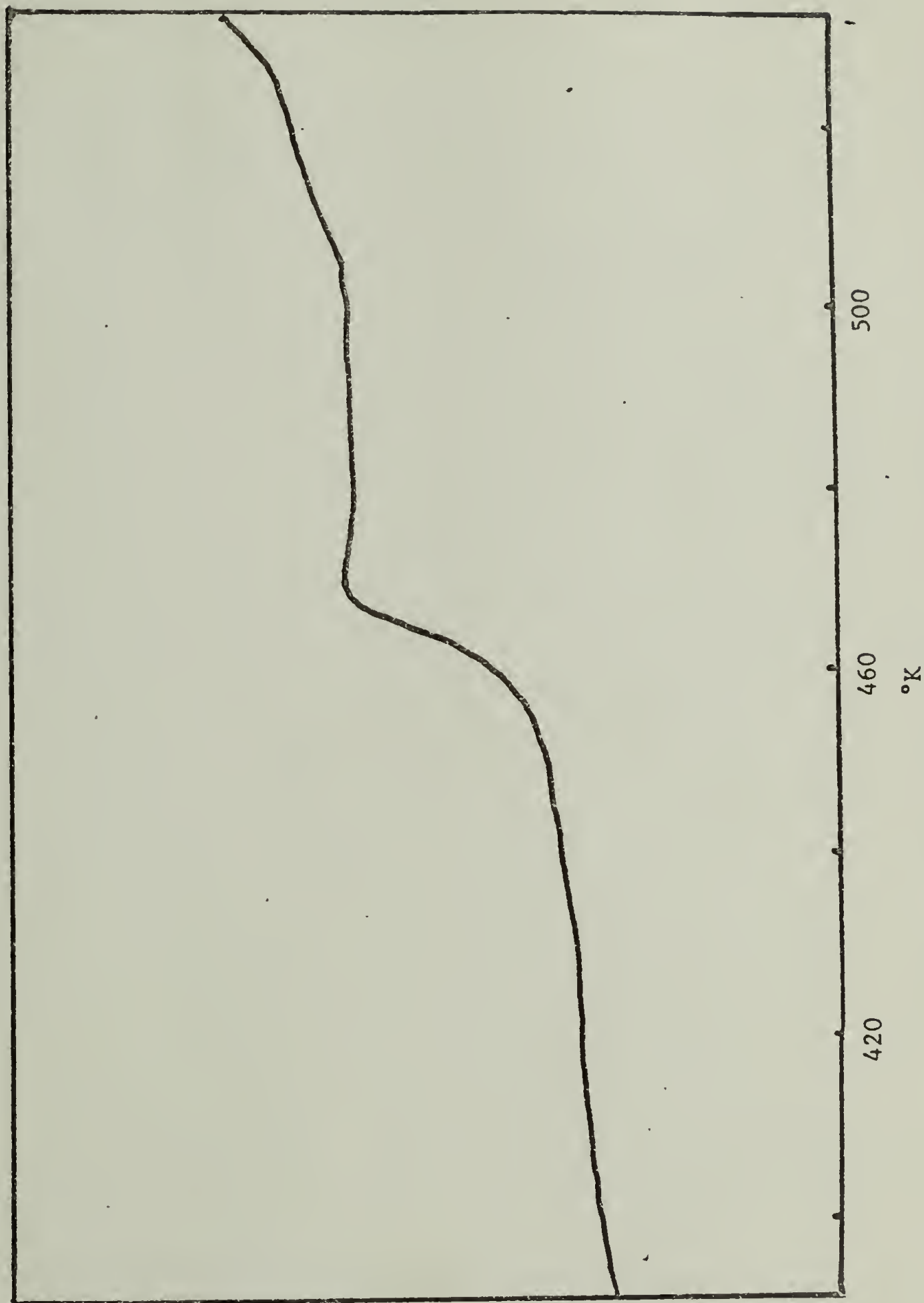


Figure 9. Typical DSC curve for poly-α-methylstyrene showing the glass transition.

these polymers by any of the annealing procedures used in this work.

The dynamic mechanical behavior of two films was examined on the Vibron at a frequency of 100 Hz. For both samples only one loss peak was observed. For the solvent-cast film in which no degradation was evident, the loss peak occurred at 160°C and for the molded film the loss peak began at 140°C.

Influence of the Solvent. It is believed that the microstructure of the polymer is not dependent upon the polarity of the solvent but on the nature of the polymerization. That is, the decrease in syndiotacticity and accompanying increase in heterotacticity is associated with the heterogeneity of the system. Kunitake and Aso²⁰ observed the same trend in the polymerization reactions done in methylcyclohexane. They reported that in a mixture of toluene and methylcyclohexane, the syndiotacticity decreased with increasing content of methylcyclohexane.

The molecular weight is also dependent upon the solubility of the polymer in the reaction diluent. The influence of solubility is more obvious when the $\overline{M}_v/\overline{M}_n$ values are compared. Thus, poly- α -methyl styrene samples prepared in hexane and in the mixed solvent containing 70% hexane had much broader molecular weight distributions than those prepared in the good solvent, toluene. One can only speculate as to what factors are operative here. The broader molecular weight distribution may be due to a chain transfer reaction which is competitive with propagation in these solvents and not toluene or there may be two different species from the ion pair equilibrium propagating simultaneously.

Influence of Initiator Reagents. There appears to be no significant difference in the microstructure of the polymers prepared with BF_3 or BF_3OEt_2 in the solvents used in this study. However, there are differences in the yields obtained, particularly in the case of n-hexane. Very low yields were obtained in the n-hexane/ BF_3OEt_2 reaction system, but in the n-hexane/ BF_3 system low molecular weight polymers were formed in 45 to 55% yields. Boron trifluoride is a gas which was present during the reaction in the volume above the reaction medium. Therefore, there was a constant source of initiator present. It is likely that the increased yields were due to the increased initiation which occurred because of the continuing source of additional initiator reagent.

Polymerization of Poly- α , β -Dimethylstyrene. Poly- α , β -dimethylstyrene precipitated during all polymerization reactions within less than a minute following addition of the initiator. The polymers were always colored and remained so until the reaction was terminated in methanol. In toluene and the mixed solvent (n-hexane/chloroform), the reaction medium had small dots of intense pink color imbedded in stiff gels which formed as the polymer precipitates. Propagation after gelation was presumably then controlled by diffusion of the monomer to the active growing end. During polymerization in hexane there was a rapid initial precipitation. In the solid-state polymerization of the frozen monomer initiated with BF_3OEt_2 , the area of frozen monomer in immediate contact with the liquid drops of initiator developed a yellow color instantly. After several hours the color slowly spread throughout the remaining frozen monomer, although when the polymerization was to be

terminated, that portion of the product which was still in immediate contact with the initiator could be distinguished from the rest of the material. In the BF_3 initiation of the solid-state polymerization where the initiator is a gas, the development of an orange color throughout the monomer was instantaneous. Table XII tabulates the data and observations for the preparation of poly- α , \underline{p} -dimethylstyrene.

All polymers prepared in solution were white granular materials which are insoluble in a wide variety of common solvents at room temperature. Table XIII lists the solvents evaluated in the solubility study for samples A-28 and A-44.

Diphenyl ether and 1,2,4-trichlorobenzene were observed to be effective solvents for this polymer at temperatures above 180°C . The polymers prepared in the solid-state reaction contained both soluble and insoluble fractions. The soluble fraction from the BF_3OEt_2 -initiated reaction was a low molecular weight polymer with a number average molecular weight of 4,200.

The thermogravimetric analysis of sample A-73 is given in Figure 10. Poly- α , \underline{p} -dimethylstyrene is more unstable than poly- α -methylstyrene. The onset of rapid degradation at a heating rate of $10^\circ\text{C}/\text{min}$ occurs in the temperature range of 210 - 220°C with a slower rate of degradation starting near 150°C . The high temperature required for solution and the thermal instability of these polymers limit the characterizations that can be made.

TABLE XII

A Summary of the Polymerization Reaction Conditions of
 α , \underline{p} -Dimethylstyrene in a Cationic System at -78°C

<u>Ref. No.</u>	<u>Solvent</u>	Monomer Conc. <u>Vol %</u>	Mole Ratio <u>[M]/[I]</u>	Yield <u>%</u>	<u>Color</u>	<u>State</u>
BF_3OEt_2						
A-44	Toluene	6	62	77	Pink	ppt
TBE	Toluene	9	44	68	Pink	ppt
A-45	Hexane	6	50	67	Pink	ppt
HBE	Hexane	11	38	46	Pink	ppt
A-28	Mixed ^a	6	9	85	Pink	ppt
MBE	Mixed ^a	11	38	77	Pink	ppt
C-12	Solid-State	100	6	48	Yellow	-
BF_3						
A-73	Toluene	8	4	77	Orange	ppt
TB	Toluene	10	11	77	Orange	ppt
A-74	Hexane	7	5	82	Orange	ppt
HB	Hexane	9	11	57	Orange	ppt
B-7	Mixed ^a	6			Orange	ppt
MB	Mixed ^a	9	10	44	Orange	ppt
B-30	Solid-State	100	6	100	Orange	-

^aMixed Solvent: n-hexane/chloroform 7:3

TBE, HBE, MBE, TB, HB, MB are reference labels. The other reference numbers are page numbers in the research notebooks.

TABLE XIII

Survey of Solvents Included in Solubility Study
for Poly- α , \underline{p} -dimethylstyrene

Solvent

Methylene Chloride
Carbon Disulfide
Chloroform
Trifluoroacetic Acid
1,1,1-Trichloroethane
Carbon Tetrachloride
Benzene
Toluene
Chlorobenzene
Xylene
1,1,2,2-Tetrachloroethane
o-Dichlorobenzene
Decahydronaphthalene
Dimethyl Sulfoxide
1,2,4-Trichlorobenzene
Hexachloro-1,3-Butadiene
 α -Chloronaphthalene
Diphenyl Ether
m-Cresol
Styrene
Acrylonitrile
Tetralin
Mesitylene
Cumene
Acetone
4,4-Thiobis-6-tert-butyl-m-cresol

Mixtures

Acetone-Carbon Disulfide (30/70 v/v)
Diphenyl Ether-Trichlorobenzene
Diphenyl Ether-Tetrachloroethane

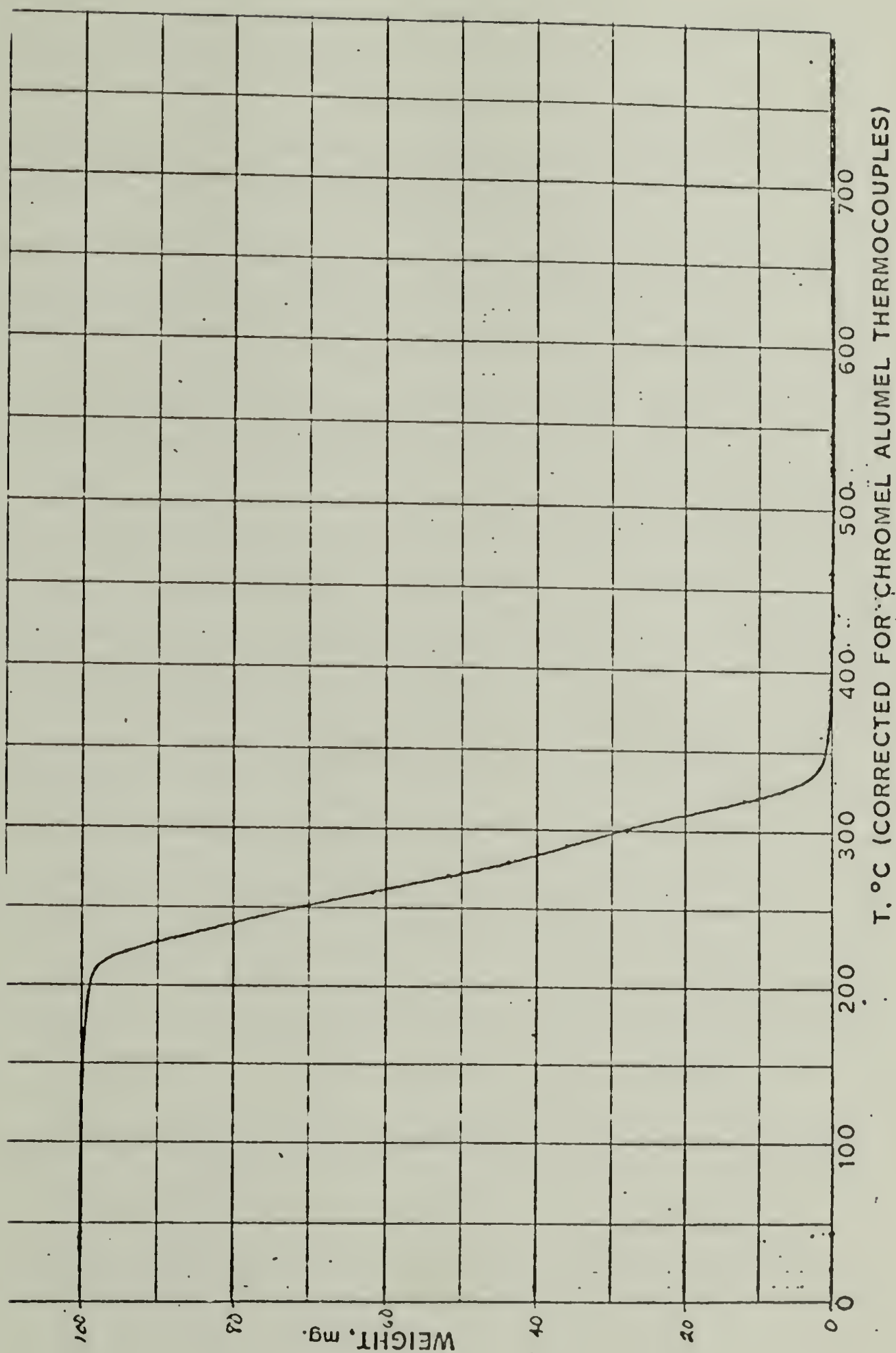


Figure 10. A TGA thermal curve of poly- α,β -dimethylstyrene at a heating rate of 10°C/min in a nitrogen atmosphere.

The infrared spectrum and elemental analysis of sample HBE and the NMR of sample A-44 confirm that the poly- α , β -dimethylstyrene is a linear, vinyl polymer. Elemental analyses were 90.30% carbon and 8.74% hydrogen [calculated for $(C_{10}H_{12})_n$: C, 90.85%; H, 9.15%].

Figure 11 reproduces the infrared spectrum of HBE which is representative of the spectra of all samples of poly- α , β -dimethylstyrene. It contains the major absorptions for p-substituted aromatic compounds at 1910, 1800 and 810 cm^{-1} and for the methyl substituents at 1470 and 1380 cm^{-1} . There are differences in the spectra of samples prepared in varying reaction conditions in the 910-840 cm^{-1} region. The absorption in this region is characteristic for the carbon-carbon bonds in alkenes; geminal substituted double bonds absorb at 895-885 cm^{-1} and trisubstituted double bonds at 840-790 cm^{-1} .

This region is reproduced for the eight samples in Figure 12. The sample prepared in the solid-state polymerization initiated with BF_3OEt_2 (C-12) and the samples prepared in toluene and mixed solvent with both initiators (TB, TBE, MB and MBE) have absorptions at both of these frequencies. These absorptions may arise from the two possible structures for the unsaturated chain end described on page 13 or possibly from residual monomer. For the latter, two of the samples were re-extracted with methanol in an attempt to remove the monomer, if any was present, but no change was observed in the infrared spectrum. A sample of the solid-state polymer was annealed on the DSC and no change in the spectra was observed after the annealing.

The two samples with an absorption peak at only one of these frequencies, 900 cm^{-1} , were HBE (hexane/ BF_3OEt_2) and B-30 (solid-state/

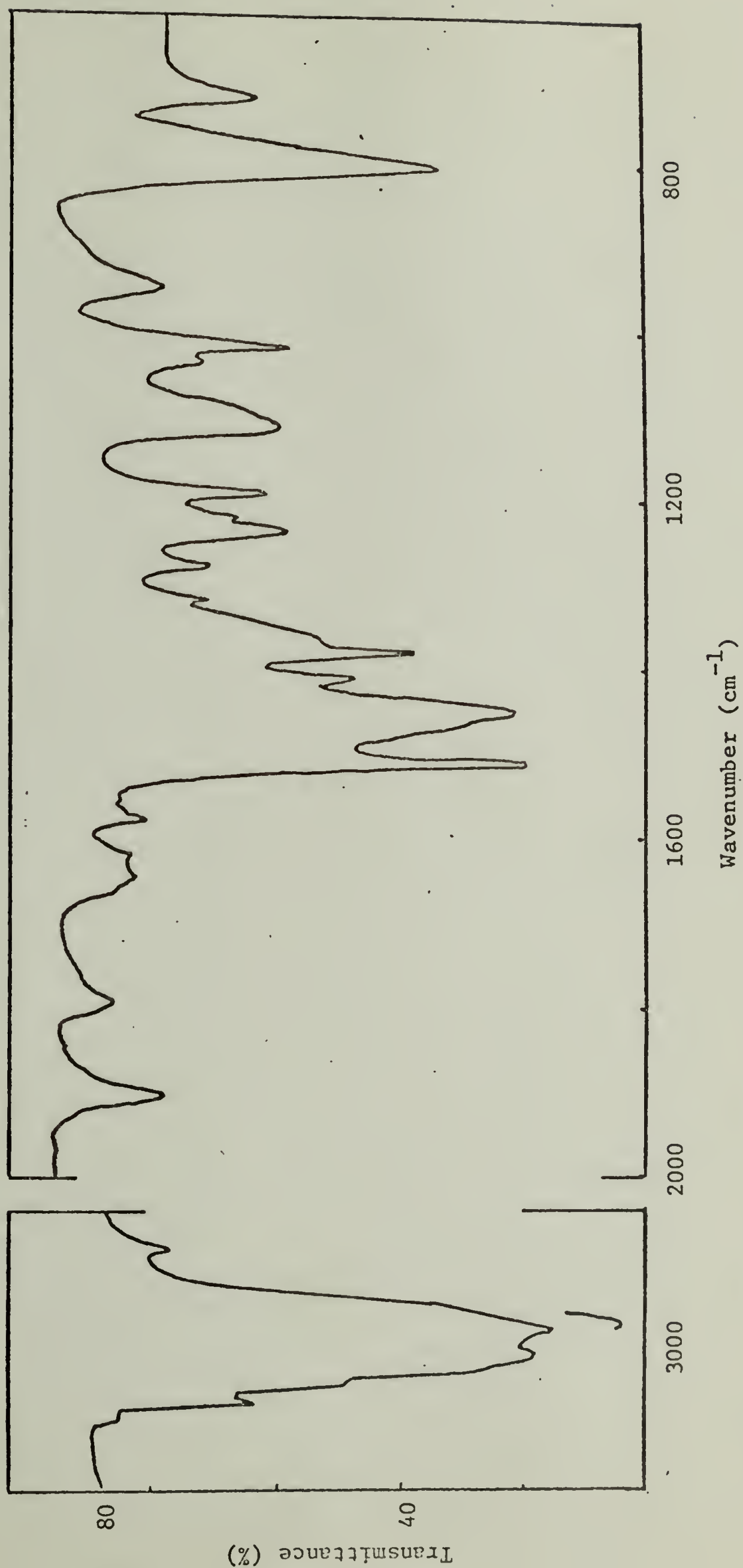


Figure 11. Infrared absorption spectra of poly- α -p-dimethylstyrene.

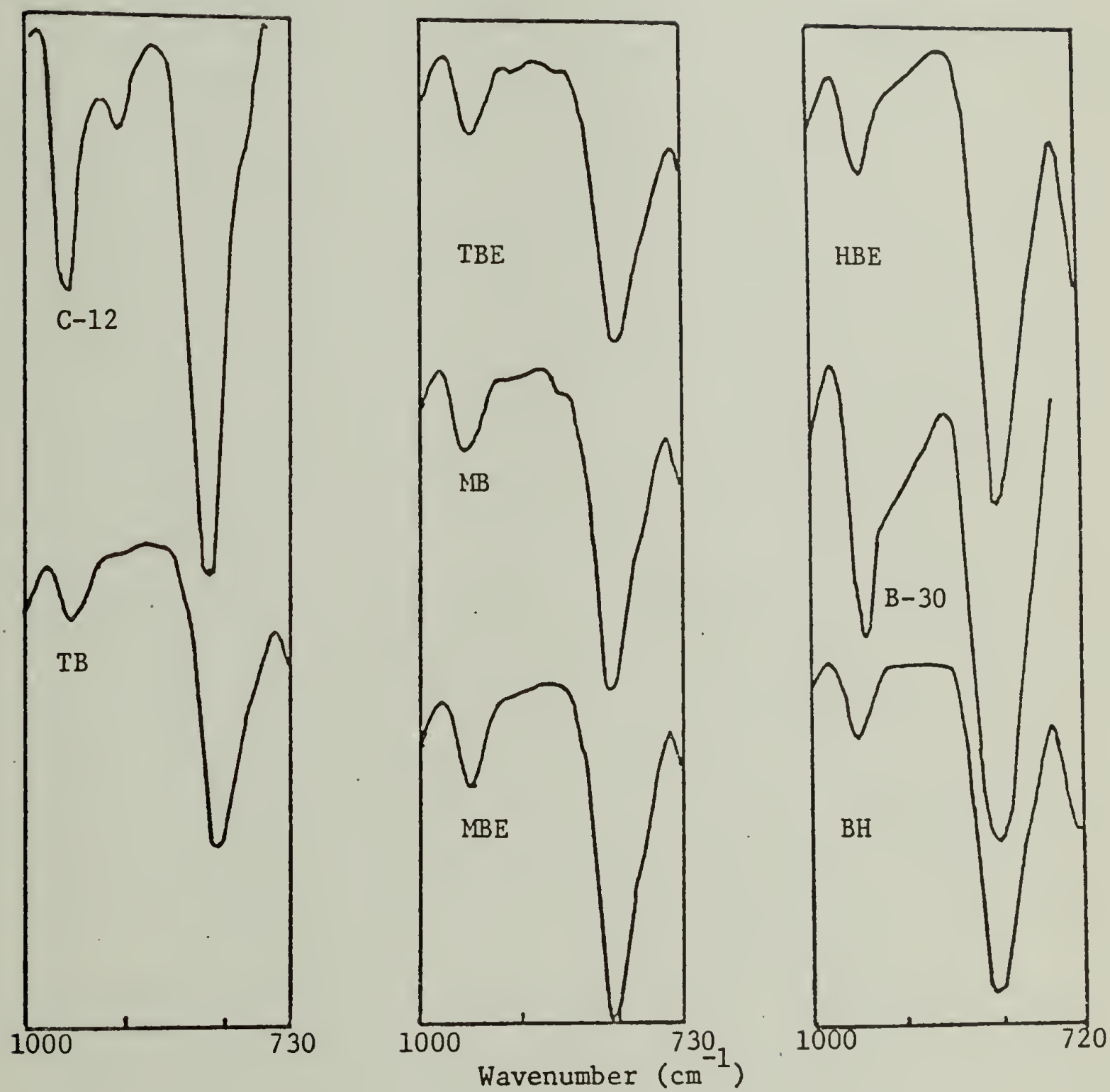


Figure 12. Infrared absorption spectra of the 1000-730 cm^{-1} region for the poly- α , p -dimethylstyrenes.

BF₃), so these polymers are believed to contain the unsaturated chain end: $\sim\text{CH}_2-\text{C}=\text{CH}_2$. The polymer prepared in hexane/BF₃ appeared to have



no absorption at either frequency, and it is assumed that this polymer contains only saturated chain ends.

The NMR spectrum of the methyl and methylene regions of poly- α , p -dimethylstyrene (A-44) in diphenyl ether at 175°C is reproduced in Figure 13. The chemical shifts (relative to hexamethyldisiloxane) and the assignments are given in Table XIV.

TABLE XIV

Chemical Shifts for Poly- α , p -dimethylstyrene

<u>Protons</u>	Chemical Shifts <u>ppm</u> ^a
α -Methyl	
Syndiotactic	-0.22
Heterotactic	-0.32
Methylene	-0.80
p -Methyl	-1.05

^aRelative to hexamethyldisiloxane, 100 MHz
spectra prepared in diphenyl ether at 175°C

The single peak observed for the methylene protons in the NMR spectrum of poly- α , p -dimethylstyrene strongly suggests that the polymer is predominantly syndiotactic. The presence of the p -substituted

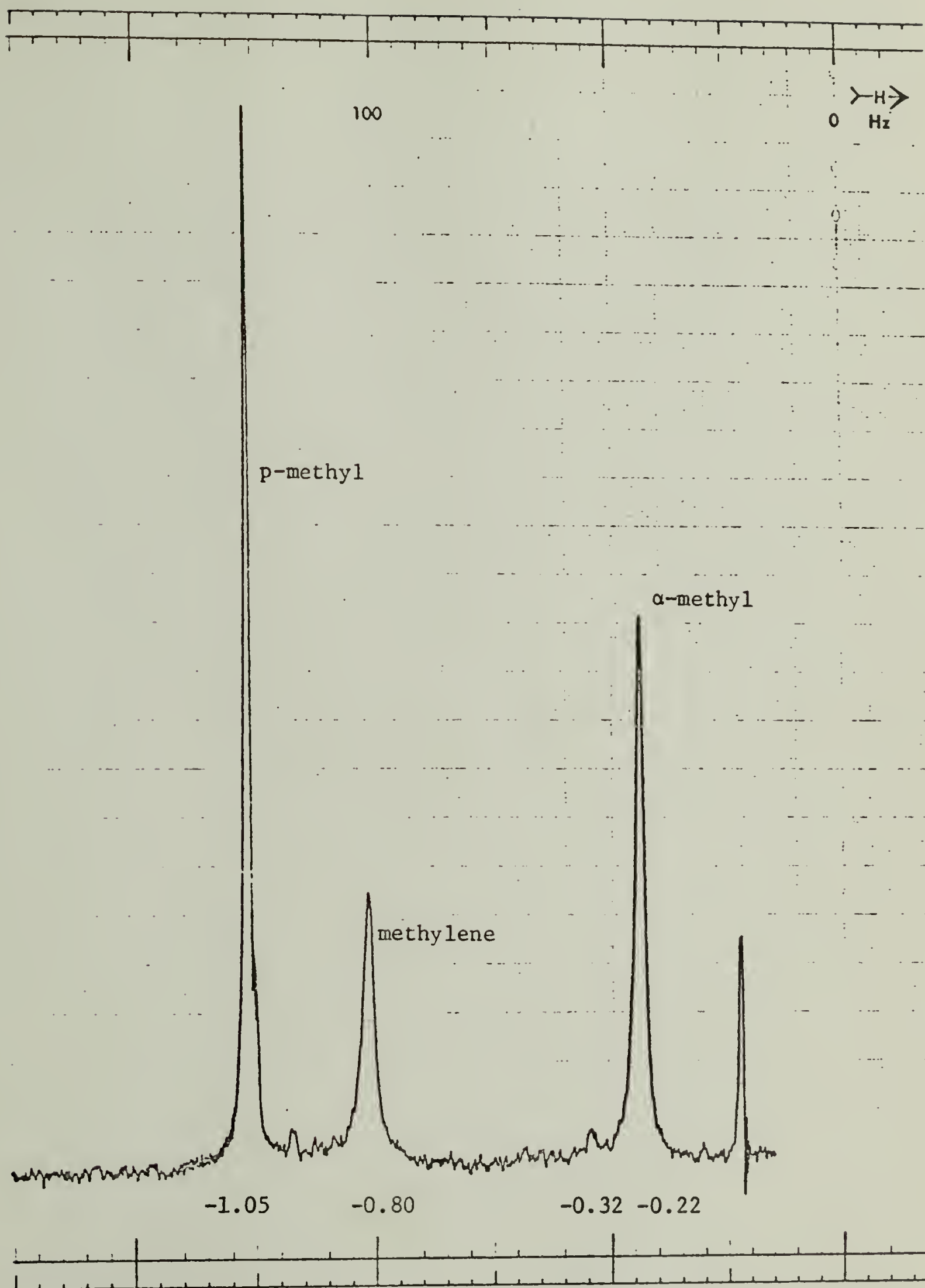


Figure 13. The NMR spectra of the α -methyl, *p*-methyl and methylene regions of poly- α ,*p*-dimethylstyrene. Spectra prepared in diphenyl ether at 175°C at 100 MHz.

methyl protons and the single peak in the methylene region is evidence that the polymerization has occurred exclusively through the vinyl group and not through the benzene ring. The resonances for the aromatic protons have not been included because the solvent, diphenyl ether, was used for the lock signal and no spectra was recorded in this region.

The sample of poly- α , \underline{p} -dimethylstyrene prepared in toluene/ BF_3OEt_2 system contained 95% syndiotactic triads and 5% heterotactic triads.

Because of the instability of the poly- α , \underline{p} -dimethylstyrene at 175°C at which this spectra was run, there are reservations about the assignment of the small resonance peaks observed in the spectra in Figure 13. The possibility exists that these peaks may be caused by impurities caused by polymer degradation.

Polymers of α , \underline{p} -dimethylstyrene prepared in toluene and in the mixed solvent with both initiators show evidence of crystallinity in the x-ray diffraction spectra of powder samples. The d-spacings of these polymers are 3.7, 5.4, 7.0, 8.7, and 10.5 Å. X-ray diffraction spectra are reproduced for sample A-28 and A-44.

Melting endotherms were observed with the Differential Scanning Calorimeter in all the samples of poly- α , \underline{p} -dimethylstyrene including those polymers prepared in hexane in which no crystallinity was detected by x-ray diffraction. The samples which were annealed above the glass transition temperatures or had been solvent extracted between 100 and 150°C had melting temperatures which were depressed apparently

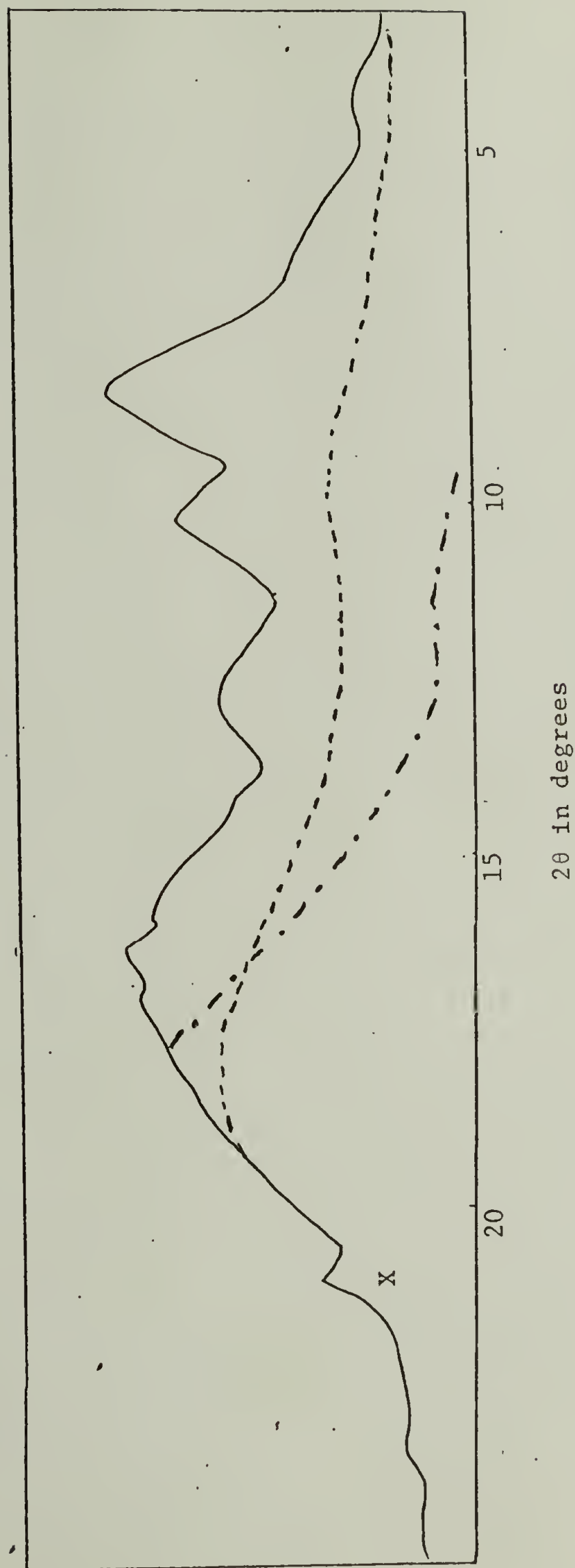


Figure 14. X-ray diffraction spectra of poly- α,β -dimethylstyrene (A-28). Powder sample mounted in vaseline. (X: reflection from vaseline.)

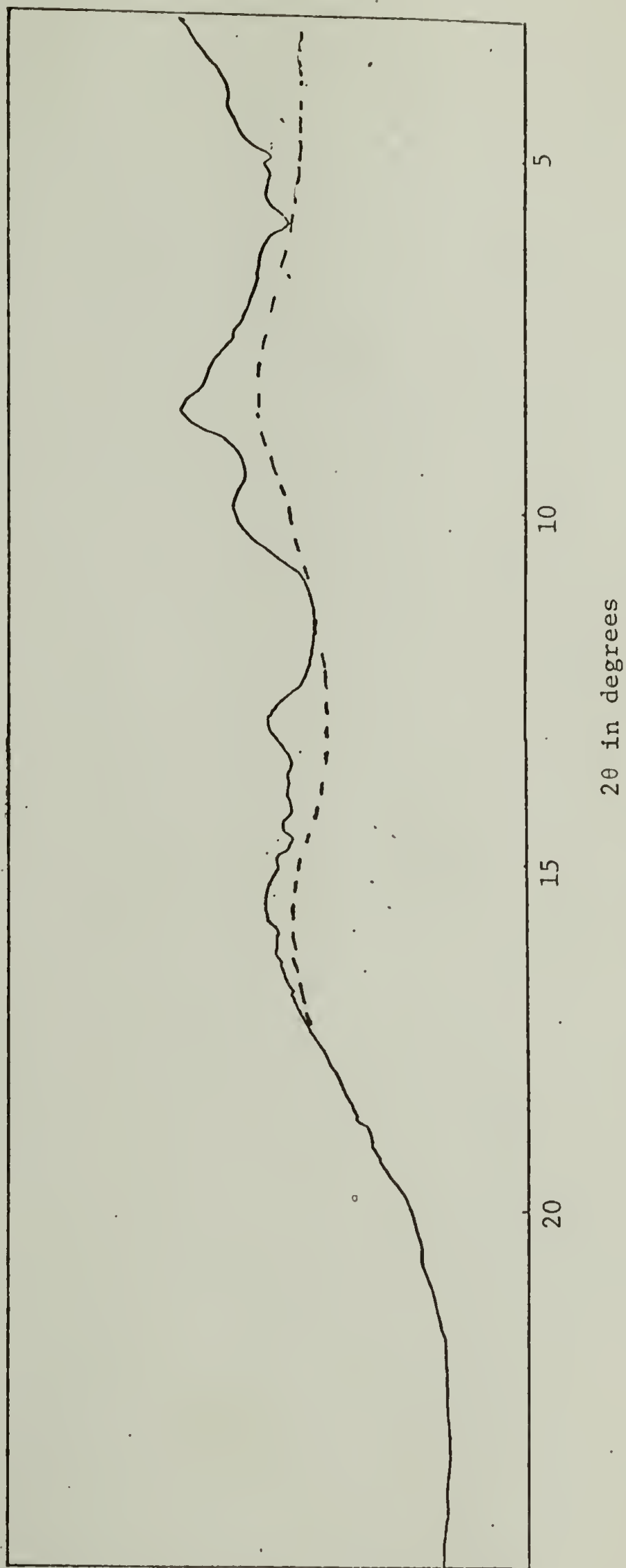


Figure 15. X-ray diffraction spectra of poly- α,β -dimethylstyrene (Sample A-44). Powder sample.

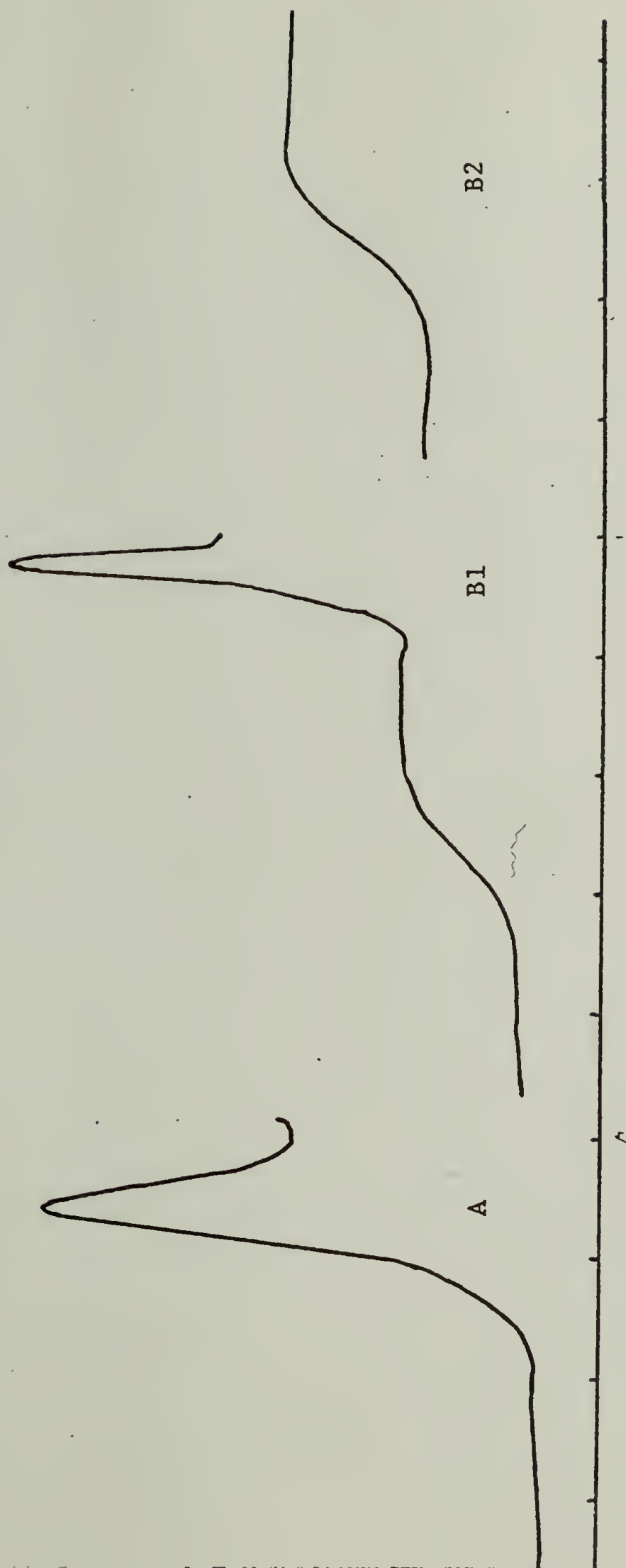


Figure 16. Typical DSC curves for poly- α,β -dimethylstyrene.

A: Melting endotherm of sample HB (first scan and no annealing).
B: Melting endotherm and glass transition of sample A-28 annealed in octanone-2. B1 - first scan, B2 - second scan.

by the presence of monomer from degradation that occurs or by the residual solvent from the annealing treatment. In all cases, the melting endotherms were measured on the first scan. There was no evidence of recrystallization either at the cooling rates as slow as 0.63°C/minute or on annealing at 177°C. Samples in which melting endotherms were initially observed on the first scan were re-examined four months later and no endotherm was observed.

Glass transitions were observed for many of the samples, although repeated annealing was often required before the transition could be recognized. It should be noted, however, that the annealing treatment was carried out in the temperature range in which degradation had been observed, and the values of the T_g were probably depressed by the presence of the monomer from depolymerization occurring during annealing. The variation in the glass transition, therefore, can be attributed to anyone or more of several factors including possible molecular weight differences, possible tacticity differences, and the possible presence of monomer. Table XV lists the glass transitions, the melting temperatures (recorded from the peak of the melting endotherms) and the melting range of the various samples.

A relative measure of the crystallinity was calculated using the relationship:

$$\%X = \frac{\Delta H_s}{\Delta H_u} \times 100$$

where %X is the percent crystallinity, ΔH_s is the enthalpy of fusion of the sample and ΔH_u is the enthalpy of fusion of a mole unit of crystalline material calculated from the copolymer data. It should be noted when evaluating the values given for the percent crystallinity that the melting endotherms used in the calculations were not equilibrium melting measurement nor was the ΔH_u value determined with equilibrium melting data. These melting endotherms were obtained at temperatures very near the onset of degradation. Full melting curves were not recorded in some cases before the onset of degradation occurred. For this data the line was extrapolated to the base line and ΔH_s values were calculated using these areas. The relative values of crystallinity are given in Table XV.

Variations in the polymerization procedure, in which the order of the addition of the reactants was changed, were tried in an attempt to produce soluble polymers. These modifications did not significantly change the solubility properties. In one procedure in which the initiator was diluted with solvent and added dropwise to the solvent-monomer mixture, the product was neither crystalline nor soluble. In another procedure a 50% monomer solution was initiated with BF_3 at room temperature and rapidly chilled to -78°C . No methanol-insoluble polymer was formed. In other cases, early termination of the reactions did not greatly reduce the yields or change the solubilities of the polymers formed.

TABLE XV
Properties of Poly- α , β -dimethylstyrene

<u>Initiator</u>	<u>Solvent</u>	<u>T_g, °C</u>	<u>Melting Range °C</u>	<u>T_m Peak °C</u>	<u>T / T_m g</u>	<u>Crystallinity</u>	
						<u>X-Ray</u>	<u>%X^a</u>
BF ₃ OEt ₂	Toluene	176	199-224	217	0.90	+	30
	Hexane	165	193-211	204	0.90	-	10
	Mixed ^b	175	184-225	225	0.90	+	50
	None	152 ^c	--	--	--		
BF ₃		--	174-212	195	--	+	50
	Toluene	175	201-227	227	0.89	+	20
	Hexane	186	203-227	227	0.91	+	30
	Mixed ^b	--	203-223	223	--	+	20
	None	170	--	--	--	-	--

^aCalculated from melting data

^bMixed: Hexane/chloroform (7:3)

^cSoluble fraction

^dInsoluble fraction

The crystallinity that was observed in the samples of poly- α , p -dimethylstyrene was in all cases in the virgin polymer. The properties of the crystalline phase of these polymer samples depend upon the condition under which the crystallinity is formed (in this case the polymerization conditions) and upon any changes that would occur as a result of the work-up procedure for analysis.

The samples of poly- α , p -dimethylstyrene melt over a broad range of temperatures. The polymer formed in the solid state polymerization, C-12, had a melting range of 38°C as compared with the 15 to 20°C range for samples prepared in the solution polymerization. This broad range for partially crystalline polymers is generally caused by a wide range of crystallite sizes present in the sample and by the lack of perfection of the crystals.

Melting temperatures are dependent upon the size and perfection of the crystallites with the larger, more perfect crystals melting at higher temperatures. Sample C-12 (BF_3OEt_2 solid state) had a melting peak at 195°C which is lower than other samples. This depression in the melting peak temperature is probably due to the smallness of the crystallites formed during the solid state polymerization.

Crystallite size is dependent upon the length of tactic sequences (syndiotactic sequences for poly- α , p -dimethylstyrene) and upon the ability of the polymer chain to assume the conformation required for molecular packing. Fox³³ in his study of crystalline poly(methyl methacrylate) found that the ability to crystallize was dependent upon

a critical sequence length of tactic units. This critical length was estimated to be 20 units for the isotactic form of poly(methyl methacrylate). If, however, the polymers were blocky, that is with long sequences of both isotactic and syndiotactic units, then the polymers would crystallize only with great difficulty or not at all.

The average sequence length of syndiotactic units, \bar{l}_s , can be calculated from the relationship:

$$\bar{l}_s = [h + 2(s + h/2)]/h$$

where h is the fraction of heterotactic triads and s is the fraction of syndiotactic triads. Using the data of the triad analysis from the NMR spectrum of sample A-44 (BF_3OEt_2 /toluene) the average sequence length in a partially crystalline poly- α , \underline{p} -dimethylstyrene was found to be 40 syndiotactic units.

Polymerization of \underline{p} -isopropyl- α -methylstyrene. The data on the polymerization of \underline{p} -isopropyl- α -methylstyrene with BF_3OEt_2 and BF_3 , each in toluene and hexane, is summarized in Table XVI. Color developed in all four systems immediately on initiation and disappeared when the reaction was quenched with methanol. The BF_3 -initiated ones were pale yellow. In hexane the polymer precipitated during the reaction, but in toluene the polymer formed a thick viscous solution with BF_3OEt_2 and a gel with BF_3 .

Sample B-51 (hexane/ BF_3OEt_2) contained both soluble and insoluble fractions on extraction with a mixture of toluene and chloroform at room temperature. The soluble portion represented a 62% yield based on initial monomer concentration. This polymer had a number average molecular weight of 11,000. It contained 90.00% carbon and 10.09% hydrogen [calculated for $(\text{C}_{12}\text{H}_{16})_n$: %C, 89.93; %H, 10.07].

Sample B-52 (toluene/ BF_3OEt_2) was soluble only in diphenyl ether and o-dichlorobenzene at 140°C. It swelled in xylene, hexachloro-1,3-butadiene, tetralin, and isopropylbenzene and was insoluble in the common organic solvents such as benzene and chloroform at reflux temperatures. The polymers prepared with BF_3 were insoluble in diphenyl ether at 185°C.

Figure 17 gives the thermogravimetric analysis of sample B-52 which shows that the polymers are not thermally stable above 210-220°C. In annealing experiments, in which the sample was held for an hour or longer at 165°C, significant degradation occurred at the lower temperature.

The glass transition temperatures for this series of polymers are given in Table XVII. A representative DSC trace is given in Figure 18. Because the glass transition temperature is dependent upon the molecular weight, no conclusions concerning the differences in stereoregularity can be drawn.

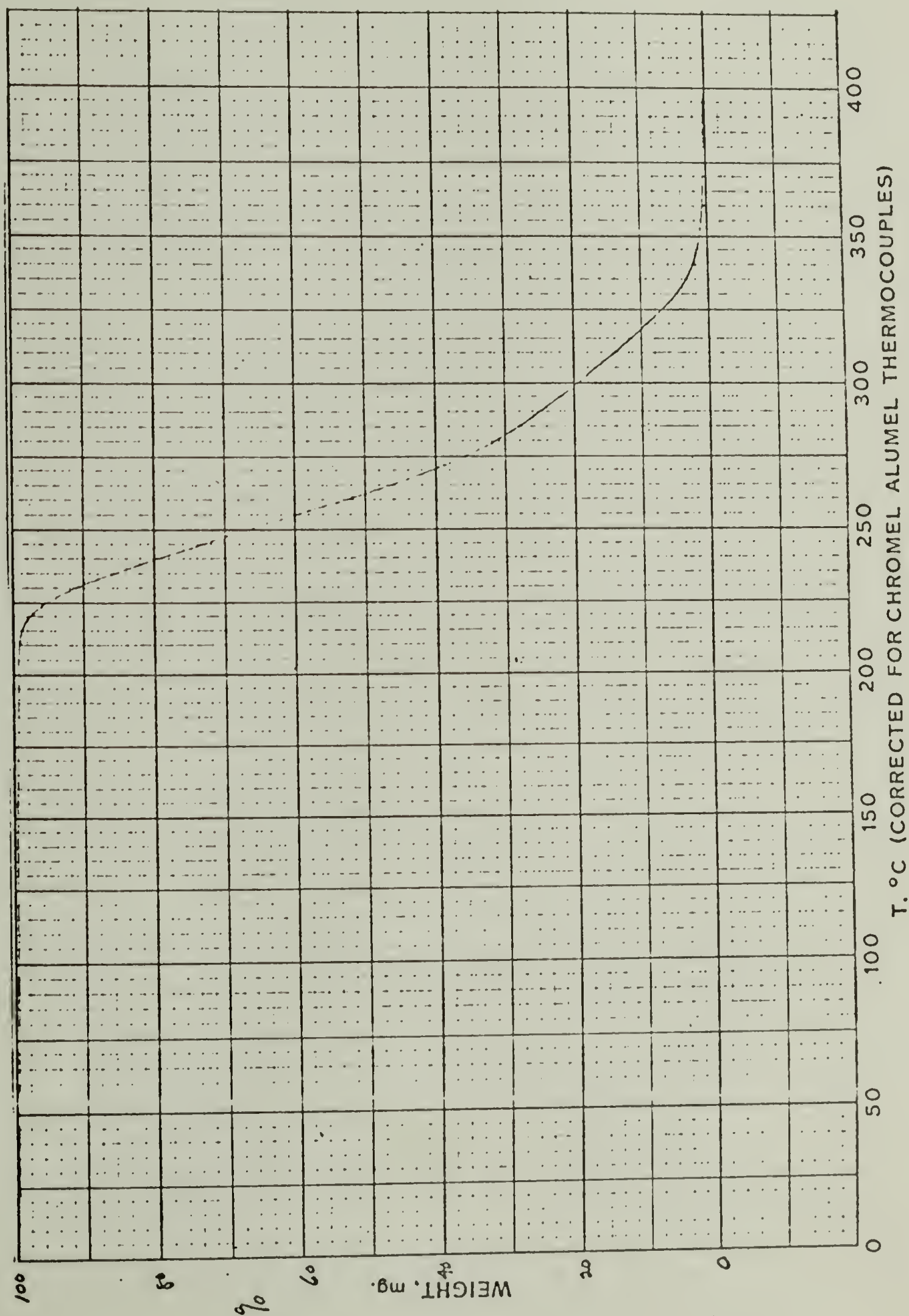


Figure 17. A TGA thermal curve for poly(p-isopropyl- α -methylstyrene) at a heating rate of 10°C/min in a nitrogen atmosphere.

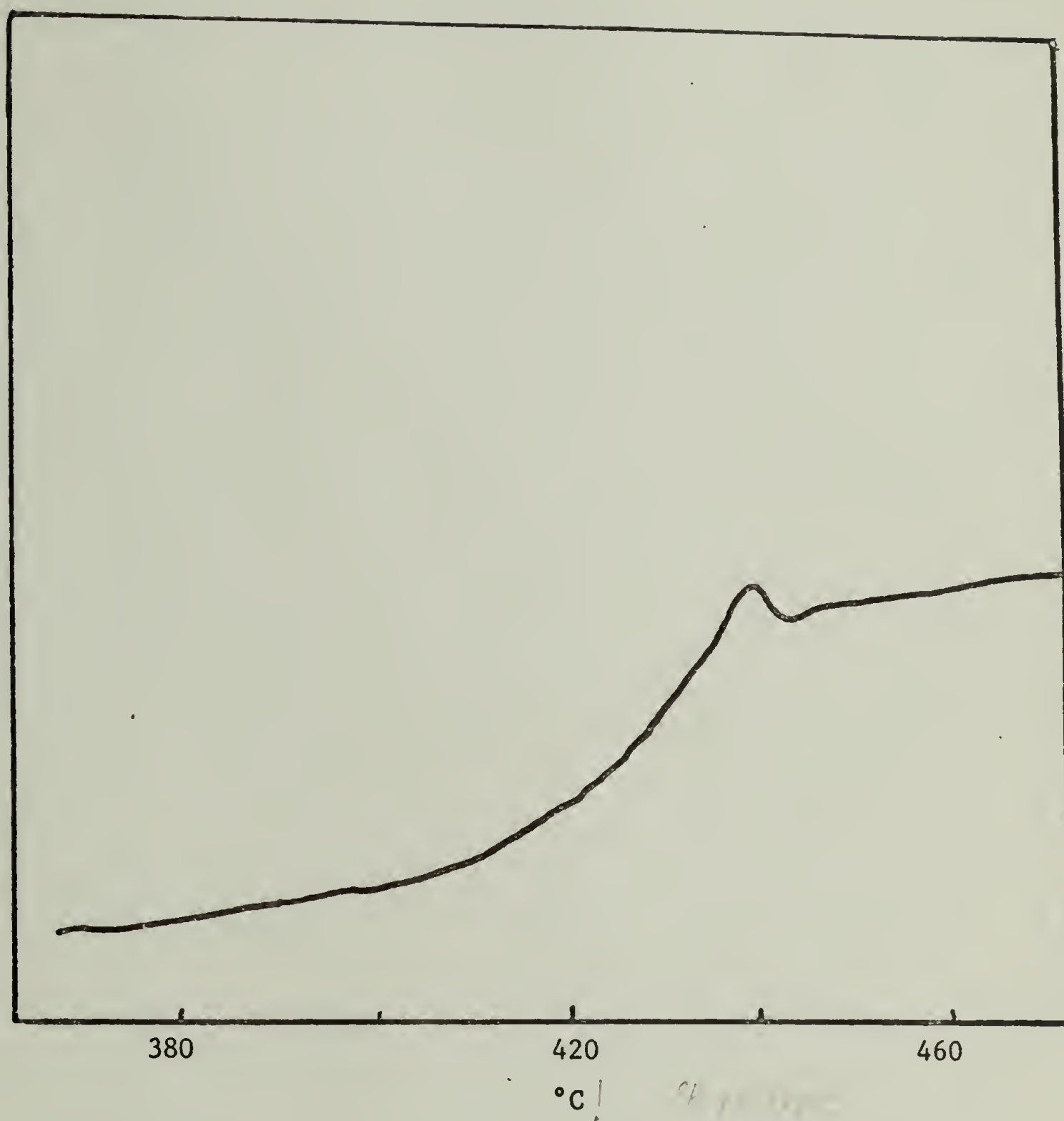


Figure 18. Typical DSC curve of poly(p-isopropyl- α -methylstyrene) showing a glass transition.

TABLE XVI

A Summary of the Polymerization Reaction Conditions
of p-Isopropyl- α -methylstyrene at -78°C

Sample No.	Solvent	Monomer Conc. Vol %	Mole Ratio [M]/[I]	Reaction Time Hrs.	Yield %	State	Color
BF ₃ OEt ₂							
B-52	Toluene	9	15	41	--	Viscous Solution	Yellow
B-51	Hexane	10	13	41	62	ppt	Yellow
BF ₃							
B-58	Toluene	9	3	23	85	Gel	Orange
B-57	Hexane	9	3	24	--	ppt	Orange
B-61	Hexane	10	3			ppt	Orange

TABLE XVII

Glass Transition Temperatures of
Poly(p-isopropyl- α -Methylstyrene)

Sample Number	Solvent/Initiator	T _g , $^{\circ}\text{C}$
B-52 (Soluble)	Toluene/BF ₃ OEt ₂	138
B-52 (Insoluble)	Toluene/BF ₃ OEt ₂	153
B-51	Hexane/BF ₃ OEt ₂	155
B-58	Toluene/BF ₃	124
B-61	Hexane/BF ₃	142

The infrared spectrum of poly(p-isopropyl- α -methylstyrene) is given in Figure 19 and confirms the presumed composition of this polymer as being a linear, vinyl polymer. The major absorption bands present are those for p-substituted benzene (1910 , 1790 and 810 cm^{-1}), for the

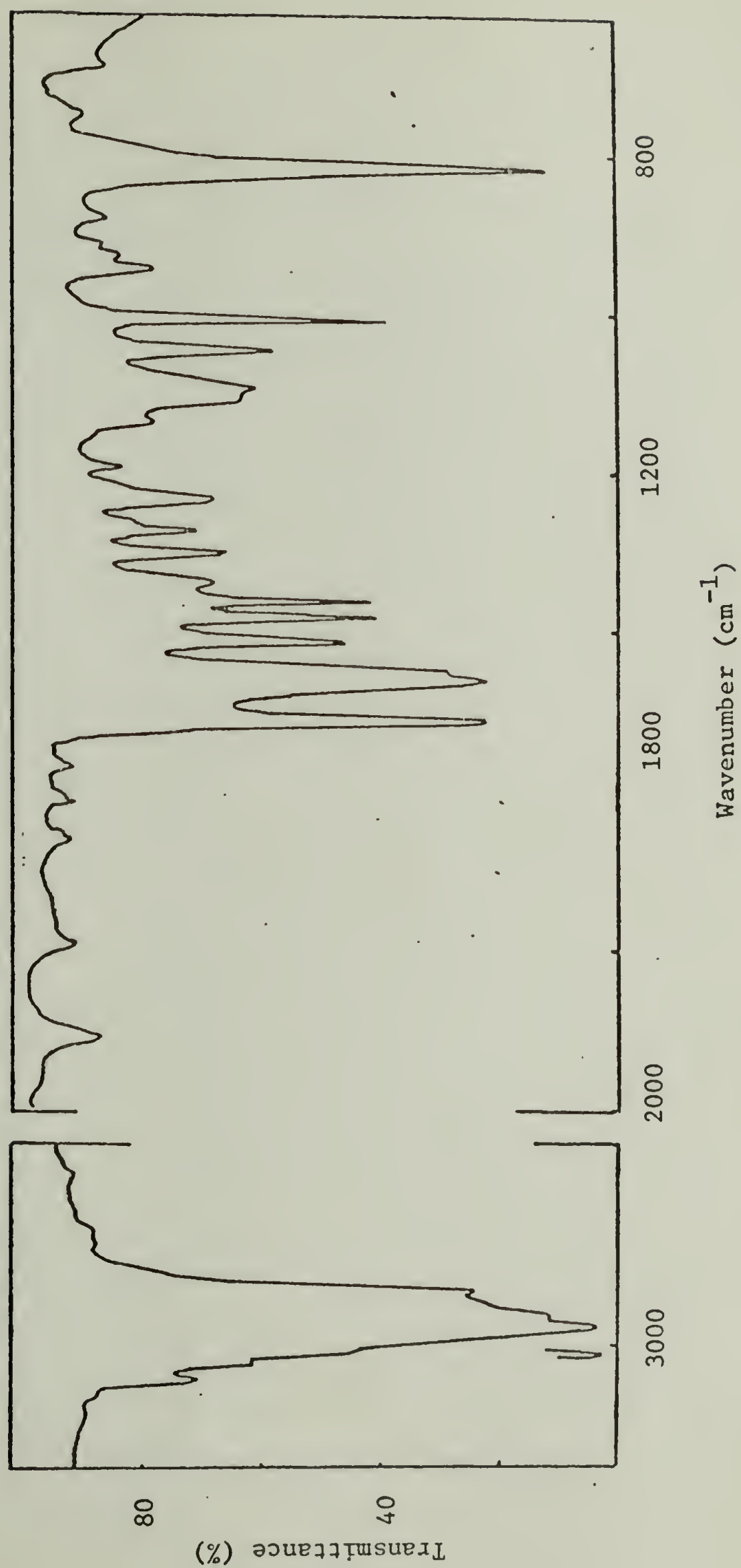


Figure 19. Infrared absorption spectra of poly(p-isopropyl- α -methylstyrene). (KBr disc)

methyl group (1460 and 1360 cm^{-1}) and for the isopropyl substituent (1100 and 950 cm^{-1}). The weak absorption peak at 870 cm^{-1} indicates that a small percentage of residual vinyl groups are still present.

Sample B-52 prepared in a BF_3OEt_2 -initiated polymerization in toluene is partially crystalline and has a melting peak at 202°C (range 197 - 217°C) in the DSC thermogram. The d-spacing obtained from the x-ray diffraction spectrum are: 3.6 , 5.1 , 5.4 , ~ 6.5 , ~ 9.3 and 13.3 \AA . The other samples in this series were amorphous. The x-ray diffraction spectra is reproduced in Figure 20.

The NMR spectra in hexachloro-1,3-butadiene of the α -methyl and methylene protons were not resolved sufficiently to make any judgment on the stereoregularity. The doublet from the methyl protons of the isopropyl substituent is well resolved and falls in the same region of the spectra as the methylene protons.

Attempted Polymerization of $\alpha,2,4$ -Trimethylstyrene. The results of attempted polymerization reactions of $\alpha,2,4$ -trimethylstyrene which were attempted by use of the same cationic systems used for the preparation of polymers with the other monomers in this study are summarized in Table XVIII. This monomer did not form any products which precipitated in methanol, although the characteristic colors which were evident in most of the other polymerization reactions were present with this monomer. The failure to polymerize was attributed to the steric hindrance of the o-substituted methyl group.

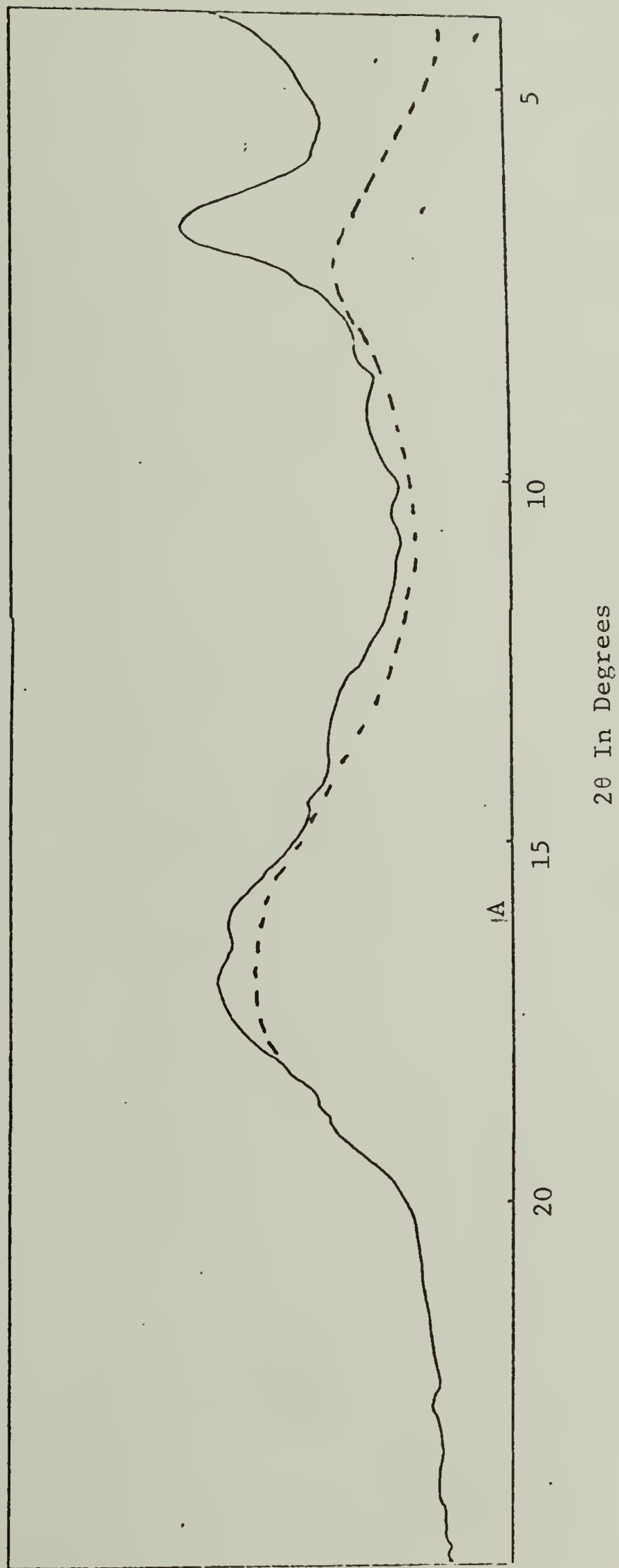


Figure 20. X-ray diffraction spectra of poly(p-isopropyl- α -methylstyrene). Powder sample mounted between mylar window. (A is reflection from mylar.)

TABLE XVIII

Summary of the Reaction Conditions for the Cationic Polymerization of $\alpha,2,4$ -Trimethylstyrene

Sample No.	Solvent	Conc. of Monomer Vol. %	Mole Ratio [M]/[I]	Reaction Time Hrs.	Yield %	Color
BF_3OEt_2						
B-93	Toluene	11	7.5	24	0	Yellow
B-94	Toluene	44	3.9	22	0	None
B-96	Hexane	11	6.9	19	0	None
BF_3						
B-96	Toluene	28	5.6	24	0	Orange
C-1	Hexane	20	7.1	24	0	Orange

Preparation of Copolymers. It was hoped that soluble polymer samples which were still at least partially crystalline could be obtained by preparing copolymers. Therefore, the following series of copolymers was prepared using the same reaction conditions which yield the samples of crystalline homopolymers of α, p -dimethylstyrene, i.e., BF_3OEt_2 in toluene:

α, p -dimethylstyrene with α -methylstyrene

p -isopropyl- α -methylstyrene with α -methylstyrene

α, p -dimethylstyrene with p -isopropyl- α -methylstyrene

Unfortunately, when the preparations yielded soluble copolymers, the samples were no longer crystalline. The copolymer compositions and characterization are summarized in Table XIX.

TABLE XIX

Composition and Properties of the Copolymers of Substituted α -Methylstyrenes

Sample Number	Monomer Composition		Soluble at RT	Crystal- linity	Melting ^a Endotherm Peak	T _g °C	Calc. ^c T _g , °C	Yield %		
	Feed	Mole % Polymer								
									Biref.*	X-Ray
Monomer A: α , <u>p</u> -Dimethylstyrene Monomer B: α -Methylstyrene Monomer C: <u>p</u> -Isopropyl- α -Methylstyrene										
B-80	A/B	A/B	-	+	220	178	185			
B-81	98/2	99/1	-	+	219					
B-87	90/10	97/3	-	+	204					
B-89	82/18	91/9	-	+	195			65		
C-3	69/31	86/14	-	+						
	57/43	78/22	b	+		165	183	73		
B-64	C/B	C/B	+	-		157	159	94		
B-74	87/13	89/11	+	-		138	157	87		
	97/3	98/2	+	-						
C-9	A/C	A/C	-	+	200	163	164	93		
C-15	94/6	85/15	-	s1	199-202	141	157	60		
	12/88	9/91	+	-						

^aDSC melting endotherm

*Birefringence

^bThis copolymer has a soluble and an insoluble fraction, 92 and 8%, respectively^cCalculated by the Gordon-Taylor equation: $Q_{AB} = xQ_A + (1-x)Q_B$ where Q is the T_g and x is the mole fraction of monomer A.

Copolymers of α , p -Dimethylstyrene with α -Methylstyrene. A series of five copolymers were prepared containing α , p -dimethylstyrene and α -methylstyrene with increasing α -methylstyrene content. All of the copolymers in this series precipitated during the polymerization reaction and exhibited the characteristic insolubility of the homopolymers of α , p -dimethylstyrene at room temperature. Like the homopolymers, the samples were soluble in diphenyl ether at 180°C. Soluble copolymers at room temperature were not formed until the mole fraction of α -methylstyrene content was increased to 0.22, and this preparation yielded both a soluble and an insoluble fraction.

All of the insoluble samples were extracted with solvents in which poly- α -methylstyrene was soluble. The presence of the phenyl band found in α -methylstyrene polymers at 1610 cm^{-1} in the infrared spectrum of the extracted copolymers confirmed that the samples were copolymers. The spectra in this region is given in Figure 21.

The composition of the copolymers, which was determined by thermally degrading the copolymer and analyzing the volatile products by gas chromatography, is given in the third column of Table XIX. In each preparation the percent of α , p -dimethylstyrene found in the copolymers was greater than the percent composition of that monomer in the feed composition.

Crystallinity could be detected in the x-ray diffraction spectra of powder samples of all the copolymers of α , p -dimethylstyrene and α -methylstyrene except the sample with 22 mole percent α -methylstyrene. The percent crystallinity in these copolymers was between 10 and 20%. On annealing sample B-80 (99% α , p -dimethylstyrene) with refluxing

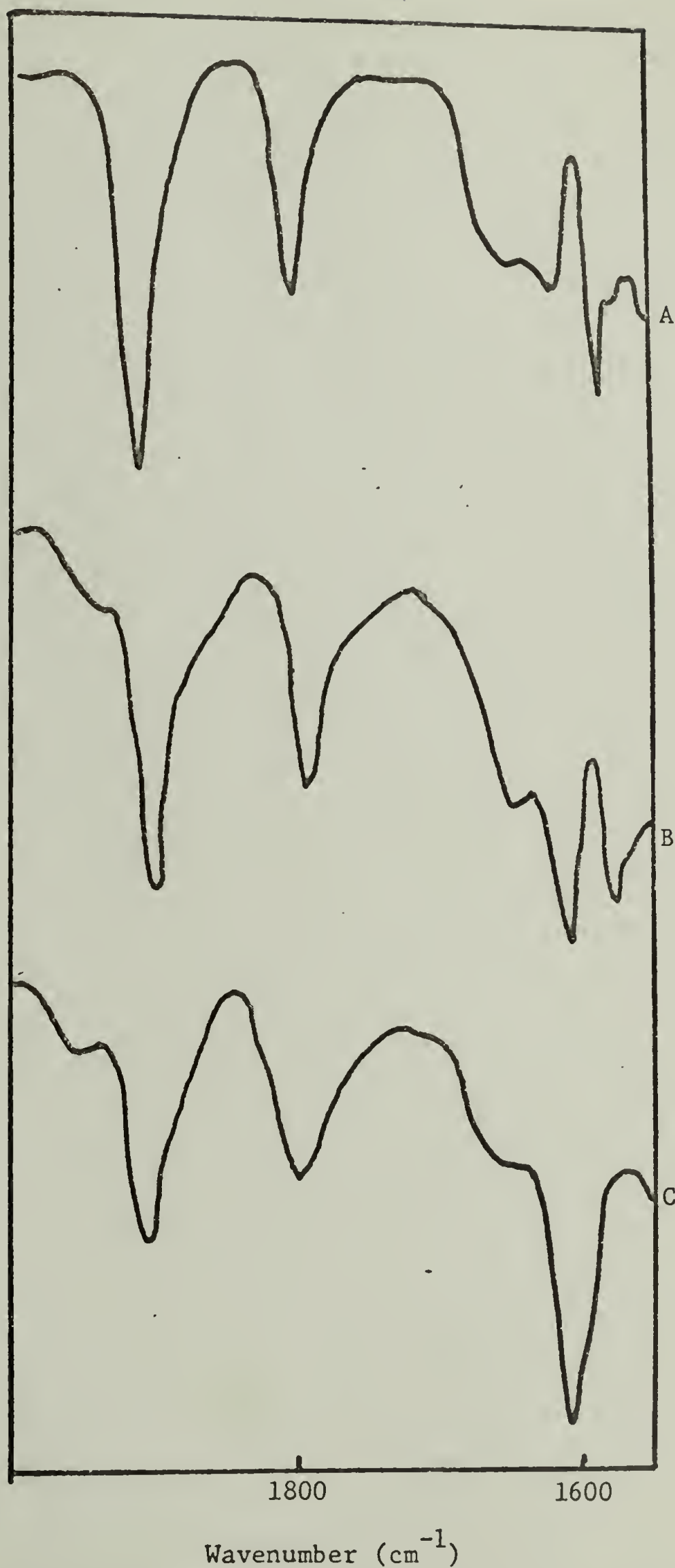


Figure 21. Infrared spectra of 2000-1550 cm^{-1} region showing increased α -methylstyrene content at 1610 cm^{-1} in copolymers of α , p -dimethylstyrene and α -methylstyrene. Mole % α -methylstyrene - A: 3, B: 9, C: 22.

octanone-2 (at 173°C) the percent crystallinity was increased to approximately 30%. At this temperature a slow rate of degradation also occurred. The d-spacings for these copolymers were: 5.5, 6.8, 8.7, 10.5 and 21.5 Å which are the same as those found for the homopolymers of α , p -dimethylstyrene.

All the copolymers exhibited melting endotherms in thermograms obtained on a Differential Scanning Calorimeter including sample C-3 (22 mole % α -methylstyrene). The temperature range and peak of these endotherms are given in Table XIX. With increasing α -methylstyrene content, the peak of the endotherm is depressed from 220°C to 195°C and the range of the endotherms become broader. In samples which were annealed above 170°C, the melting peak is apparently depressed by the monomer formed in the slow degradation that occurs.

Birefringence observed in these samples under the polarizing microscope disappeared in the same temperature range as that of the melting endotherm for all the samples. Two or three degrees beyond the disappearance of the birefringence, the sample changed from its powder form to a liquid. After an additional 10° increase in temperature, bubbles formed and a strong order of monomer would be detected as the sample degrades.

Glass transitions were observed in only two samples, B-80 and C-3, on the DSC after the polymers had been heated through the melting range and are given in Table XIX.

Copolymers of p -Isopropyl- α -Methylstyrene and α -Methylstyrene.

The copolymers of p -isopropyl- α -methylstyrene and α -methylstyrene, B-64

and B-74 in Table XIX, remained in solution during polymerization and were low molecular weight, soluble products. No crystallinity was detected in the x-ray diffraction spectra of powder samples nor was birefringence observed under the polarizing microscope.

The analysis of the composition of the copolymers by thermal degradation shows that the mole fractions of the two monomers was very nearly the same as the feed composition. The presence of bands for mono-substituted aromatics ($1610, 760, 690 \text{ cm}^{-1}$) in the infrared spectra confirmed the presence of α -methylstyrene in the copolymers.

Copolymers of α , p -Dimethylstyrene and p -Isopropyl- α -Methylstyrene.

In the last series, copolymers were prepared using two feed compositions of p -methyl and p -isopropyl substituted α -methylstyrene monomers. A comparison of the results for samples B-89 and C-9 (Table XIX) with those for similar α , p -dimethylstyrene contents in the α -methylstyrene copolymers shows that substitution of the p -isopropyl- α -methylstyrene for the α -methylstyrene in the copolymer composition did not alter the solubility. The copolymer of α , p -dimethylstyrene with p -isopropyl- α -methylstyrene with only 9% α , p -dimethylstyrene was soluble and not crystalline.

For the first and third series, crystallinity was observed in all copolymers containing 85% or more α , p -dimethylstyrene which were prepared in toluene with BF_3OEt_2 at -78°C . Assuming that the copolymers of α , p -dimethylstyrene and α -methylstyrene were random, the relationship derived by Flory³⁴ for the depression of the melting point could be used to obtain values of T_m° , the melting point of pure crystalline

poly- α , \underline{p} -dimethylstyrene, and of ΔH_u , the enthalpy of fusion for one mole of crystalline units.

$$1/T_m - 1/T_m^\circ = - [R/\Delta H_u] \ln X_A$$

where X_A is the mole fraction of α , \underline{p} -dimethylstyrene and T_m is the depressed melting temperature from the copolymer data. The melting points for this equation should be equilibrium melting points; however, these are not available for these copolymers. Figure 22 gives a plot of $1/T_m$ versus $\ln X_A$. The intercept gives the value of $T_m^\circ = 497.8^\circ\text{K}$, and from the slope, ΔH_u is calculated to be 2,400 cal/mole of crystalline units. The entropy of fusion, ΔS_u , is obtained from the relationship: $\Delta S_u = \Delta H_u/T_m^\circ$, and is 4.8 cal/°K mole of repeating units.

The enthalpy and entropy of fusion are differences between the enthalpy and entropy of the liquid and crystals at the melting temperature and are dependent upon structural properties. The ΔH_u is dependent upon the structure and composition of the repeating unit and intermolecular attraction such as found in hydrogen bonding in polyesters and polyamides. The ΔS_u value reflects the destruction of the long-range order in the crystal lattice and an increase in the freedom for segmental rotation. Therefore, ΔS_u will depend upon the energy difference between the rotational isomers, and in turn to any structural factors introducing steric hindrance to rotation, and to the motion of translation of the molecules. There are two contributions in the ΔS_u term for poly- α , \underline{p} -dimethylstyrene. The effect of the steric hindrance to rotation should decrease the number of bonds changing conformation and

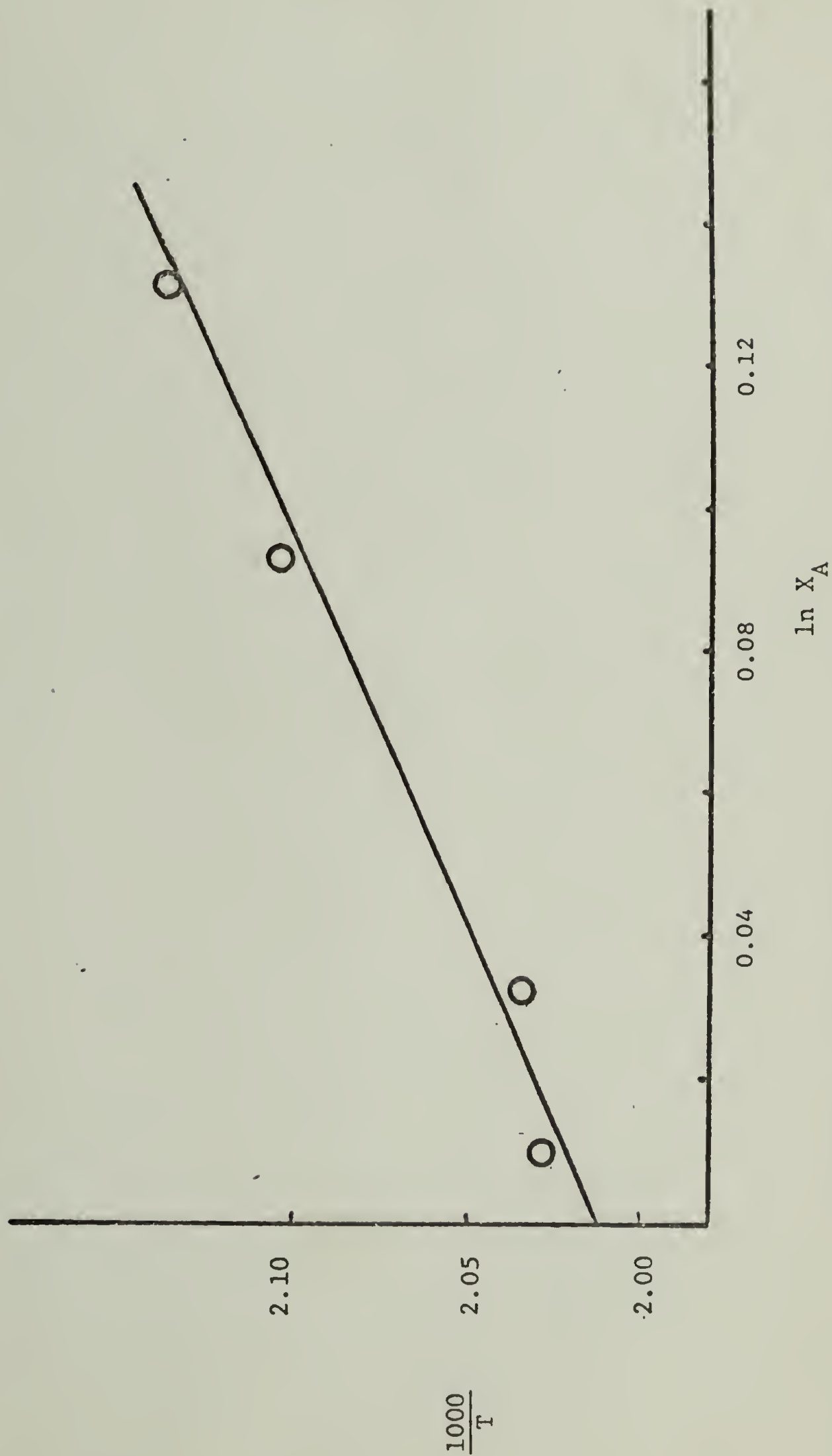


Figure 22. The reciprocal melting point versus mole fraction of monomer A for copolymers of poly- α , p -dimethylstyrene and α -methylstyrene.

and decrease the ΔS_u term. The motion and translation of polymer molecules with large, bulky, stiff substituents tend to disrupt the crystal lattice. Therefore, these polymers do not gain entropy by premelting which is reflected in the larger ΔS_u term.

Polyethylene and polypropylene are two examples with different repeating structures, $\sim\text{CH}_2\sim$ and $\sim\text{CH}_2-\underset{\text{CH}_3}{\underset{|}{\text{C}}}\sim$, and different degrees of

steric hindrance to rotation. The values for ΔH_u for these polymers are 950 and 2,600 cal/mole of crystalline unit and for ΔS_u are 2.3 and 5.8 cal/mole of repeating unit. The values for poly- α , \underline{p} -dimethylstyrene compare in magnitude to the values of polypropylene.

Comparison of Polymer Properties. The p-substituted polymers were insoluble at room temperature and thermally unstable at temperatures where solution occurred. Therefore, characterization of these polymers was necessarily limited, and correlation of the microstructure and the properties with changes in the polymerization reaction was not possible.

Table XX gives the comparison of the properties of the polymers for each monomer prepared in the toluene/ BF_3OEt_2 system.

On the basis of the NMR spectra both poly- α -methylstyrene and poly- α , \underline{p} -dimethylstyrene are highly syndiotactic polymers. The infrared spectra and the NMR spectra indicate that the polymers are formed exclusively by a 1,2-addition reaction and that they are linear. Examination of infrared spectra of low molecular weight samples shows that the unsaturated group, $\sim\text{C}=\text{CH}_2$, is probably the structure of the chain end.



TABLE XX

Properties of the Polymers of α -Methylstyrene,
 α ,p-Dimethylstyrene and p-Isopropyl- α -Methylstyrene
 Prepared in Toluene/BF₃OEt₂ System at -78°C

<u>Properties</u>	para-Substituent		
	<u>H</u>	<u>Methyl</u>	<u>Isopropyl</u>
Percent Syndiotacticity	89%	95%	Not Resolved
Glass Transition, °C	187	176	153
Melting Temperature, °C (DSC)	---	212	203
Crystallinity, X-Ray	No	Yes	Yes
Infrared	Linear	Linear	Linear
Chain Ends		Unsat	Unsat
Solubility at Room Temperature	Yes	No	No

The differences in the glass transition temperatures should be correlated with the changes in the monomer structure, but, in fact, the differences in this data also include molecular weight and tacticity effects. If the effect of tacticity is neglected in two low molecular weight samples, the effect of the structure can be observed in the molecular weight-glass transition data for sample pair prepared in different polymerization systems. Poly- α -methylstyrene prepared in a hexane/BF₃ system and a poly- α , p -dimethylstyrene prepared in the BF₃OEt₂-initiated bulk polymerization had number average molecular weights of 4,000 and 4,200 and glass transition temperatures of 157 and 152°C, respectively. This decrease in the glass transition temperature with the p -substituent is in the direction to be expected. The bulk of the p -substituent would decrease the density of the polymer chains in a given volume by reducing the efficiency of molecular packing. The glass transition temperature would then be lowered because of an increase in free volume.

Comparison of Monomer Reactivities. The order of overall reactivities of the four monomers in this series as indicated by polymer yield as a function of time was α ,2,4-trimethylstyrene \ll α -methylstyrene $<$ α , p -dimethylstyrene $<$ p -isopropyl- α -methylstyrene. α ,2,4-Trimethylstyrene does not polymerize presumably because of steric hindrance between the o -methyl substituent with the α -methyl substituent. From

the analysis of composition of the copolymers, which is given in Table XIX, the p-isopropyl- α -methylstyrene and the α ,p-dimethylstyrene monomer are shown to be more reactive than α -methylstyrene. This is attributed to the inductive effect of the two p-substituents.

From observations of the polymerization reactions, differences were observed in the rates of polymerization of α -methylstyrene and α ,p-dimethylstyrene. The polymerization of α ,p-dimethylstyrene was very rapid in appearance. These polymers precipitated within seconds after the addition of the initiating reagent and were obtained in yields 77% within minutes. This behavior is in marked contrast to that observed in the preparation of α -methylstyrene. After four hours the yield in this case was still only 73%.

The increased rate for the p-substituted monomer is attributed to the increased stability of the carbonium ion attributable to the inductive effect of the p-methyl substituent. This increased stability should lead to a lower energy of activation for formation of the transition state and, therefore, a faster rate of polymerization. In an analogous system with p-methylstyrene and styrene, the rate of propagation of p-methylstyrene is reported to be 25 times faster than that of styrene in a cationic polymerization²⁶.

This difference in reactivity was observed again in the hexane/ BF_3OEt_2 systems. Both α ,p-dimethylstyrene and p-isopropyl- α -methylstyrene polymerized rapidly to give polymers in yield of 60%, while the α -methylstyrene monomer did not polymerize readily in this system and only trace amounts of product were formed. Other interactions may be important

factors in affecting polymerization rate in addition to the reactivity of the monomers. The interaction of the monomer with the initiator depends upon the nature of solvation of the latter in hexane, and solvation is also a factor in the stabilization of the positive charge of the carbonium ion and in the extent of dissociation of the ion pairs.

In the bulk polymerization initiated with BF_3OEt_2 , both monomers formed products which had very low molecular weights. α -Methylstyrene and the soluble fraction of α ,p-dimethylstyrene polymers had number average molecular weights of 785 and 4200 or degrees of polymerization of 6.7 and 40, respectively. The average degree of polymerization, $\overline{\text{DP}}$, is the ratio of the rate of propagation compared to the rate of termination and transfer, and the value of $\overline{\text{DP}}$ gives an indication of the importance of chain termination reactions to monomer or to the initiating species in these polymerizations. The increased stability of the carbonium ion can account for the favorable k_p/k_t ratio of α ,p-dimethylstyrene. With the lower energy of activation in the formation of the transition state, the rate of propagation is increased relative to the rate of termination.

Thermal Instability. The thermal measurements for evaluating glass transition and melting behavior have been very difficult to make and to interpret in this study because of the thermal instability of poly- α ,p-dimethylstyrene. In the early part of the study, the lack of reproducibility of the measurements was dismaying. The polymer samples were observed to degrade with repeated scans on the DSC. There was early evidence that pre-annealing was required, but in fact, it only

contributed to the degradation. Some polymer samples had well-defined endotherms which were characteristic of melting, but with other samples there was evidence of degradation before the melting was completed.

Nevertheless, DSC measurements are reproducible from sample to sample when precautions are taken to limit the number of heating and cooling scans in order to minimize degradation. At heating rates of 20°C/min, the glass transitions were reproducible for two or three scans but at 10°C/min, the values for the T_g were depressed 2-3° with each additional scan. The melting endotherms generally occur approximately 10°C before the onset of rapid degradation. In every case the endotherm was detected on the first scan in the DSC measurement but not on the second scan, although if the scans were interrupted before the sample was completely melted, the melting from the residual crystallinity in the sample would be observed on the next scan. If the polymer was annealed before measuring the melting point, the value for T_m was depressed but there was no evidence of weight loss. Table XXI summarizes the data illustrating this type of depression of the melting point. The depression of the melting point is attributed to the diluent effect of the monomer which is formed in a degradation reaction.

To determine, if possible, whether the endotherm that was observed was due to melting or to degradation the following experiment was done. The crystallinity of powder samples of the copolymer of α , p -dimethylstyrene and α -methylstyrene (99/1) which had been annealed in octanone-2 was determined by x-ray diffraction spectroscopy. The sample which was used for the x-ray analysis was then examined on the Differential

Scanning Calorimeter. The melting endotherm was observed at 475-496°K with a peak at 487°K on the first scan but not on the second. Care was taken to terminate the scan at 496°K. To determine whether thermal degradation may be prevented recrystallization, the samples were recovered from the DSC scan and examined for weight loss. None was detected after the two scans nor was the characteristic order of monomer observed that occurs when the polymer unzips in thermal degradation. A second x-ray diffraction spectrum was then obtained for these samples and the crystallinity was observed to have disappeared confirming the DSC results. Hence, it was concluded that the endotherm observed for poly- α , p -dimethylstyrene on the Differential Scanning Calorimeter that occurred at 475-496°K was a melting endotherm.

TABLE XXI

Summary of the Data for the Copolymer of α , p -Dimethylstyrene with α -Methylstyrene Showing the Depression of the Melting Point with Annealing

<u>Sample Number</u>	<u>Number of Annealing Scans</u>	<u>Maximum Temperature °K</u>	<u>T_m °K</u>
1	None	--	493
2	1	460	489
3	1	480	487
4	3	460	475
5	Refluxing Octanone-2 (450°C)		487

Summary. Crystalline polymers were prepared with the two *p*-substituted monomers, α ,*p*-dimethylstyrene and *p*-isopropyl- α -methylstyrene, but no crystalline polymers were prepared with α -methylstyrene in any of the cationic systems examined in this work. α ,2,4,-Trimethylstyrene did not polymerize presumably because of the steric hindrance of the *o*-methyl substituent with the α -methyl substituent.

Copolymers of α ,*p*-dimethylstyrene with α -methylstyrene, α ,*p*-dimethylstyrene with *p*-isopropyl- α -methylstyrene, and *p*-isopropyl- α -methylstyrene with α -methylstyrene were crystalline when they contained 85% or more α ,*p*-dimethylstyrene.

Reaction heterogeneity appears to be associated with crystallinity because the *p*-substituted polymers and the copolymers which were crystalline were all prepared in heterogeneous polymerization systems. However, the three poly- α -methylstyrenes, which were prepared in an heterogeneous polymerization, were not crystalline.

Crystallinity is also believed to be dependent upon the physical state of the initiator and upon the ability of the solvent to swell the growing polymer chain.

The nuclear magnetic resonance spectra of poly- α -methylstyrene and α ,*p*-dimethylstyrene were obtained on the Varian A-100 and for *p*-isopropyl- α -methylstyrene on the Varian A-60. The chemical shifts of the α -methyl protons in poly- α ,*p*-dimethylstyrene relative to HMDS were: $\delta = -0.22$ and -0.32 for the heterotactic and syndiotactic triads, respectively; -0.80 for the methylene protons and -1.05 for the *p*-methyl protons. The chemical shifts of the α -methyl protons in poly- α -methylstyrene relative to dioxane were: $\delta = +3.05$ and 3.27 for the heterotactic

and syndiotactic triads, respectively; +1.99 for the methylene protons and -3.50 and -3.36 for the aromatic protons. The proton spectra of the backbone carbons of poly-(p-isopropyl- α -methylstyrene were not resolved in the NMR spectra.

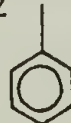
Both poly- α -methylstyrene and poly- α ,p-dimethylstyrene were predominantly syndiotactic with 89 and 95% syndiotactic triads, respectively. The tacticities of the poly- α -methylstyrenes depended upon the polymerization solvent with the degree of stereoregularity decreasing in the following order: toluene > n-hexane/chloroform (7:3) > n-hexane.


The tacticity of the poly- α -methylstyrenes did not vary with the two initiators, BF_3 and BF_3OEt_2 .

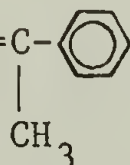
The molecular weight distribution, $\overline{M}_v/\overline{M}_n$, observed in the poly- α -methylstyrene series depended upon the solvent. The value of $\overline{M}_v/\overline{M}_n$ decreased in the following order: toluene > n-hexane/chloroform (7:3) > n-hexane.

On the basis of the infrared spectra and the NMR spectra, the polymers of α ,p-dimethylstyrene and α -methylstyrene were linear, and on the basis of the infrared spectra alone the poly-(p-isopropyl- α -methylstyrene) was a linear polymer.

On the basis of the infrared spectra, the chain ends were predominantly the unsaturated group $\sim\text{CH}_2-\text{CH}=\text{CH}_2$, but an absorption peak



for a trisubstituted alkene, $\sim\text{CH}=\text{C}-$  was also observed in the



spectra for poly- α ,p-dimethylstyrene prepared in toluene and the mixed solvent.

Glass transition temperatures, $T_g(\infty)$, for poly- α -methylstyrene prepared in toluene and the mixed solvent were not sensitive to slight variation in tacticity, e.g., a change of 2° for a difference in the syndiotactic triads of 8%. Glass transition temperatures, however, were very much dependent upon the nature of the para-substituent in the repeating unit. The T_g decreased in the following order:
 α -methylstyrene > α ,p-dimethylstyrene > p-isopropyl- α -methylstyrene.

Melting points, T_m , were obtained for the crystalline polymers and copolymers by differential scanning calorimetry. The T_m for poly- α ,p-dimethylstyrene obtained by extrapolating the data from the copolymer experiments was $224\text{--}225^\circ\text{C}$, while for poly-(p-isopropyl- α -methylstyrene) was 203°C .

The enthalpy and entropy of fusion of poly- α ,p-dimethylstyrene, ΔH_u and ΔS_u , respectively, were found to be 2400 cal per mole of repeating unit and $4.8 \text{ cal } ^\circ\text{K}^{-1}$ per mole of repeating unit.

X-ray diffraction spectra were obtained for poly- α -methylstyrene, poly- α ,p-dimethylstyrene, and poly(p-isopropyl- α -methylstyrene). The x-ray diffraction spectra of poly- α -methylstyrene showed two amorphous halos with maximum occurring at 2θ of 10° and 16° . The d-spacings for poly- α ,p-dimethylstyrene were: 3.6, 5.1, 5.4, 7.0, 8.7 and 10.5 \AA and for poly(p-isopropyl- α -methylstyrene) were: 3.6, 5.1, 5.4, ~ 6.5 , ~ 9.3 and 13.3 \AA ; and for the copolymers of α ,p-dimethylstyrene and α -methylstyrene were: 5.5, 6.8, 8.7, 10.5 and 21.5 \AA .

Conclusion. There are two possibilities to account for the crystallinity that has been observed in the p-substituted α -methylstyrene

polymers. The first is that the crystallinity observed in these polymers is due to crystallization that occurs during the polymerization reaction. This phenomena³⁴ has been observed in a number of polymerization systems, notably, the radical polymerization of polytetrafluoroethylene and the cationic polymerization of polyoxymethylene. According to Wunderlich, crystallization during polymerization requires the spontaneous nucleation of solid crystalline polymer followed by chain growth on the crystal surface. In crystallization during polymerization, both the configuration and the conformation are determined at the time of the reaction. Polymers formed by this mechanism would preferentially have the extended chain conformation.

The alternate explanation for the formation of crystalline p-substituted polymers depends upon increased stereoregularity which is conducive to crystallization. Syndiotactic poly- α -methylvinylmethylether³⁵ have been prepared and has been reported to be moderately crystalline. The x-ray analysis indicates that this polymer chain assumes a helical conformation in the crystalline state. This polymer, however, was polymerized in a homogeneous system. The mechanism of stereoregulation proposed by the authors is the formation of pseudo-six-membered rings in which the configuration of the two preceding units determines the orientation of the incoming monomer.

Both the α -methylstyrene and the α ,p-dimethylstyrene polymers are syndiotactic, linear polymers. The differences in the stereoregularity may account for the lack of crystallinity in poly- α -methylstyrene. However, there are visual differences in the polymerization reactions of the two monomers which are evidence that polymerization is occurring

by a different mechanism, such as crystallization during the overall polymerization reaction. In addition, the crystallinity is observed in the samples of virgin polymers without any pretreatment usually required to develop crystallinity in polymers.

It appears that the differences in crystallinity arise from differences in the mechanism of polymerization which, in turn, is due to the subtle differences in the stability of the carbonium ion.

Recommendations. The work which has been reported in the literature for the cationic polymerization of poly- α , β -dimethylstyrene cannot be adequately evaluated because the results depend upon the specific reaction conditions, the methods of characterization and the techniques of the individual research worker. Although there is a general agreement in the trends of stereoregulation, there is no agreement upon the specific tacticities obtained. In this study, when the isotactic content of poly- α -methylstyrene was increased, the polymer was either a very low molecular weight polymer or had an increased fraction of low molecular weight species. Therefore, it is recommended that in any future study of the stereoregularity of poly- α -methylstyrene, the relationship of molecular weight and the molecular weight distribution and tacticity should be examined.

Future studies with poly- α , β -dimethylstyrene should examine the solution properties of the amorphous polymers. It was observed in this study that a soluble poly- α , β -dimethylstyrene was prepared at room temperature when the monomer was slurried with Linde Molecular Sieve-3A. It is also reported² that soluble, amorphous poly- α , β -dimethylstyrene was formed in polymerization reactions initiated with H_2SO_4 .

Finally, polymers of substituted α -methylstyrene with other p-substituents should be examined to determine whether crystalline polymers can be formed. Specifically, p-ethyl, p-tert-butyl-, p-methoxy- and p-chloro-substituted α -methylstyrenes should be examined.

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