To the Graduate Council:

I am submitting herewith a thesis written by Chester M. Vandergriff, Jr. entitled "Synthesis and Microstructure of Poly(p-Methoxystyrene)." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

James F. Kinstle
James F. Kinstle, Major Professor

We have read this thesis
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SYNTHESIS AND MICROSTRUCTURE OF POLY(p-METHOXYSTYRENE)

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee

Chester M. Vandergriff, Jr.

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ABSTRACT

In an attempt to ascertain the microstructure of poly(p-methoxystyrene), p-methoxystyrene was made in a multistep synthesis from p-methoxyacetophenone. The monomer was then polymerized thermally and cationically and used in subsequent reactions. Poly(p-methoxystyrene was reacted with Br_2 to exchange the meta protons. This reaction gave an insoluble polymer which could not be used in this study. Exchange of the meta protons was then attempted by reacting poly(p-methoxystyrene) with n-butyllithium and quenching the reaction with D_2O. This proved to be a low yield reaction and was abandoned in favor of a deuterated monomer synthesis.

Several synthetic routes were attempted in making 3,5-dideuterio-4-methoxystyrene. Of these routes, the following was chosen. Para methoxyacetophenone was reduced to p-methoxyethylbenzene. The product was repeatedly treated with n-butyllithium and subsequently D_2O until 3,5-dideuterio-4-methoxyethylbenzene resulted. This product was then brominated and dehydrohalogenated to give 3,5-dideuterio-4-methoxystyrene. This monomer was polymerized as before, and nmr spectra of the ortho protons were studied for microstructure information. From these spectra, tentative conclusions, which are in agreement with earlier work, were drawn.

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CHAPTER I

INTRODUCTION AND BACKGROUND INFORMATION

A. Polymer Stereochemistry

1. Definitions

In 1932 Staudinger pointed out that a monosubstituted vinyl monomer forms a polymer in which alternate carbon atoms are asymmetric.[1] Since that time, many studies have centered on elucidation of polymer stereochemistry and on the relations between microstructure and macroscopic properties.

It is now understood that the atoms of the polymer backbone are not truly asymmetric and are, therefore, not optically active. Two of these substituent groups on the "asymmetric" carbon are equivalent for five to seven or more carbons. Consequently, there is no resultant optical activity; and these carbons are called "psuedo asymmetric." It was quickly found that the prefixes d and l used to designate stereoisomers in low molecular weight compounds would be very unwieldy for use on polymeric materials. To circumvent this problem, stereoregular polymers were said to be tactic polymers.[2]

It is easily shown that there are three different arrangements obtainable when linking monosubstituted vinyl units in a head-to-tail fashion. These are displayed in

Figure 1, in which the polymer segments are depicted in their fully extended, all-trans conformations. Figure 1, structure a, is an isotactic polymer segment, in which each substituted carbon has the same configuration as its neighbors. Each R substituent is on the same side of the chain. Structure b is a syndiotactic segment in which each substituted carbon has the opposite configuration of its neighbors. The R groups are thus on alternating sides of the extended chain. Structure c is one of many possible atactic segments.

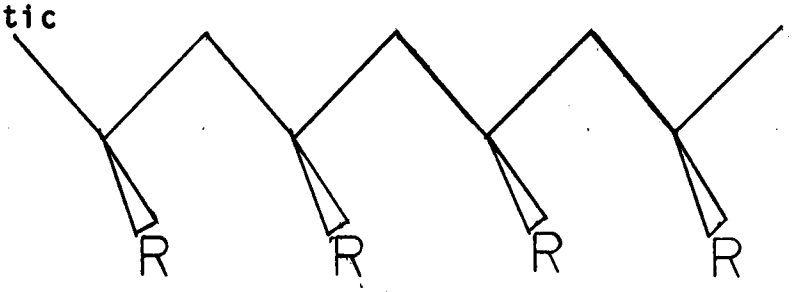
By using the tacticity convention, one can clearly designate the stereoregularity of a polymer chain.

2. Mechanism

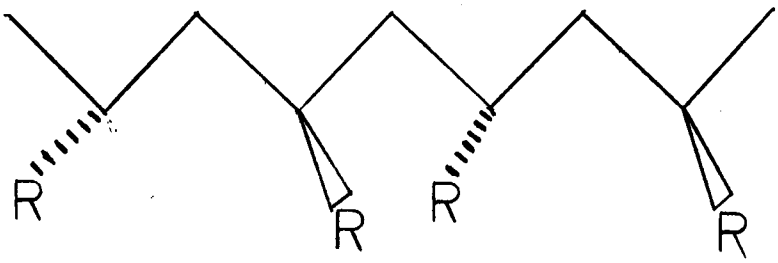
A knowledge of the stereochemistry of a polymer provides an insight into the mechanism of placement that must occur to give different tactic forms. Figure 2 shows a schematic diagram of two consecutive propagation events during polymerization and illustrates the formation of each possible three unit segment (triad). Consecutive meso placements lead to isotactic segments, and consecutive racemic placements lead to syndiotactic segments.

Since most polymerization reactions do not proceed in a stereoregular fashion, placement mechanisms and sequence formation are usually described by a statistical approach.

a. Isotactic



b. Syndiotactic



c. Atactic

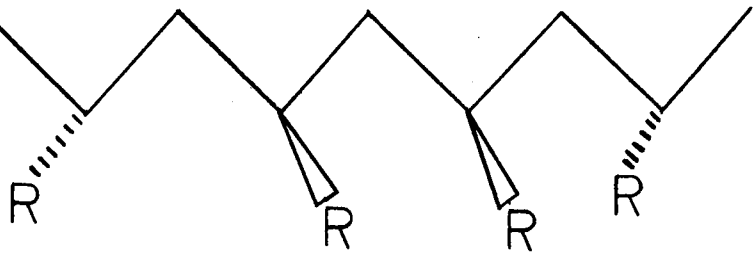


Figure 1. Tacticity of polymer from monosubstituted vinyl monomer.

(a) Isotactic segment, (b) Syndiotactic segment, and (c) One of the possible atactic segments.

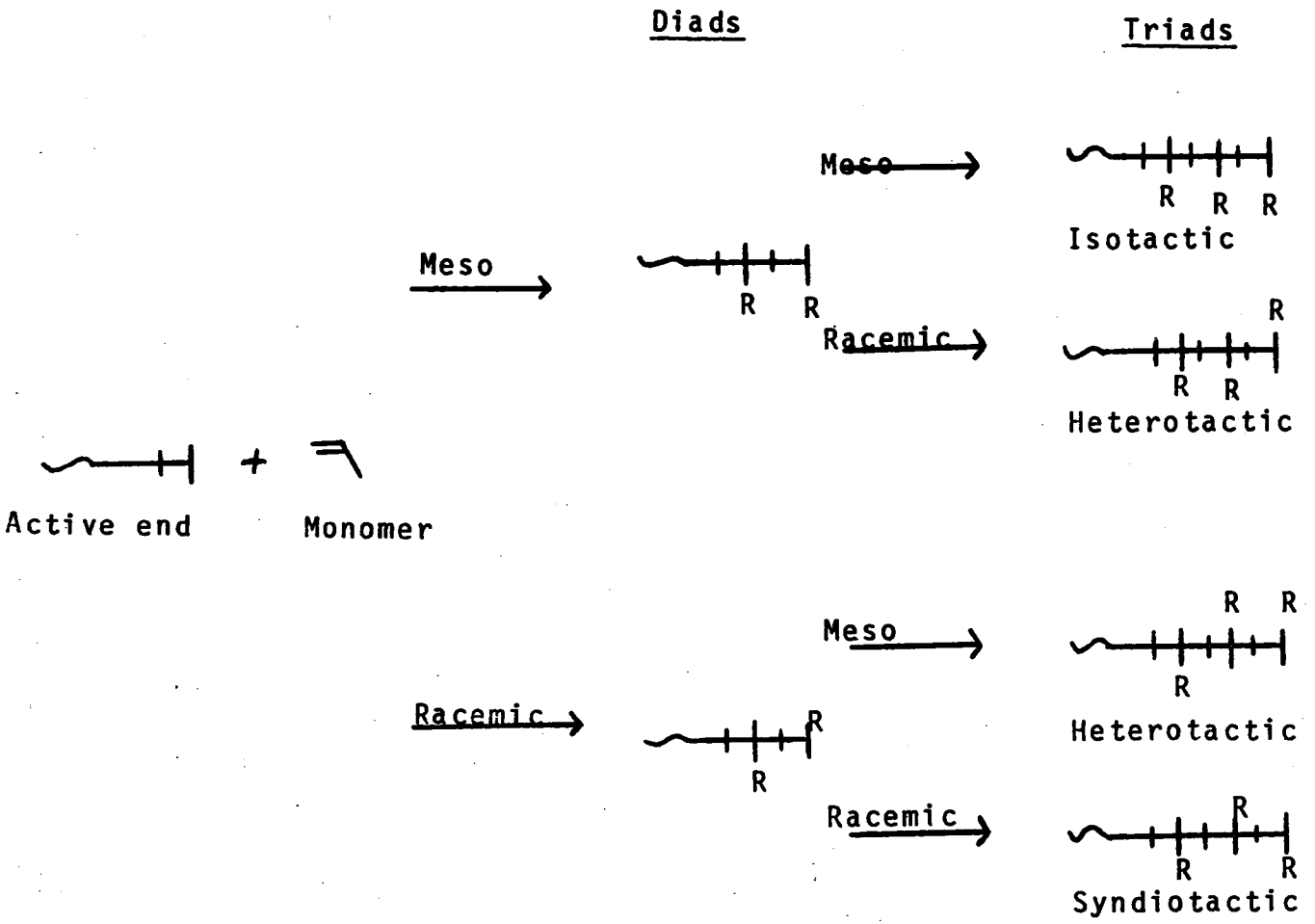


Figure 2. Schematic diagram of stereochemical diad and triad formation during polymerization.

The stereochemical placements that occur during polymerization can usually be described in terms of either Bernoullian or first order Markoffian statistics.

The Bernoullian approach utilizes a one-parameter model; the placement of the incoming monomer unit is independent of the preceding placement. Bernoullian statistics describe most free radical and many uncomplexed ionic polymerization reactions. In polymerization reactions where Bernoullian statistics are not sufficient to describe a polymerization, first order Markoffian statistics often apply. First order Markoffian statistics describe placement probabilities when the stereochemical placement of an incoming monomer unit depends on the relationship of itself with the end monomer unit on a growing polymer chain. This type of statistical approach is useful in some ionic polymerizations in which the active chain and its counter ion influence the mode of addition of an incoming unit.

Higher order statistical treatments include second and third order Markoffian approaches. These are unwieldy due to a large number of parameters. Also noted are Coleman and Fox two state models, which appear to describe certain poly(methyl methacrylates) prepared by anionic initiators.[3,4,5]

3. Analysis

Since the development of methods for producing highly stereoregular polymers, methods for deducing polymer tacticity have been sought. A versatile method with applicability to both crystalline and amorphous polymer was not available until the development of nuclear magnetic resonance (nmr) spectroscopy. Nmr spectroscopy has proven to be a valuable tool in establishing the stereochemistry of many vinyl polymers. The basis of nmr is the ability to detect subtile differences in the magnetic environments of atoms--in our case protons. If two distinct (non-interacting) protons are in identical magnetic environments, the protons will exhibit a single resonance (singlet). This is the case for the methylene protons centered between racemic placements in a polymer from $CH_2{=}CRX$, where $R{\neq}X$ and neither is H (see Figure 3a). Proton H_o is affected through bonds or through space by R_o, X_b, X_o, and R_b. Likewise, proton H_b is affected in exactly the same way by atoms R_b, X_o, X_b, and R_o, respectively. Therefore, H_o and H_b experience identical magnetic environments and are displayed as a singlet on the nmr readout. If the two protons were in different magnetic environments, they would each exhibit their own individual resonance signal. However, since adjacent (and to a lesser degree more distant) atoms mutually affect each other's resonance, a phenomenon called coupling occurs. The methylene protons centered

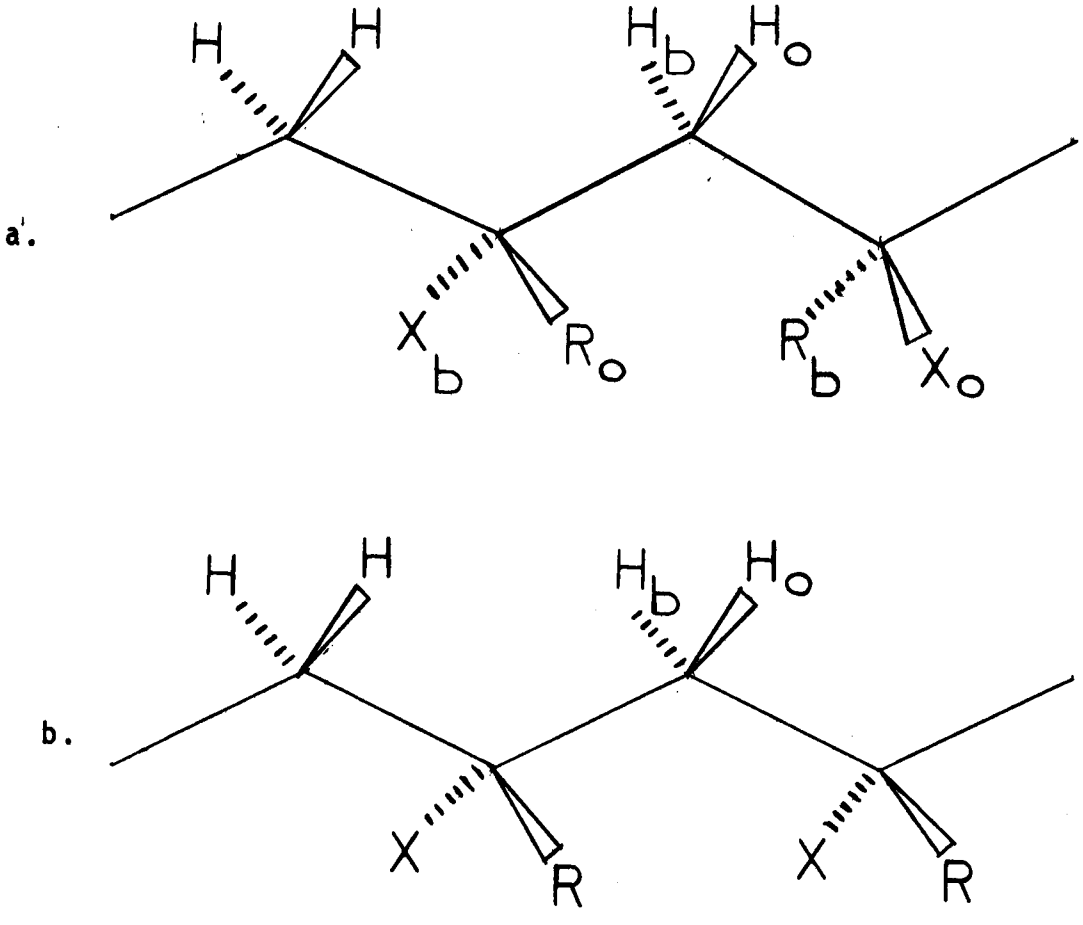


Figure 3. Influence of substituents on adjacent methylene protons as a function of stereochemistry.

between meso placements in a polymer from monomer $CH_2{=}CRX$ illustrate these phenomena. As can be seen in Figure 3b (p 7), H_o is closer to the R groups and H_b is closer to the X groups, so H_o and H_b are nonequivalent. This non-equivalence leads to display of two resonances, but coupling causes these two to each be split into a doublet, so the net signal is a quartet. These principles allow nmr analysis to be used as an absolute measure of polymer stereochemistry in a stereoregular polymer. Nmr analysis is also useful in studies of non-stereoregular polymers as detailed in the following sections.[6]

B. Nmr Studies of Polymer Stereochemistry

1. Poly(methyl methacrylate)

The first quantitative measurement of polymer tacticity by use of nmr spectroscopy was reported in 1960.[7] Polymers were prepared from methyl methacrylate under various conditions. The best polymers for comparison are those from anionic polymerization using n-butyllithium at -62° and from the free radical polymerization using benzoyl peroxide initiation at 100°. Figure 4 shows the 60 MHz proton nmr spectra of these two polymers. The large peak at the left is due to chloroform solvent. The peak at 3.60 δ is due to the estermethyl group and appears as a singlet in the same position in both spectra. When one looks at the remainder

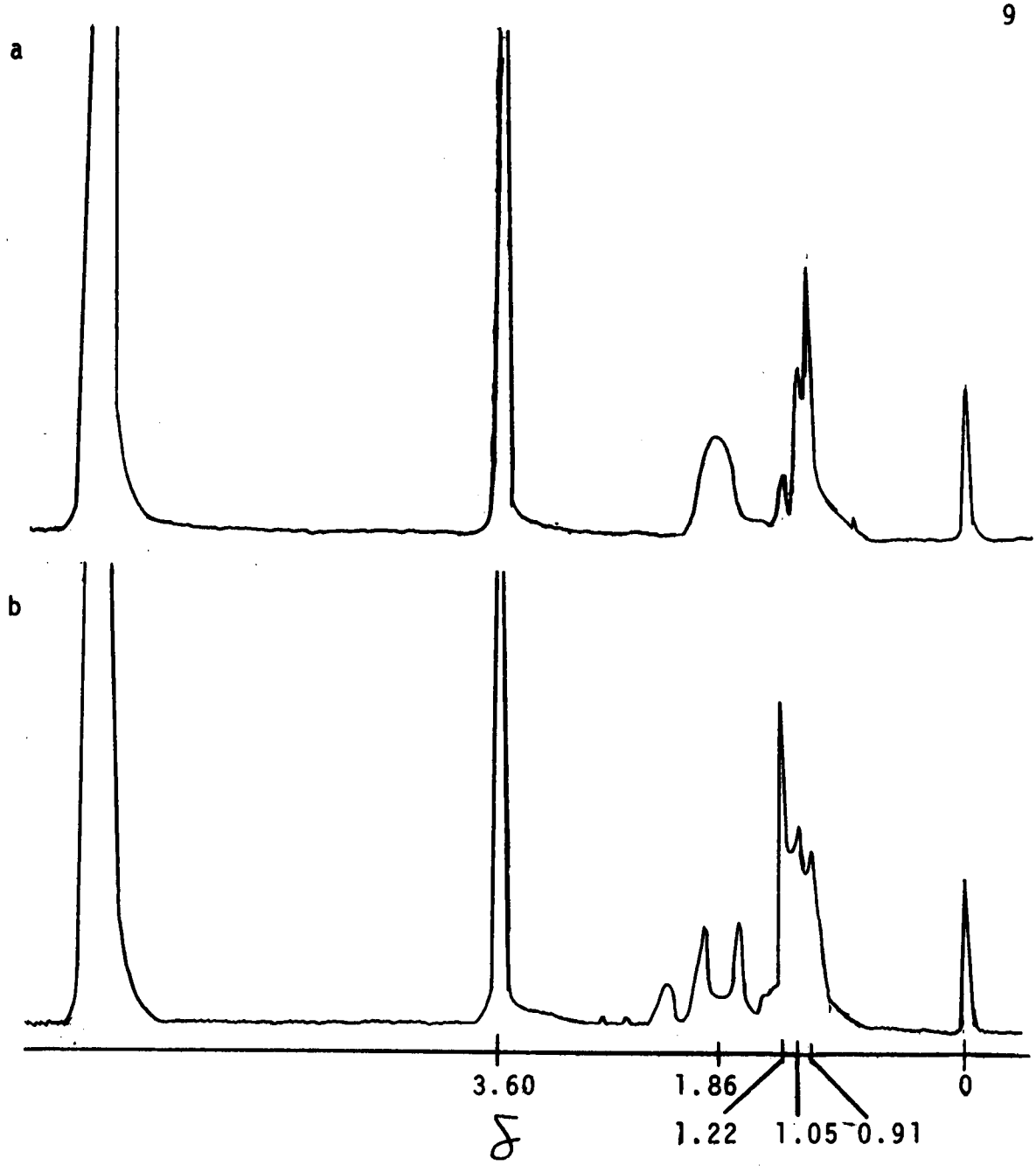


Figure 4. Nmr spectra of methyl methacrylate polymers in chloroform solvent with TMS reference.

Polymers formed by (a) benzoyl peroxide at 100° and (b) n-butyllithium in toluene at -62°.

of the spectra, one sees many differences. The greatest differences, which appear in the α methyl resonance at 1.2 δ to 0.9 δ, are explained as follows. The three peaks of the α methyl resonance are attributed to the tactic triad fractions of the polymer; isotactic at 1.22 δ, heterotactic at 1.05 δ, and syndiotactic at 0.91 δ. This is reasonable because in syndiotactic polymer the α methyl group is the most shielded by adjacent ester moieties and would be most upfield. This assignment also agrees with work on low temperature free radical polymerization, where it was noted that due to minimal propagation energies, the thermodynamically most stable product, syndiotactic polymer, predominates.[5,8] In the case of the isotactic peak at 1.22 δ, one has the α methyl group situated in space as far away as possible from the carbonyls, so little if any influence is seen on the isotactic fraction. This is consistent with later findings where poly(methyl methacrylates) prepared by n-butyllithium initiation in hydrocarbon solvent were predominately isotactic.[10]

The nmr spectra of the "backbone" methylene resonance also confirm the assignment. In spectrum 4b (Figure 4, p 9) the methylene resonance is split--showing that the methylene hydrogens are in different environments (predominately isotactic polymer). The methylene resonance in spectrum 4a is not split; i.e., the methylene hydrogens are equivalent.

(predominately syndiotactic polymer). The assignments were also confirmed by use of X-ray analysis from which the absolute stereochemical configuration can be assigned.

2. Polystyrene

Although the configurations of many vinyl polymers have been determined by the use of high resolution nmr spectroscopy, until recently it has not proven entirely successful in the study of polystyrene.[10] It has been known for several years that the nmr spectrum of polystyrene shows features which are not seen in small molecule analogues like cumene. Relative to cumene, all resonances from polystyrene are broadened and shifted upfield. For polystyrene, the methine and methylene resonances overlap.[11] Also, the protons of the phenyl groups in polystyrene do not appear as a narrow resonance as they do in cumene. Kern and Pustinger were the first to observe that the α and β resonance could be separated in isotactic polystyrene and later Yoshino and coworkers separated the resonances in the atactic polymer as well.[12,13] It was also shown that the chemical shift difference between α and β protons in isotactic polymer is greater than in atactic polymer, but is never large enough to allow simplification of the spectrum by double resonance techniques.[14] Brownstein and coworkers observed that in the α proton spectrum of poly(β , β , d_2-styrene) one could discern resonances

corresponding to the three tactic forms.[7,11,14] However, resolution of the peaks was poor; and quantitative interpretation was not obtainable. Later, in 1965, Bovey and coworkers reported improved nmr resolution of polystyrene and compared both isotactic and syndiotactic polymers with model compounds.[15] However, none of these methods gave unambiguously the stereochemistry of polystyrene.

It should be noted that in all of the studies above, only the resonances of the polymer backbone are considered.

In 1969 Kinstle and Harwood investigated the possibility of using the phenyl group in determination of polymer tacticity.[16] Since the ortho protons of the phenyl group appear upfield of the other aromatic protons, these workers reasoned that the apparent high sensitivity of the ortho protons to intramolecular shielding may allow their use for a measurement of the stereochemistry in the polymer. However, study of these protons are complicated by overlap of signals from meta and para protons and by coupling of the ortho and meta protons. This was overcome by substitution of deuterium atoms for the meta and para protons. Deuterium atoms do not exhibit a signal in the proton nmr range and do not couple with adjacent protons. Further, they are near enough to hydrogen in steric and electronic characteristics that they can be substituted on the monomer without affecting the propagation mechanism.

The appropriate monomer, 3,4,5-trideuteriostyrene, was prepared in a multistep synthesis. Poly(3,4,5-trideuteriostyrene) was prepared by free radical, cationic, and Ziegler-Natta techniques. The aromatic resonance obtained from the polymers prepared by free radical and cationic initiation appeared as a multiplet of peaks which were ascribed to syndiotactic, heterotactic, and isotactic triads, respectively, with increasing field. This assignment, which is in the reverse order observed for the methyl resonance of poly(methyl methacrylate), is reasonable because here one is looking not at a proton between two anisotropic groups, but at a proton on the anisotropic group. Therefore, in syndiotactic polymer the ortho hydrogens are least shielded and most downfield, whereas the ortho hydrogens in the isotactic triads are most shielded. The polymer from free radical polymerization was predominately syndiotactic, with increasing randomness observed in cationically prepared polymer. Very pure isotactic polymer was obtained from the Ziegler-Natta polymerization. Thus, the nmr signals from the protons ortho to the chain juncture can provide a method of assigning stereochemical configuration to polystyrene chains.

3. Poly(o-methoxystyrene)

Poly(o-methoxystyrene) is another phenyl-substituted polymer which has been analyzed stereochemically. In one of

the earlier investigations by Natta, it was found that the ortho and para isomers of methoxystyrene polymerized well via cationic initiation to give amorphous polymers.[17] One sample of amorphous poly(o-methoxystyrene), prepared at -78° in toluene with $EtAlCl_2$ initiator, was thought to be highly isotactic. This sample was hydrogenated using Raney-nickel catalyst at 100 atmospheres pressure and 180° for 65 hours, to give poly(2-methoxy vinyl cyclohexane). The derived saturated polymer crystallized. This indicated that lack of crystallinity in the parent polymer was probably not due to lack of stereoregularity. It was also proposed that the most probable mechanism for production of isotactic polymer under these conditions was coordination of initiator with the methoxy group. Such coordination in the para isomer would be far removed from the polymerizing group and would exert minimal influence on propagation mechanism. A good test of this proposal would have been to hydrogenate the poly(p-methoxystyrene). If this polymer were not crystalline after hydrogenation, the proposal would have been, at least in part, verified. However, poly(p-methoxystyrene) resisted all attempts at hydrogenation. Further questions were posed in 1965 by Kern and Braun, who proposed that the highly regular polymer formed by the Natta group may have been syndiotactic rather than isotactic.[18] Also, in 1968, workers at Kyoto University prepared poly(o-methoxystyrene) under conditions supposedly identical to those used by the

Natta group and studied its nmr spectrum. They concluded that the polymer was predominately heterotactic.[19] This first nmr study of the stereochemistry of poly(o-methoxystyrene) involved o-methoxystyrene polymers prepared by a variety of initiators under various conditions (see Table I). Three methoxy peaks were observed, whose areas were taken as a measure of tacticity. The order of appearance of the o-methoxy resonances was syndiotactic, heterotactic, and isotactic, in order of increasing field. The authors also concluded that the solvent had no effect on the tacticity of the resulting polymer and that temperature change affected the tacticity of polymer formed in toluene, but not that of polymer formed in methylene chloride. The results of this study disagree with earlier studies. For example, their conclusion that polymer prepared by $EtAlCl_2$ initiation was heterotactic is inconsistent with Natta's findings that polymer prepared in the same way crystallized after hydrogenation. They did not comment on such points of disagreement.

There are other nmr studies of poly(o-methoxystyrene) such as the one by Yuki and coworkers.[20] These workers prepared poly(o-methoxystyrene) with various anionic initiators under various conditions and attempted to use the methoxyl resonance as a measure of tacticity. Tacticities were assigned using the order heterotactic, isotactic, and syndiotactic in order of increasing field. This

TABLE I[19]

TACTICITIES OF POLY(o-METHOXYSTYRENES) PREPARED UNDER VARIOUS CONDITIONS

Initiator	Solvent	Temperature (°)	Tacticity (%) S	H	I
AIBN	Toluene	30	40	46	14
AIBN	Toluene	60	39	48	13
AIBN	Toluene	80	35	47	18
$BF_3:OEt_2$	Toluene	-78	39	49	12
$BF_3:OEt_2$	Toluene	-20	55	36	9
$BF_3:OEt_2$	Methylene Chloride	Varied	52	41	7
$SnCl_4$	Toluene	-78	49	41	10
$AlEtCl_2$	Toluene	-78	40	50	10

unconventional assignment was different from the Kyoto workers' assignment, but this difference was not resolved in the paper. It is obvious that the stereochemical analysis of poly(o-methoxystyrene) is questionable at best; before any absolute conclusions may be drawn, more work must be done and existing studies must be re-analyzed.

C. Prior Studies of Poly(p-methoxystyrene)

1. Introduction

In the literature one will find several references to poly(p-methoxystyrene). These references contain information concerning polymerizability, reactivity, and solution data.[17,21-25] However, unlike poly(o-methoxystyrene), no information concerning stereochemistry has been published.

2. Radical Polymerization and Polar Effects

In 1965 Ayrey and coworkers published their work on radical polymerization of p-methoxystyrene and other styrene derivatives.[21] Isotopic C^{14} AIBN was used to determine the mode of termination. This was done by radioactive end group tracer analysis. The workers assumed that if termination occurred only by disproportionation (abstraction of a beta hydrogen), or by radical coupling of two growing chains, then the relative proportion of each type termination could be determined by counting the number of initiator fragments per polymer chain. This study also gathered

information on rates of initiation and propagation and came to the following conclusions. Para methoxystyrene showed lower rates of initiation and propagation than did para chlorostyrene or styrene. Where it was found that styrene and para chlorostyrene terminated predominately by a coupling or combination mechanism, p-methoxystyrene exhibited an increasing tendency to terminate by disproportionation, especially as the temperature increased. These results on termination reactions for p-methoxystyrene were rationalized by saying that in the systems studied both p-chlorostyrene and p-methoxystyrene are more reactive than styrene and therefore, have slightly less reactive polymer radicals. The increase in termination by disproportionation by poly(p-methoxystyrene) radicals was attributed to the electron donating effect of the p-methoxy group. Szwarc had stated that although radicals are neutral species, changes in structure could invoke slight nucleophilic or electrophilic character.[26] According to Ayrey, the growing poly(p-methoxystyrene) radical would be essentially an electronegative radical. This electronegative nature purportedly induced repulsion polarizing the transition state. These polar effects on rates of polymerization and initiation are in general agreement with earlier work of Imoto, et al., but the latter workers' assumption that termination is solely by coupling rules out comparison of data on the termination reaction.[22]

3. Cationic Polymerization

Stereospecific cationic polymerization of p-methoxystyrene was attempted by Natta and coworkers in 1962.[17] In this study ortho, meta, and para methoxystyrene monomers were individually subjected to polymerization via homogeneous Friedel-Crafts catalysts. The meta isomer failed to give polymer under any conditions studied. The ortho methoxystyrene required strongly cationic catalysts for polymerization, but para methoxystyrene could be polymerized with catalysts showing much weaker cationic activity. It was also found, as previously mentioned, that poly(o-methoxystyrene) could be hydrogenated to poly(2-methoxy vinyl cyclohexane), but poly(p-methoxystyrene) resisted all attempts at hydrogenation even under severe reaction conditions. From these results, the authors state that no conclusions could be drawn about stereospecific cationic polymerization of para-methoxystyrene.

Cationic polymerization of para-methoxystyrene under the influence of an electric field was reported by Sakurada and coworkers in 1966.[23] These workers attempted to resolve the question of whether cationic polymerization proceeded via ion pairs or free ions. To do this, they logically assumed that polymerization of free ions would be faster than by ion pairs. It was known that under the effects of a strong electric field, ion pairs tend to

dissociate and become free ions. Therefore, if the rate of polymerization under an electric field was greater than the rate of polymerization with no applied field, then the ion pair mechanism could be operative in the latter. They polymerized p-methoxystyrene with iodine in ethylene dichloride under an electric field. After carefully resolving all possible influences which could distort the results, it was found that the rate and degree of polymerization did increase in an electric field. From these results, it appears that the probable mechanism for cationic polymerization of p-methoxystyrene is via ion pair.

4. Heterogeneous (Anionic) Polymerization

Anionic polymerization studies on p-methoxystyrene were reported in 1959 by Natta and coworkers.[27] Several para substituted styrenes were polymerized using aluminum alkyls and titanium halides as catalysts; they found that p-methoxystyrene was a more reactive monomer than other monomers in the study. The authors concluded that the higher reactivity of p-methoxystyrene is due to the strong electron donating effects of the p-methoxy group.

5. Solution Properties

Kotera and coworkers compared the behavior of poly(p-methoxystyrene), poly(p-chlorostyrene), and polystyrene in toluene and butanone.[24] They concluded that toluene is a

good solvent for poly(p-methoxystyrene) and butanone is a poor one. The authors also found that the solubility characteristics of poly(p-methoxystyrene) are more similar to polystyrene than to poly(p-chlorostyrene). The workers also found that the unperturbed dimensions of poly(p-methoxystyrene) are larger than that of polystyrene. The workers attribute this to an increase in the chain extension of the polymer molecule.

The study of the dimensions of poly(p-methoxystyrene) was continued in 1971 by Ceccoruilli and coworkers.[25] Various theories pertaining to the unperturbed dimensions of the polymer chain were evaluated. Polymer viscosities were evaluated in three solvents of different solvent power. From these measurements they concluded that the unperturbed dimensions of the polymer chains are constant and are not influenced by the specific solvent effect.

CHAPTER II

EXPERIMENTAL PROCEDURES

A. Materials

$LiAlH_4$ - Ventron Corporation, used as received.

p-Methoxyacetophenone - (reagent) Aldrich Chemical Company, redistilled before use.

$NaHCO_3$ - (anhydrous reagent) Fisher Scientific, used as received.

HCl - (concentrated reagent) Mallinkrodt, used as received.

K_2CO_3 - (anhydrous reagent) Fisher Scientific, used as received.

Diethyl Ether - (anhydrous, electronics grade) Mallinckrodt, used as received, or redistilled from $LiAlH_4$ if used in a reaction.

Benzene - (reagent, thiophene free) J. T. Baker or Fisher Scientific, dried over 4Å molecular sieves before use or distilled from $LiAlH_4$.

$KHSO_4$ - (reagent) Mallinckrodt, used as received.

CCl_4 - (reagent) Fisher Scientific, used as received, or dried over 4Å molecular sieves if used in a reaction.

D_2O - (99.7% isotopic purity) Aldrich Chemical Company, used as received.

NaOH - (reagent, pellets) Fisher Scientific, used as received.

P_2O_5 - (reagent) Fisher Scientific, used as received.

N_2 gas - (anhydrous) Selox Corporation, passed through P_2O_5 and NaOH drying train as used.

Br_2 - (reagent) Mallinckrodt VBM, used as received.

Methyl Alcohol - (anhydrous reagent) J. T. Baker Chemical Company, used as received.

Hexanes - (reagent, mixture of isomers) J. T. Baker Chemical Company, dried over 4Å molecular sieves.

$CDCl_3$ - (99.8% isotopic purity) Merck, Sharp, and Dohme, used as received.

Iron Powder - (100 mesh) Baker and Adamson Chemical Company, used as received.

Anisole - (reagent) Aldrich Chemical Company, used as received.

D_2SO_4 - (99.5% isotopic purity) Aldrich Chemical Company, used as received.

H_3PO_4 - (85% reagent) Fisher Scientific, used as received.

Tetrahydrofuran - (reagent) Fisher Scientific, redistilled from $LiAlH_4$.

n-Butyllithium - (reagent) Matheson, Coleman and Bell, 1.0 mole in 300 ml benzene solution or Ventron, 2.0-2.4 molar in hydrocarbon, used as received.

$AlCl_3$ - (reagent) J. T. Baker Chemical Company, used as received.

N-Bromosuccinimide - (powder) Aldrich Chemical Company, recrystallized from H_2O and dried under vacuum at 25-40°C.

Quinoline - (refined, b p 235-237°) Matheson, Coleman and Bell, redistilled before use.

$SnCl_4$ - Eastman red label, redistilled from P_2O_5 before use.

4-Tertiarybutylcatechol - (reagent, lump) Aldrich Chemical Company, used as received.

$HgCl_2$ - (reagent) Fisher Scientific, used as received.

Zn - (Mossy) Baker and Adamson Chemical Company or Mallinckrodt Chemicals, used as received.

p-Ethylaniline - Aldrich Chemical Company, redistilled before use.

$NaNO_2$ - (reagent) J. T. Baker Chemical Company, used as received.

HBF_4 - (Purified 40-50% Solution) J. T. Baker Chemical Company, used as received.

Nitrobenzene - (reagent) Fisher Scientific, dried over 4Å molecular sieves before use.

Na_2CO_3 - (anhydrous reagent) Fisher Scientific Company, used as received.

Molecular Sieves - (4Å) Fisher Scientific, used as received.

B. Synthesis of p-Methoxystyrene

1. p-Methoxy- α methylbenzylalcohol

Following the method of Everard, Kumar, and Sutton, a solution of p-methoxyacetophenone (28 g, 0.19 mole) in 100 ml anhydrous diethyl ether was added slowly (1 hour) to a nitrogen-blanketed, mechanically-stirred suspension of 8.0 g (0.21 mole) $LiAlH_4$ in 400 ml diethyl ether.[28] The reaction mixture was stirred for an additional hour. The mixture was quenched by the dropwise addition of water, the layers were separated, and the aqueous fraction was extracted twice with 50 ml portions of ether. The combined organic layer was washed with saturated $NaHCO_3$, dried over anhydrous K_2CO_3, filtered to remove drying agent, and condensed by evaporation of ether. Distillation of the residue at reduced pressure gave 27.1 g (96%) of p-methoxy- α -methylbenzylalcohol, b p 103-105° @ 0.35 mm (literature 104 @ 0.35 mm).[29] The product identification and purity were verified by nmr analysis. The effect of varying reaction time may be seen in Table II.

2. p-Methoxystyrene

According to the method of Overberger and Saunders, 28.4 g (0.19 mole) p-methoxy- α -methylbenzylalcohol in a

TABLE II

$LiAlH_4$ REDUCTIONS OF p-METHOXYACETOPHENONE

Run	Starting Material (g)	Reaction Time (hr)	Product (g)	b p °/mm	Yield (%)
A 1	28.0	2.0	27.1	103-105/0.35	96
A 2	10.0	3.0	6.1	109-112/0.4	60
A 3	20.0	3.5	14.6	113-117/1.0	72
A 4	28.0	2.5	24.1	113-116/1.0	85
A 5	56.0	2.5	42.6	105-110/0.95	75
A 6	28.0	2.0	26.1	104-106/0.85	92
A 7	28.0	2.0	25.5	103-105/0.35	90

125 ml addition funnel was placed on a distillation apparatus which contained 1.0 g fused $KHSO_4$.[30] The pressure was reduced and heat was applied to the flask. When the heating bath temperature reached 200°, alcohol was added slowly so that a slow distillation of the p-methoxystyrene occurred. At the end of the reaction, 17.1 g of impure p-methoxystyrene had been collected. This material was redistilled at reduced pressure from 0.1 g tertiarybutylcatechol to give 12.2 g (48.6%) p-methoxystyrene, b p 49-51° @ 0.85 mm (literature 92-93° @ 13 mm).[31] This process was repeated several times at various temperatures, and the product identification and purity verified by nmr analyses. The results are summarized in Table III. The nmr spectrum of the product is shown in Figure 5.

C. Polymerizations

1. Thermal

The polymers prepared from p-methoxystyrene and from 3,5-dideuterio-4-methoxystyrene are listed in Table IV.

Thermally initiated polymers P1 through P7 were prepared in Pyrex tubes which were sealed by a screw cap; the procedure used for polymer P1 is typical. A 2.0 g portion of p-methoxystyrene was weighed into a baked Pyrex tube. The monomer and the tube were flushed for 15-20

TABLE III

$KHSO_4$ DEHYDRATION OF p-METHOXY-α-METHYLBENZYLALCOHOL

Run	Starting Material (g)	Temperature (^{o})	Product (g)	Yield (%)
K 1	24.8	200	12.2	48.6
K 2	14.6	200	10.2	79.0
K 3	24.1	200	16.2	76.1
K 4	54.6	200	20.2	37.4
K 5	26.7	210	14.3	54.1

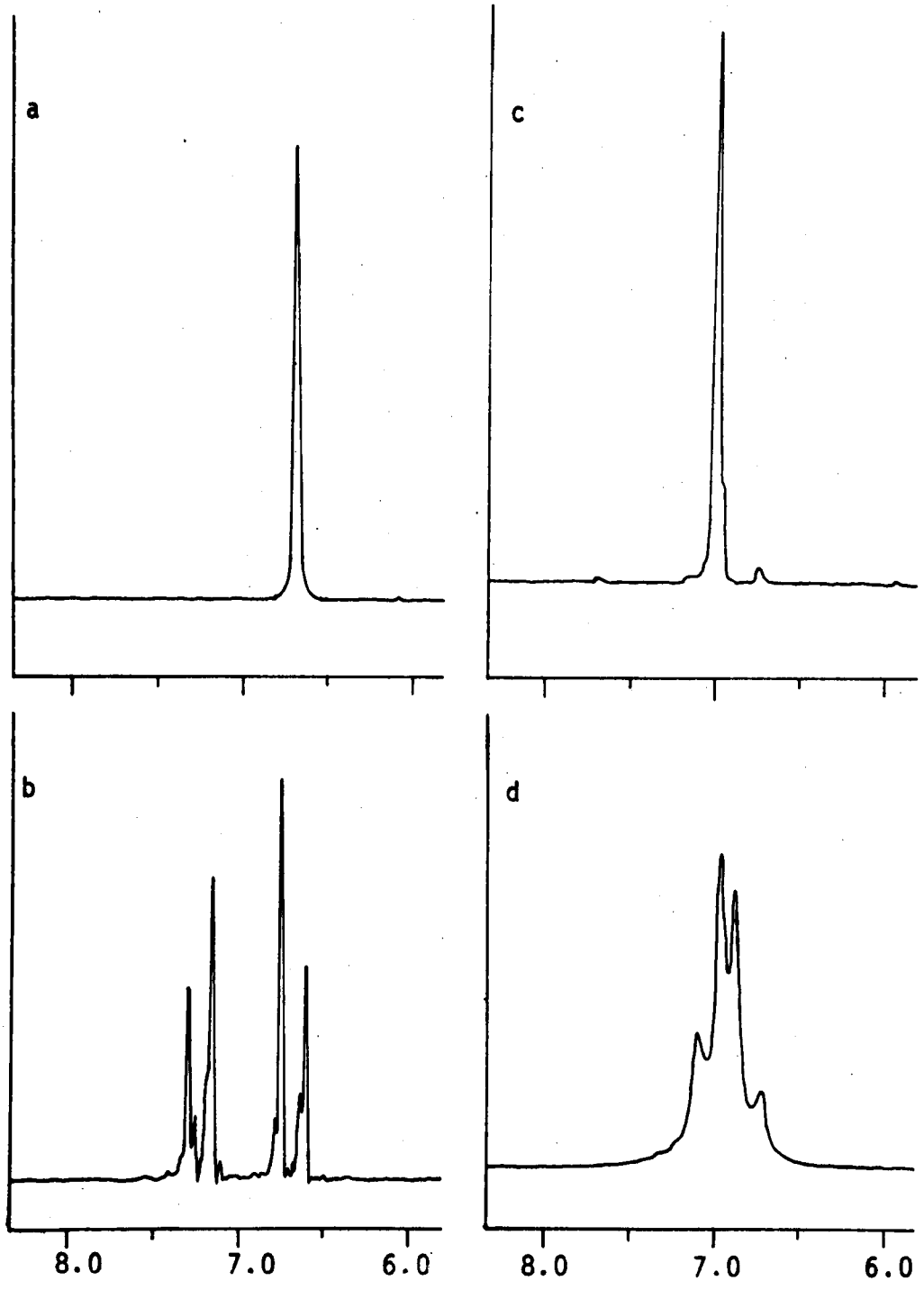


Figure 5. Aromatic proton nmr spectra.

All at 60MHz neat at 40°: (a) N, N, 2,6-tetradeuterio-4-ethylaniline (b) 4-ethylaniline (c) 0,2,6-trideuterio-4-ethylphenol (d) 4-ethylphenol.

TABLE IV

POLYMERIZATIONS OF p-METHOXYSTYRENE AND 3,5-DIDEUTERIO-4-METHOXYSTYRENE

Run	Monomer (g)	Initiator	Time (hr)	Solvent	Temperature (°)
P 1	2.0	-	17	-	160±5
P 2	2.0	-	17	-	160±5
P 3	2.5	-	17	-	160±5
P 4	3.6	-	17	-	160±5
P 5	5.7	-	17	-	160±2
P 6[a]	0.9	-	24	-	160±2
P 7	5.0	-	24	-	160±2
P 8	6.5	$SnCl_4$	5	CCl_4-$ØNO_2$	0-5
P 9[a]	1.1	$SnCl_4$	5	CCl_4-$ØNO_2$	0-5

[a]Represents deuterated monomer.

minutes by a rapid stream of dry nitrogen. The tube was sealed and immersed in a $160 \pm 5^{\circ}$ silicone oil bath for 17 hours. The solid polymer was dissolved in benzene and precipitated by adding the benzene solution to ten times its volume of hexane. The polymer was filtered, purified twice by precipitation from benzene into hexane, air dried, and dried under vacuum at 50°. The nmr spectra of representative polymers are shown in Figure 6.

2. Cationic

The catalyst for cationic polymerization was prepared by mixing 76.0 g CCl_4 and 1.66 g freshly distilled $SnCl_4$ in a 2-ounce bottle equipped with a septum closure.[32] This 2.14 weight percent solution was chilled in an ice bath while a solution of 1.1 ml 3,5-dideuterio-4-methoxystyrene in 4.0 ml nitrobenzene and 3 ml CCl_4 was being prepared. After chilling the monomer solution, 1.1 ml initiator solution was added through the septum closure; and the reaction mixture was chilled in ice for 5.0 hours. The solution was then added to 500 ml methanol with vigorous stirring. The precipitated polymer was collected by filtration and purified twice by precipitation from benzene into first methanol and then hexane. The polymer was air dried, then dried under vacuum at 50°. The nmr spectra of representative polymers are shown in Figure 6.

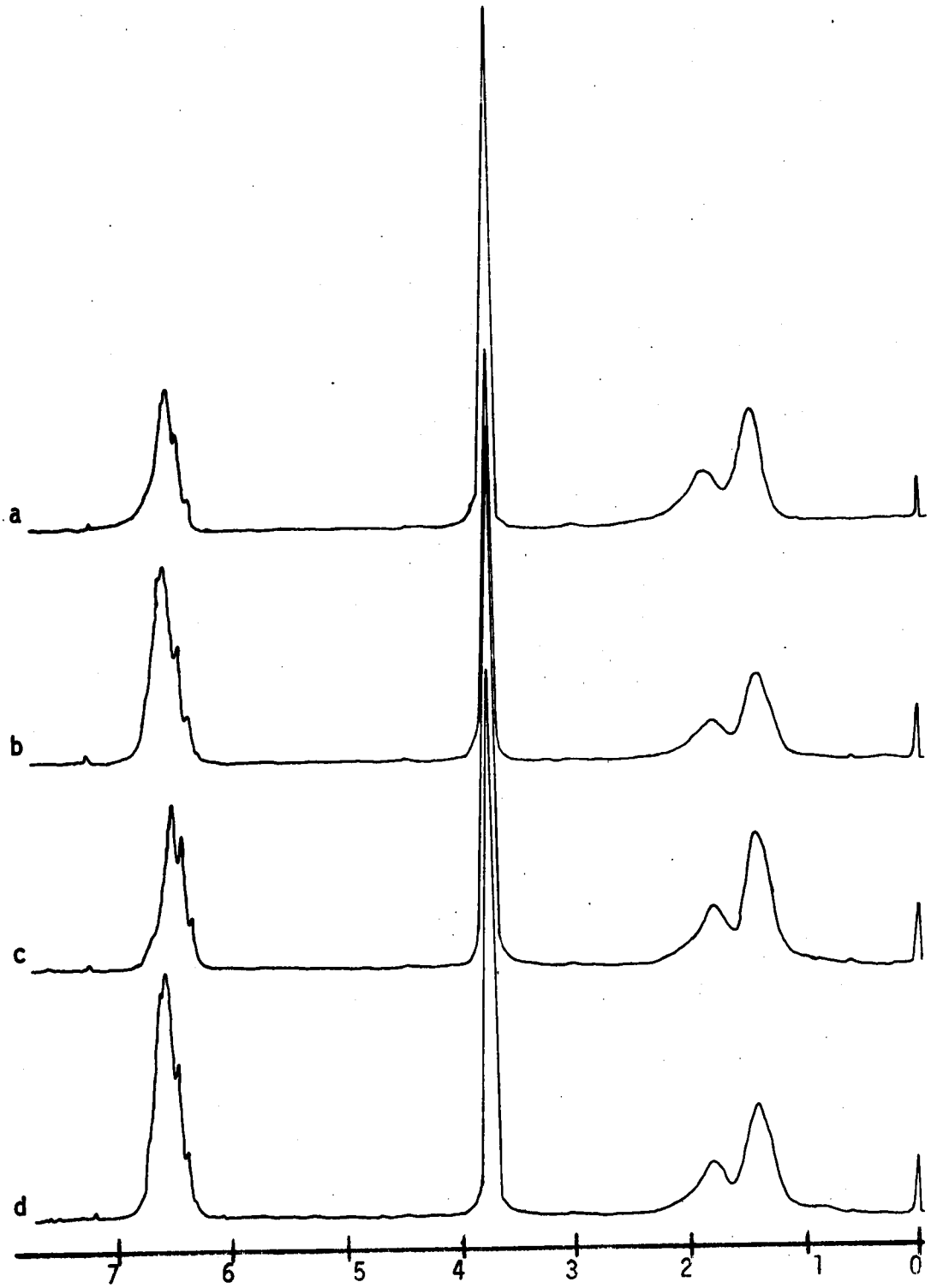


Figure 6. Proton nmr spectra of representative polymers. All at 100 MHz in CCl_4 at 60°; (a) P 6 (b) P 7 (c) P 9 (d) P 8.

D. Reactions on Poly(p-methoxystyrene)

1. Bromination

A solution of 0.53 g (4.0 mmole methoxyaryl units) of poly(p-methoxystyrene) in 6.0 ml (5.2 g, 60 mmole) benzene was placed in a 20 ml foil-wrapped test tube that contained a trace of iron catalyst. This solution was stirred with a mechanical stirrer, and 7.0 ml (20.9 g, 0.13 mole) bromine was added dropwise. After the bromine addition, the suspension was stirred for seven hours, and purified by repeated additions to 200 ml methanol and subsequent filtration. The polymer thus obtained was air dried and then dried under vacuum at 50°. This reaction was repeated several times under different conditions and with different solvents. The results and conditions of these reactions may be seen in Table V.

2. n-Butyllithium-D_2O Exchange

Several reactions of this type were run on the polymer. Of these reactions tabulated in Table VI, P1 is typical. A 2.21 g (16.5 mmole methoxyaryl units) portion of poly(p-methoxystyrene) was freeze-dried in a three-inch standard taper glass tube. This tube was affixed on one neck of a three-necked 250 ml flask which had been nitrogen flushed and baked dry. The flask was equipped with an N_2 inlet, a reflux condenser, a septum port, and was

TABLE V

BROMINATION OF POLY(p-METHOXYSTYRENE)

Run	Solvent	Catalyst	Molar Ratio Br_2/ Methoxyaryl Units	Time (hr)	Results
B 1	THF	None	3.20	24	No Reaction
B 2	THF	None	0.86	24	No Reaction
B 3	C_6H_6	None	25.80	30	No Reaction
B 4	C_6H_6	Fe	16.30	7	Insoluble Polymer
B 5	C_6H_6	Fe	9.79	24	Insoluble Polymer

TABLE VI

DEUTERIUM EXCHANGE ON POLY(p-METHOXYSTYRENE)

Run	Polymer (g)	Solvent	Molar Ratio RLi/ Methoxy	Time (hr)	No. Times Reaction Repeated
P 1	2.6	C_6H_6	1.5	56	2
P 2	1.7	THF	1.5	6	1
P 3	2.8	C_6H_6	3.2	47	3

magnetically stirred. Dried benzene (100 ml) was added to the apparatus and heated at reflux until all the polymer was in solution. After cooling the solution to room temperature, 7.5 ml of 3.33 M (25 mmole) n-butyllithium in benzene was injected via the septum port; and the reaction mixture was stirred at room temperature for 56 hours. The reaction was quenched with excess D_2O (1.6 ml, 80 mmole) and stirred with 50 ml of 3M HCl. The layers were separated and the polymer was precipitated from the benzene by addition of 1.0 l of hexane. After filtration, the polymer was purified twice by precipitation from benzene into hexane, filtered, air dried, and then dried under vacuum at 50°.

E. Synthesis of 3,5-Dideuterio-4-methoxystyrene

1. Synthesis of p-Ethylanisole

As shown in Table VII, p-ethylanisole was prepared several times, using the Clemmensen reduction as described by Johnson and Hodge.[33] Of these reactions, R1 is characteristic.

The zinc amalgam for the reaction was made by mixing 5.0 g mercuric chloride, 100 g mossy zinc, 75 ml water, and 175 ml HCl. This solution was shaken for about ten minutes and the aqueous layer decanted. The amalgam was immediately covered with 50 g p-methoxyacetophenone, 175 ml HCl, and 75 ml H_2O. This mixture was refluxed for 13

TABLE VII

CLEMMENSEN REDUCTION OF p-METHOXYACETOPHENONE

Run	Ketone (g)	Time (hr)	Product (g)	Yield (%)
R 1	50	13	36.7	81
R 2	100	23	62.0	68
R 3	100	14	64.0	71
R 4	200	15	152.0	81

hours, with addition of 50 ml HCl every three hours, cooled to room temperature, separated, and the aqueous layer extracted with 100 ml diethyl ether. The combined organic layers were washed with saturated $NaHCO_3$, dried over K_2CO_3, filtered, and the ether was evaporated. Distillation at reduced pressure yielded 36.7 g (81%) p-ethylanisole, b p 57-58° @ 1.0 mm (literature 195-196° @ 760 mm).[34]

2. Direct Exchange

Several deuterium exchanges were run to check the feasibility of direct exchange. Of these reactions, which are listed in Table VIII, reaction E1 is characteristic. A 1.0 ml portion (7.0 mmole) of p-ethylanisole was placed in a tube along with 10.0 ml of 0.93 M D_2SO_4 in D_2O. The tube was sealed and heated in a steam bath for 24 hours. After cooling to room temperature, the degree of reaction was checked by nmr analysis. In cases where reaction occurred, the nmr spectra of reactants and products are shown in Figure 5, p 29.

3. Diazonium Salt: Synthesis and Decomposition

Para-ethylanilinium hydrochloride was prepared by treating freshly distilled p-ethylaniline with three times its volume of cold 37% HCl. The material was filtered to remove excess HCl and then 47.0 g (0.29 mole) of p-ethyl-

TABLE VIII

DIRECT DEUTERIUM EXCHANGE REACTIONS

Run	Substrate	Deuterium Source	Vol. Ratio: Deuterium Source/ Substrate	Time (hr)	Reaction
E 1	p-Ethyl-anisole	0.93 M D_2SO_4/D_2O	10	24	No
E 2	Anisole	D_3PO_4	6	24	No
E 3	p-Methyl-anisole	D_3PO_4	6	24	Decomposed
E 4	p-Methyl-anisole	14.5 M D_2SO_4	1	96	No
E 5	p-Ethyl-phenol	0.93 M D_2SO_4/D_2O	10	24	Yes

anilinium hydrochloride was treated with D_2O at 100° according to the procedure outlined by Best and Wilson.[35] After 24 hours the D_2O was removed under vacuum and the residue was subsequently treated with D_2O and heated until nmr analysis of the free amine (see Figure 5, p 29) showed the reaction complete. When the reaction was complete, the reaction mixture was chilled to 0° and diazotized by treatment with aqueous $NaNO_2$. The cold diazonium salt was then converted to a diazonium fluoroborate salt by addition of cold aqueous HBF_4.[36] The reaction mixture was stirred for 30 minutes at 0°, filtered, washed with 5 ml of cold diethyl ether and air dried for 24 hours. The dry white diazonium fluoroborate salt was then added to 400 ml of hot methanol and stirred for 2.0 hours. The red reaction mixture was then poured into 2.0 l of a saturated aqueous solution of NaCl, extracted four times with 100 ml each of diethyl ether, evaporated to residue, and distilled at reduced pressure to give 6.4 g (15.7% 2,5-dideuterio-4-ethylanisole), b p 39° @ 0.025 mm (literature 38-40° @ 0.025 mm).[37] This reaction was repeated several times under slightly varied conditions. (All literature boiling points for deuterated compounds are for their all-proton analogs.)

4. n-Butyllithium-D_2O Exchange

Several of these reaction sequences were done. In Table IX, which shows the data in each reaction sequence,

TABLE IX

LITHIATION-HYDROLYSIS EXCHANGE REACTION
ON *p*-ETHYLANISOLE

Run	Equivalent Ratio RLi/Substrate	Average Reaction Time Per Run (hr)	No. of Reactions
L 1	1.8	33	3
L 2	1.8	30	3
L 3	3.2	41	5
L 4	1.0	30	8
L 5	1.0	24	2
L 6	1.0	24	3

series L5 is characteristic. A 13.6 g (100 mmole) portion of p-ethylanisole was added to a baked, nitrogen-flushed, one liter three-necked flask equipped with a Dean-Stark trap with a condenser, a nitrogen inlet, an inlet for solvent, and a magnetic stirrer. The system was sealed, 200 ml dried ether was distilled in, and 50 ml 2.0 M (0.10 mole) n-butyllithium in hexane was added. After heating this system at 40° for 24 hours, the reaction was slowly quenched with excess D_2O (5.0 g, 0.25 mole). When all evidence of reaction had ceased, the system was opened, washed first with 50 ml 3.0 M HCl, then with 50 ml 2.0 M NaOH, and finally with 50 ml H_2O. After drying the organic layer with K_2CO_3, the hexane was evaporated and the sequence was repeated. When the nmr spectrum showed that the desired exchange had occurred, the material was purified by distillation. The nmr spectra of the reactants and products are shown in Figure 7.

5. Bromination with NBS

A 13.8 g (100 mmole) portion of 3,5-dideuterio-4-methoxyethylbenzene was added to a mixture of 19.8 g (110 mmole) N-bromosuccinimide (NBS) in 140 ml CCl_4. This mixture was heated and stirred at reflux, with simultaneous irradiation with an unfrosted 250 watt lamp for 2.0 hours. After cooling, the mixture was filtered to remove succinimide

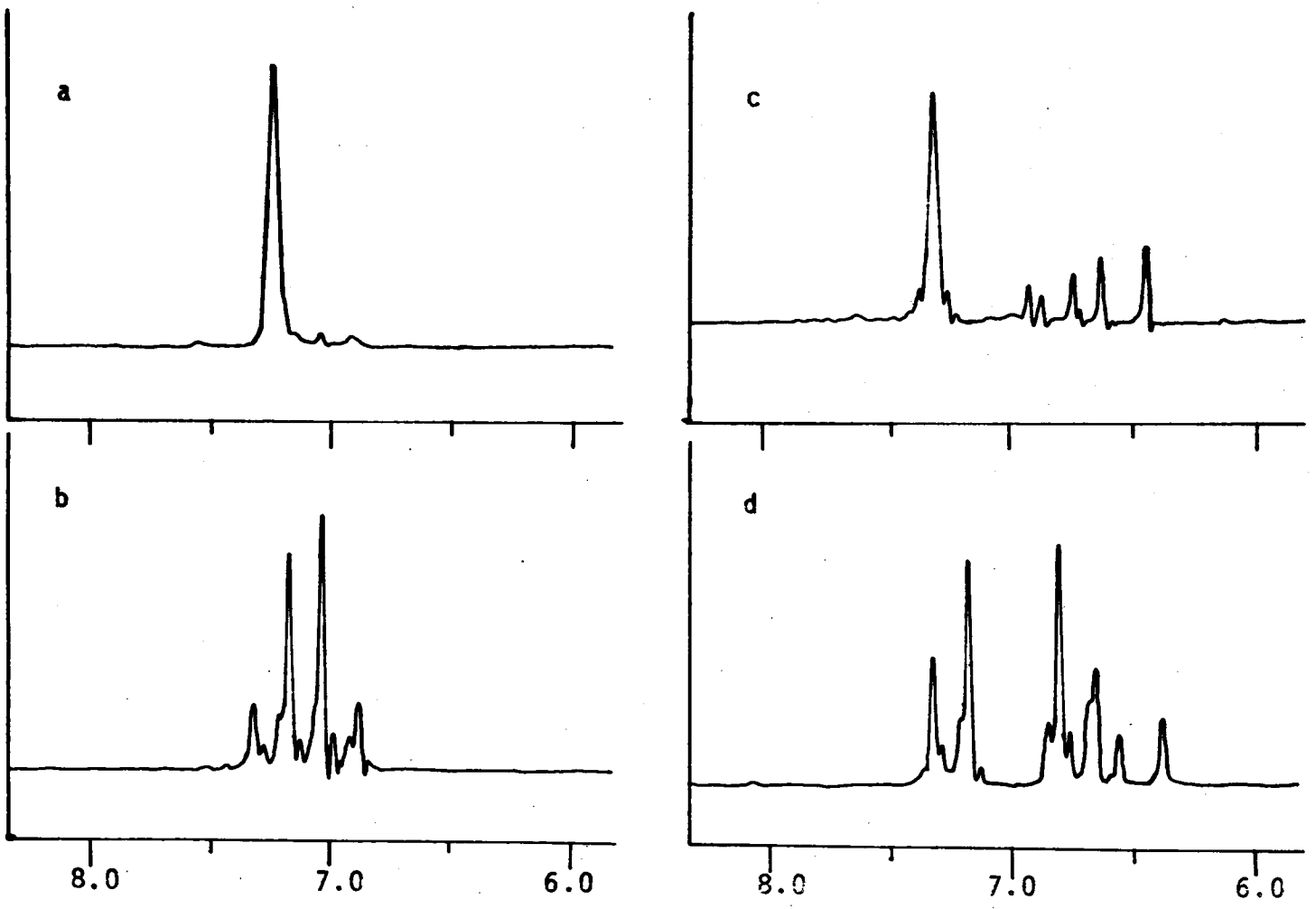


Figure 7. Aromatic proton nmr spectra.

All at 60MHz neat at 40°; (a) 2,5-dideuterio-4-ethylanisole (b) 4-ethylanisole (c) 3,5-dideuterio-4-methoxystyrene (d) 4-methoxystyrene.

and the CCl_4 was removed by evaporation. The product was used in the next step without further purification.

6. Dehydrohalogenation

The approximately 21.5 g (100 mmole) 3,5-dideuterio-4-methoxy-α-bromoethylbenzene was added all at once to a 250 ml flask containing 32.3 g (0.25 mmole) quinoline and 0.1 g 4-tertiarybutylcatechol that had been preheated to 135°. After stirring for 15-20 minutes, the pressure was reduced; and the temperature slowly increased to 160° over a one-hour period. The distillate was collected in an iced receiver. The impure 3,5-dideuterio-4-methoxystyrene was placed in 100 ml ether and washed with 100 ml 3.0 M HCl, 50 ml saturated $NaHCO_3$, and 50 ml H_2O. After drying the organic layer over anhydrous K_2CO_3, the solution was evaporated; and the residue was distilled at reduced pressure to give 5.5 g (13.4% based on p-ethylanilinium hydrochloride) 3,5-dideuterio-4-methoxystyrene, b p 39-41° @ 0.025 mm (literature 92-93° @ 13 mm).[31] The nmr spectra of this product and its nondeuterated analog are shown in Figure 7 (p 43).

CHAPTER III

RESULTS AND DISCUSSION

A. Introduction

As noted in an earlier chapter, nmr analysis is a very useful tool in polymer microstructure studies. Since it was not possible to obtain crystalline samples of poly(p-methoxystyrene), it was decided that in this study nmr analysis would be used in an attempt to gain microstructure information. Previous studies of methylene and methine proton resonance did not give quantitative information for polystyrene, but Kinstle and Harwood showed that nmr signals of protons ortho to the chain juncture could yield quantitative microstructure information.[16,43] Therefore, it was reasoned that nmr signals of similarly positioned protons might yield microstructure information on poly(p-methoxystyrene) as well. To use the ortho protons as a source of information, it would be necessary to uncouple these protons from the meta protons by replacement of the latter with groups that were not proton nmr active. There were two available routes to obtain the desired goal. One could either synthesize the polymer and then exchange the meta protons, or one could synthesize the deuterated monomer and then polymerize.

B. Synthesis of and Reactions on Poly(p-methoxystyrene)

If the alternative of exchanging the protons meta to the chain juncture on a preformed polymer were to be utilized, it would be necessary to first make p-methoxystyrene. Of the many synthetic routes available, the ones shown schematically in Figure 8 were chosen as the most convenient routes for making the non-deuterated monomer. The qualitative procedures in this section should suffice for continuity; detailed procedures are outlined in Chapter II.

The first step in the synthesis involved $LiAlH_4$ reduction of p-methoxyacetophenone (I). This reduction occurred in very high yield as long as mild reaction conditions were maintained. Under vigorous reaction conditions, oils or tars were obtained due to polymerization and other undesirable side reactions. In the second step--dehydration at elevated temperature and reduced pressure--conditions were all important. The alcohol (II) must be added sufficiently fast to maintain distillation, but at a rate so that reaction occurs without codistillation of starting material with product. If the proper conditions were not utilized, the inhibitor was quickly exhausted and polymerization occurred. Purification of the p-methoxystyrene (III) was accomplished by drying over K_2CO_3 in an

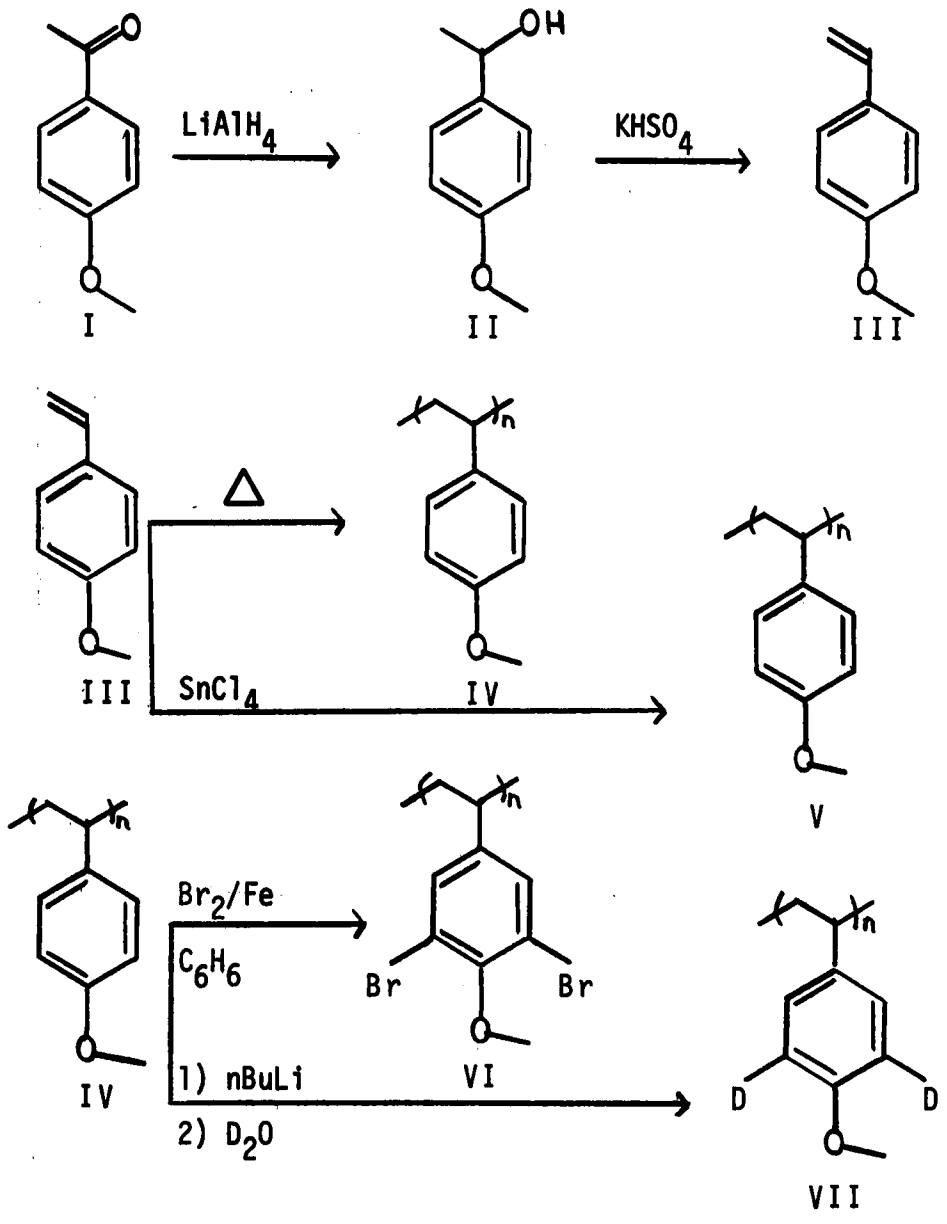


Figure 8. Synthesis and reactions of poly(p-methoxystyrene).

ethereal solvent with subsequent evaporation of ether and distillation of III from inhibitor at reduced pressure.

The monomer (III) thus obtained was polymerized both thermally at 160° with no initiator and cationically at 0° with $SnCl_4$ initiator to yield amorphous polymers. Of these two types of polymers, only the thermally initiated polymers were used in the following reactions. Upon obtaining the polymer (IV), the next step was to exchange the meta protons with groups that were not proton nmr active. In the first attempted route, the polymer (IV) was reacted with molecular bromine under various reaction conditions. From these reactions, which may be seen in Table VI (p 35), it was found that although the anisole pendant group should be far more reactive than benzene, high conversions to brominated polymer were obtained only if the reaction was done in benzene with iron catalyst. Since it was also known that the benzene solvent could also be mono and di-brominated, excess bromine was used in all of these reactions to insure complete reaction. These homogeneous reactions were done in foil-coated tubes to reduce free radical reaction. Although the reaction proceeded smoothly, as the degree of bromination increased so did the degree of insolubility. As a result of this, the polymer obtained was insoluble in all common solvents and, therefore, useless as a source of nmr data.

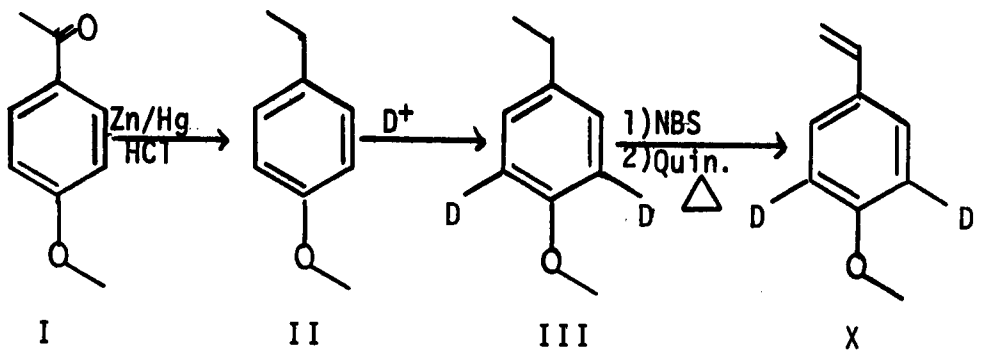
In the next exchange, data from the research of Shirley and Hendrix was used.[38] In their research, para substituted anisoles were reacted with alkyl lithium and quenched by carboxylation. It was found that the predominate site of lithiation was ortho to the methoxyl function. A variation of this technique--that is lithiation and subsequent reaction with D_2O--was potentially useful for replacing the protons ortho to the methoxy group (meta to chain juncture) with deuterium. This reaction would have advantages over bromination in that deuterium is a small group that would cause no steric crowding; and since the properties of deuterium closely resemble those of hydrogen, no solubility problems were foreseen. When the lithiation of the polymer with n-butyllithium was attempted under several sets of conditions (see Table VI, p 35), it was found that a low degree of exchange per reaction had occurred. This was due to solubility problems. The poly(aryllithium) was much more polar than the parent polymer. In addition, organolithiums are known to aggregate; in our case such aggregation acts as virtual crosslinks in the polymeric material. Hence, as the reaction proceeded, the polymer formed a precipitate on the bottom of the flask. This precipitate was not accessable to more than surface reaction, so the degree of exchange was very low. As a result, the number of reactions needed to obtain high isotopic purity was

prohibitive; and this reaction scheme was abandoned. Incorporation of the more polar solvent THF, while potentially useful in solvation, allowed side reactions to occur and was, therefore, not helpful.

C. Synthesis of Deuterated Monomer and Nmr Analysis

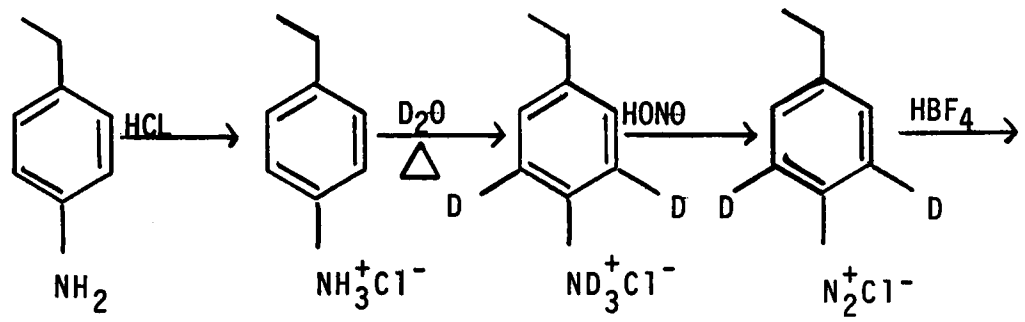
Since polymer synthesis and then exchange had many difficulties, synthesis of a high purity deuterated monomer was investigated. Since 3,5-dideuterio-4-methoxystyrene had not been previously reported in the chemical literature, several routes, shown in Figure 9, were investigated.

The first step in Sequence A (Figure 9) is the reduction of p-methoxyacetophenone (I) to p-ethylanisole (II) by Clemmensen reduction. This reaction gave very good yields (see Table VII, p 37) in all cases. Since the most straightforward way of obtaining 3,5-dideuterio-4-methoxyethylbenzene (III) was by direct deuterium exchange, the second step in Sequence A was to react 4-ethylanisole (II) with different deuterio-acids at elevated temperatures. These reactions, which were all two-phase, were carried out with vigorous turbulent stirring, using different acids and different reaction times. However, as is shown in Table VIII (p 39) no reaction occurred with the methoxy substituted compounds.

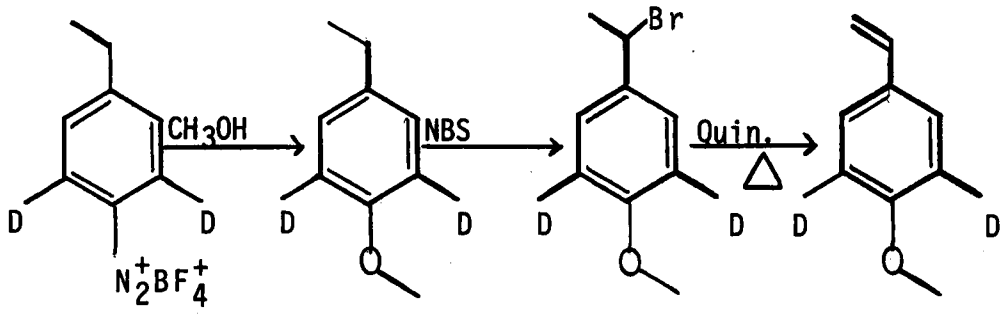


I II III X

Sequence A



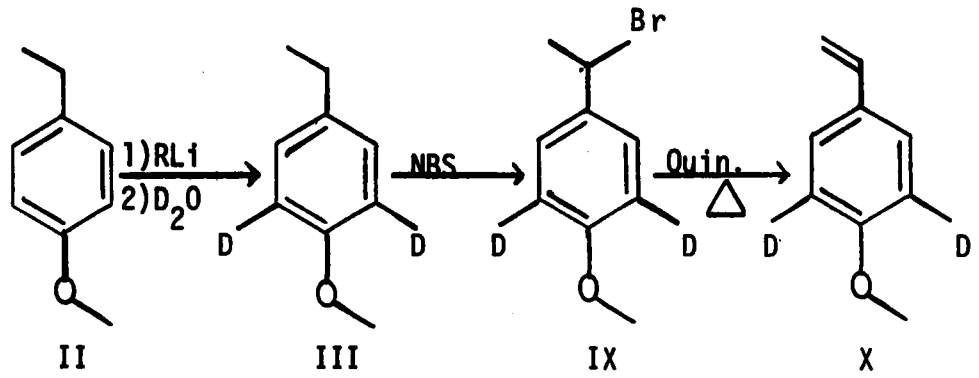
IV V VI VII



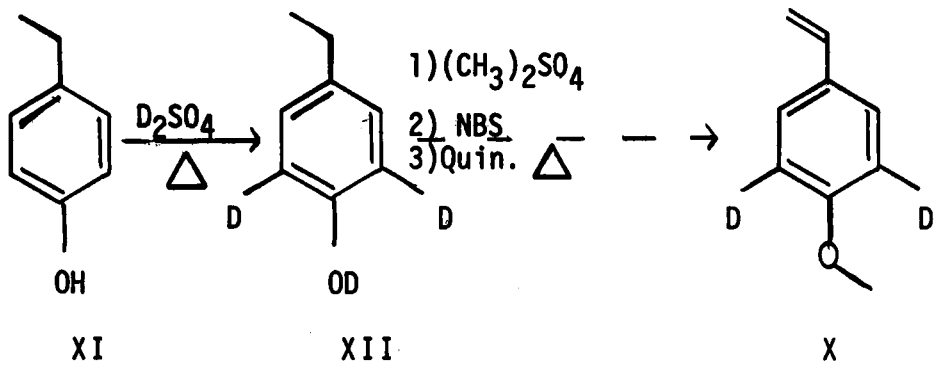
VIII III IX X

Sequence B

Figure 9. Synthetic routes to 3,5-dideuterio-4-methoxy-styrene.



Sequence C



Sequence D

Figure 9. Continued.

The next attempt at synthesis of the deuterated monomer involved a diazonium salt decomposition (Sequence B, Figure 9, p 51).

The first step of Sequence B was the conversion of p-ethylaniline (IV) to p-ethylanilinium hydrochloride (V) by treatment of the distilled ethylaniline with 37% HCl. The hydrochloride salt (V) was treated repeatedly with D_2O at 100^0 to yield the pentadeuterio derivative (VI) of high isotopic purity. The equilibrium constant for this exchange, which occurs within 24 hours, is 0.84.[39] The pentadeuterio derivative (VI) was converted to the diazonium chloride (VII) by treatment with aqueous $NaNO_2$ at $0\text{-}5^0$. When this conversion was complete, VII was converted to the stable diazonium fluoroborate (VIII) by treatment with aqueous 40-50% HBF_4 at 0^0.[37] This salt, VIII, was filtered, air dried for 24 hours, and decomposed in hot methanol to give III, which was purified by distillation at reduced pressure.[39] The 3,5-dideuterio-4-methoxyethylbenzene (III) was brominated at the benzylic site using N-bromosuccinimide (NBS) in CCl_4 under UV irradiation, yielding 3,5-dideuterio-4-methoxy- α -bromoethylbenzene (IX) in excellent yield. This reaction proceeded smoothly if the NBS were recrystallized from water and dried at 40^0 under vacuum prior to use.[40] The dehydrohalogenation of IX with quinoline at 160^0, using tertiarybutylcatechol as inhibitor,

was a low yield reaction due to the extreme reactivity of X. Yields of 3,5-dideuterio-4-methoxystyrene were optimized by using excess inhibitor.

This synthetic route gave very low yields. Factors contributing to this problem were high solubility of the diazonium fluoroborate salt (VIII) in water and many competing side reactions in the decomposition of VIII to III. Repeating this reaction gave no significant increase in yields, and it was decided that this was not a practical route for the monomer synthesis.

The third route of monomer synthesis is shown in Sequence C (Figure 9, p 52). This sequence involved repeated reaction of p-ethylanisole (II) with n-butyllithium and quenching of the reaction with excess D_2O. The deuterated p-ethylanisole (III) was brominated at the benzylic site with NBS and reacted with quinoline as in an earlier procedure to give 3,5-dideuterio-4-methoxystyrene (X). Several of these reaction sequences were done (see Table IX, p 41) due to difficulties with the lithiation step. In the earlier reaction sequences, excess n-butyllithium was used in an attempt to insure high yields. Upon analysis of the products of these reactions, it was found that the excess n-butyllithium had cleaved the methylaryl ether and given a high boiling product of unknown composition.

These side reactions were mitigated in later reactions by increasing the mole ratio of substrate to

alkyllithium to 1.0 and by changing workup procedures so that the most harmful side product, p-ethylphenol, which would use two equivalents of alkyllithium per equivalent substrate, was removed by washing with 2.5 M NaOH. The high boiling byproduct, which formed in small amounts, was removed before bromination by distillation at reduced pressure. By using these procedures 3,5-dideuterio-4-methoxyethylbenzene (III) was made in reasonable amounts in as few as three reactions. This reaction sequence was used to make the deuterated monomer in reasonable yields. It was not until after sufficient monomer was prepared that reaction Sequence D, (Figure 9, p 51) which was delayed due to unavailability of D_2SO_4, was tried. Sequence D was the only possible route to deuterated monomer which might be superior to Sequence C. The p-ethylphenol underwent deuterium exchange (see nmr c, d, Figure 6, p 32) in only two reactions to yield O,3,5-trideuterio-4-ethylphenol of very high isotopic purity. Possibly, this material could be methylated under basic conditions to give III faster and of higher purity.

Polymers were prepared from nondeuterated and deuterated monomers, using both cationic and thermal initiation. The 100 MHz nmr spectra of the polymers were compared. These spectra (Figure 10) all show multiple resonance signals. The multiple resonances seen in the

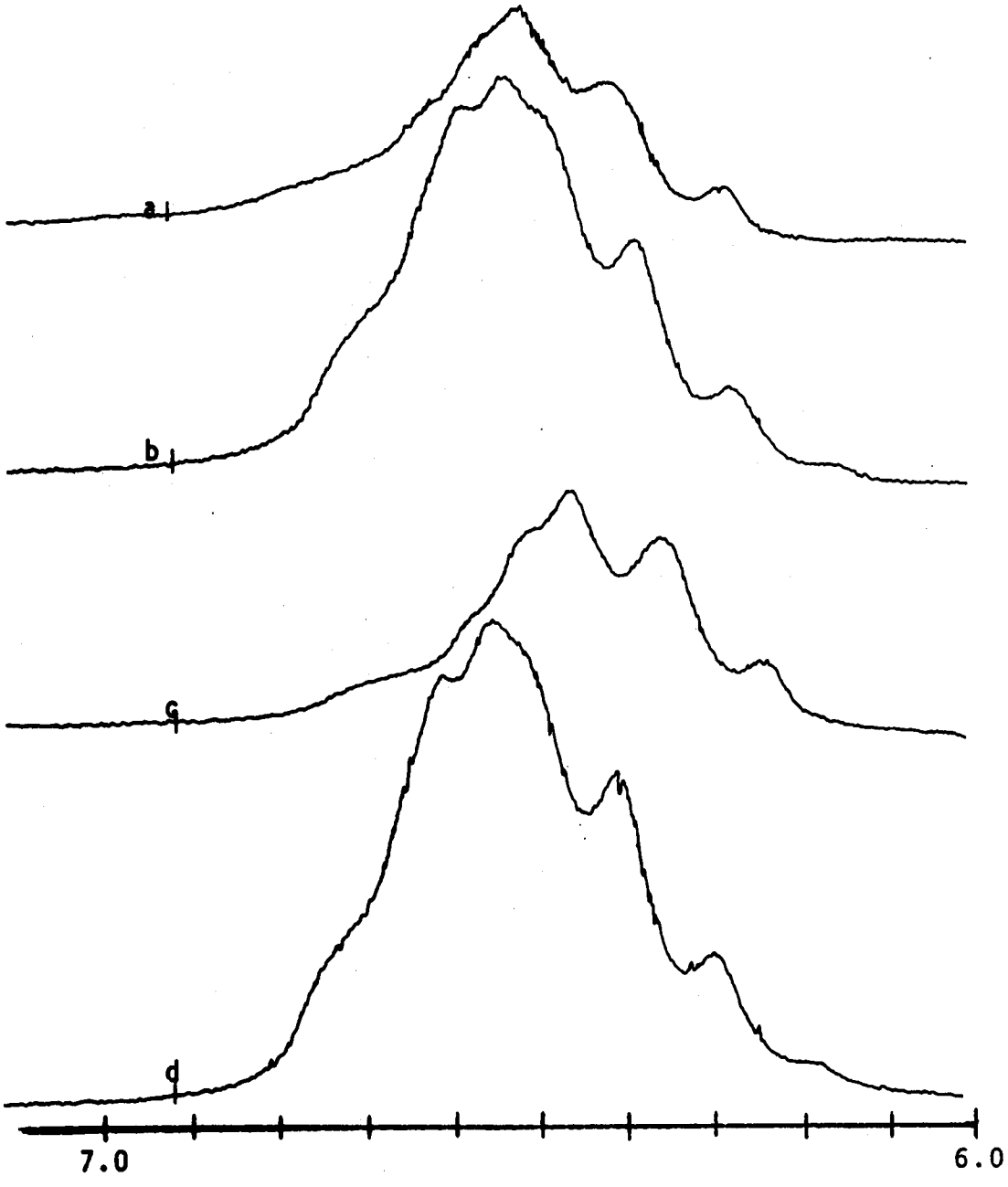


Figure 10. Expanded aryl regions of representative polymers.

All at 100 MHz in $CDCl_3$ at 60°C: (a) P 6 (b) P 7 (c) P 9 (d) P 8.

nondeuterated material P 7 and P 8 are of a complex nature. As an example, the nmr of the aryl region of p-ethylanisole will suffice (Figure 7, p 43). Here one sees a complex multiplet of peaks due to differences in the environment of the ortho and meta proton fractions. Resolution of this complex multiplet into ortho and meta fractions is further complicated by different coupling constants for the two types of protons. In the polymer spectra of the nondeuterated material, the multiplicity of signals may be assigned to the same factors. However, in the polymer spectra the complexity of the signal is amplified due to small magnetic shifts resulting from the different tactic fractions in the polymer chain. The combination of these factors make resolution of the nondeuterated material into its component signals impossible.

The situation for the deuterated polymers is greatly simplified. Here one has only one type of proton, so the explanation of different coupling values is not valid; and the phenomenon of multiple resonance now needs to be explained.

The multiple signals seen for the deuterated polymers, P 6 and P 9, are due to the protons ortho to the chain juncture. These show that the ortho protons do not all experience an identical environment. These resonances, which occur at 6.3, 6.4, and 6.5 δ, will be

referred to as resonance signals I, II, and III respectively. The intensities of the signals increase in the order I < II < III.

The phenomenon of multiple resonance may be explained by (1) coupling of the ortho protons on a given ring with each other, with meta or para isotopic impurities, or with the deuterium nuclei; or (2) differences in chemical shift due to sensitivity of the ortho protons to their magnetic (stereochemical) environment. In aromatic compounds, one often sees long range coupling. However, this coupling usually has very small coupling constants, (1-3 Hz) which would not account for the magnitude of peak separation seen here.[41] Separation arising from coupling to deuterium nuclei may also be ruled out, since deuterium-proton coupling is 6.54 times weaker than proton-proton coupling.[42]

Hindered rotation of the anisyl group along the polymer backbone could also cause multiple resonance signals for the ortho protons. However, since this type of conformation multiplicity usually has a high degree of temperature dependence, their effects may be minimized by increasing the temperature at which the spectrum is taken and thereby merge the multiple resonance signal into a single resonance. Varying the temperature at which the spectra were observed over a 25° range had no measurable

effect on the separation distances or on the relative areas of the three signals. Further evidence against multiplicity due to hindered rotation was found in studies on polystyrene.[43] Here temperature at which the spectra were taken was varied over a 100° range; and again, no measurable effect on separation distances were seen.

The results of these investigations suggest that the three signals may be a measure of stereochemical configuration of poly(p-methoxystyrene) as they were in the case of polystyrene.[16]

The resonances of the deuterated cationic and thermally prepared polymers were separated by use of a Dupont curve resolver (using Lorentzian curves), and the resultant peak areas determined by use of a polar planimeter. The expanded and resolved aryl region of thermally prepared deuterated polymer is shown in Figure 11 as an example. This procedure gave the following normalized areas: thermally initiated polymer--(I) 5.98, (II) 32.9, (III) 61.1; cationically initiated polymer--(I) 6.52, (II) 34.2, (III) 59.2. Using the work of Kinstle and Harwood as a reference, signal III was assigned to syndiotactic triads, signal II was assigned to heterotactic triads, and signal I was assigned to isotactic triads. This assignment is in accordance with the expected shielding influences of neighboring aryl groups and with studies on polystyrene.[16,43]

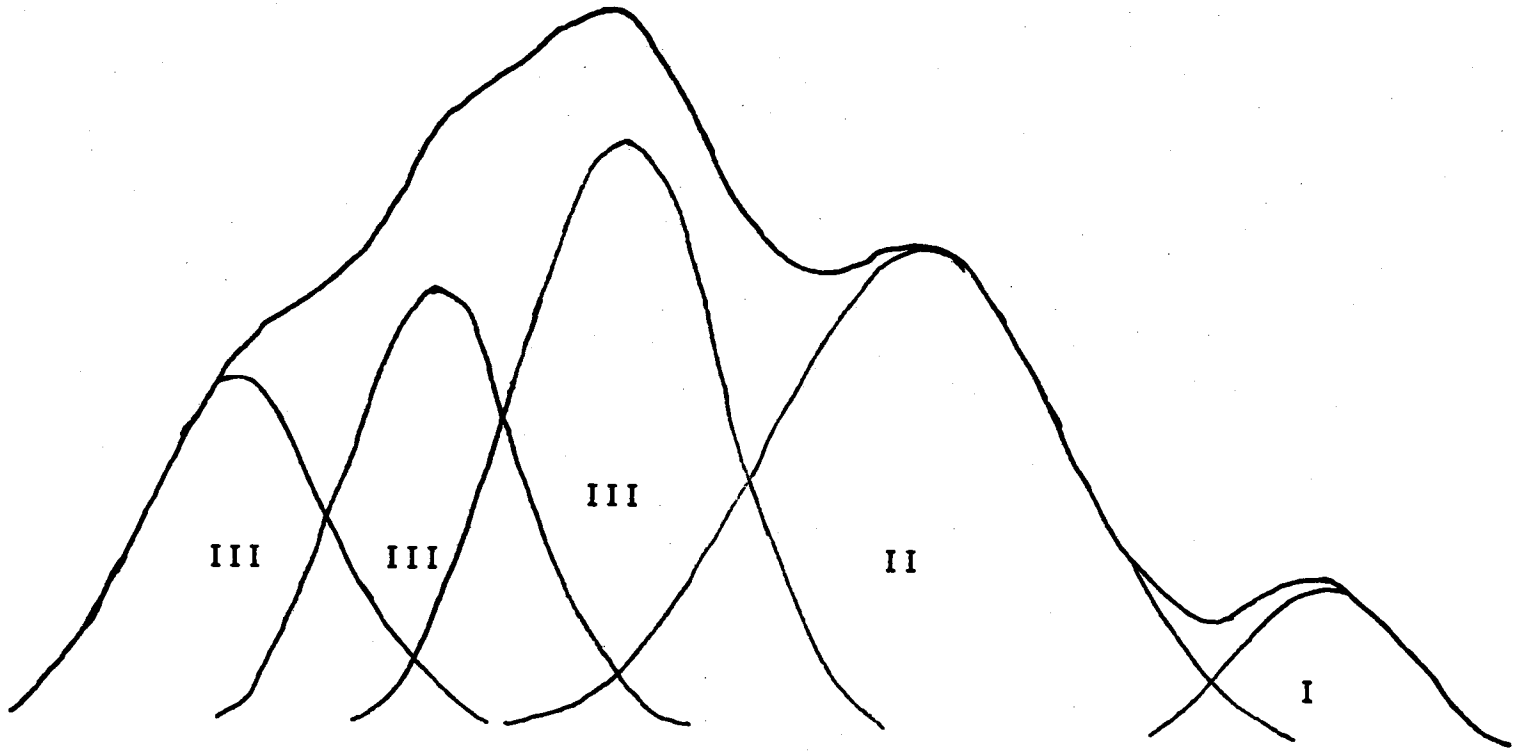


Figure 11. Component peaks of deuterated polymer.
Nmr taken at 100 MHz and 60° in $CDCl_3$.

Due to lack of standards for comparison and the fact that signals II and III cannot be unambiguously resolved, only limited conclusions may be drawn from this work. However, if one compares area I in the thermal and cationic deuterated polymers, the following conclusion may be drawn. A small increase in the isotactic fraction is seen when one compares cationic with thermal initiation. This increase is reasonable because when one goes to an ionic reaction where counter ions, solvent effects, and other factors must be considered, then an increase in randomness should occur and the isotactic fraction increase. This increase in the isotactic fraction with cationic initiation was also seen in the work of Kinstle and Harwood where the polymerization conditions were essentially the same.[43] Therefore, the small increase in the isotactic fraction further supports the statement that the three resonance signals in the deuterated polymers are a measure of tacticity.

The above assignments and conclusions rest on assumptions. It is true that the nmr analysis follows that made on polystyrene; however, the effect of the para methoxyl group is not known and the resolution of signals or variation of polymerization conditions were not different enough to permit absolute analysis. Therefore, since no standards or references exist, the S, H, I, assignment and stereochemical evaluation of poly(p-methoxystyrene) is only tentative.

CHAPTER IV

SUMMARY

Past studies have shown tnat characterization of stereochemistry of vinyl aromatic polymers is a difficult task. If a polymer were very stereoregular so that a high degree of crystallinity was achieved, X-ray analysis could be used to obtain stereochemical information. However, unless special methods of catalysis were used, most polymers were amorphous and did not lend themselves to X-ray studies.

This situation was relieved somewhat through the development and use of nmr analysis. Nmr analysis has proven to be a powerful tool for the analysis of polymer stereochemistry.

It has been known for some time that nmr resonance signals of aromatic protons are very sensitive to their environment in a molecule. In polystyrene, this effect is strongest for aromatic protons which are ortho to the polymer backbone.

Assuming the effect was seen in other aromatic vinyl polymers, this research was designed to use the ortho aromatic protons as a source of microstructure information. To achieve this goal some group or atom, which was not proton nmr active, must be substituted for the protons meta to the

polymer backbone. The first group which was tried was bromine. It was found that the use of this group resulted in insoluble polymer which was of no further use as a source of microstructure information. The next attempt at substitution used deuterium due to its similarity in size and properties with hydrogen. This route could be attempted either as a reaction on the polymer or as a synthesis of a deuterated monomer.

To use deuterium in a reaction on the polymer, the monomer (p-methoxystyrene) was made from p-methoxyacetophenone and polymerized both thermally with no initiator at 160° and cationically at 0° using $SnCl_4$. The thermally prepared polymer was then reacted a series of times under varying conditions with n-butyllithium and subsequently D_2O. This process proved to be a low yield reaction and was abandoned in favor of deuterated monomer synthesis.

Several routes of making the desired monomer were tried. The one which proved most favorable was a multistep synthesis from p-methoxyacetophenone. The p-methoxyacetophenone was reduced by Clemmensen reduction to p-ethylanisole in very good yields. The product, p-ethylanisole, was then reacted several times with n-butyllithium and quenched with D_2O to give 2,6-dideuterio-4-ethylanisole of high isotopic purity. The 2,6-dideuterio-4-ethylanisole

was then converted to 3,5-dideuterio-4-methoxystyrene by benzylic bromination with NBS and dehydrohalogenation by use of quinoline. These reactions gave high purity monomer with minimal side reactions. The monomer thus obtained, 3,5-dideuterio-4-methoxystyrene, was polymerized as before; and the 100 MHz spectra of the aryl region analyzed through use of a Dupont curve resolver and a polar planimeter.

The aryl resonance consisted of three major signals. These signals were not due to coupling of the ortho protons with each other or to meta or to para impurities or with deuterium nuclei. It is believed that these resonance orders which coincide with other studies, are measures of the ortho protons in different stereochemical environments. The predominant lowest field signal (III) was ascribed to snydiotactic structures. Signal (II) (intermediate in position and intensity) was ascribed to heterotactic structures and the smallest upfield resonance (I) was ascribed to isotactic structures.

Unfortunately, at the conclusion of this work there are no standards available for direct comparison. The polymers, being amorphous, do not lend themselves to X-ray analysis so that comparison could be made. Comparison of nmr analysis could only be done indirectly, because where Kinstle and Harwood were able to make comparisons to very stereoregular polymers prepared by Ziegler-Natta catalysts,

no such comparisons could be made here.[43] However, the resonance positions and the changes seen under available conditions do agree with theory and earlier work.[16]

The new monomer, 3,5-dideuterio-4-methoxystyrene, has shown to be of use in microstrucutre studies. Although this study is not conclusive, it indicates that microstructure information is available on poly(p-methoxystyrene) by extentions of this route.

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VITA

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In September 1972, he accepted a teaching assistantship from the University of Tennessee, Knoxville and began study toward a Master's degree. He will receive the degree of Master of Science, with a major in Chemistry, in March 1975. Since December 1974, he has been employed by Tennessee Eastman Company in Kingsport, Tennessee. He is a member of the American Chemical Society.

He is married to the former Cheryl Jean Roberts of Chattanooga, Tennessee.