

- (7) Levi, M.; Asad-Yellin, A.; Green, B. S.; Gedanken, G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 847.
- (8) Bertucci, C.; Lazzaroni, R.; Salvadori, P.; Johnson, W. C., Jr. *J. Chem. Soc., Chem. Commun.* **1981**, 590.
- (9) Ledwith, A.; Chiellini, E.; Solaro, R. *Macromolecules* **1979**, *12*, 240.
- (10) Chiellini, E. *Macromolecules* **1970**, *3*, 527.
- (11) Luis, P. L.; Chiellini, E.; Franchini, P. F.; Orienti, M. *Makromol. Chem.* **1968**, *112*, 197.
- (12) Delfini, M.; Conti, F.; Paci, M.; Segre, A. L.; Solaro, R.; Chiellini, E. *Macromolecules*, in press.
- (13) Johnson, W. C., Jr. *Rev. Sci. Instrum.* **1971**, *42*, 1283.
- (14) Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1974; Vol. 1, p 265.
- (15) Salvadori, P.; Bertucci, C., to be published.
- (16) Ciardelli, F.; Chiellini, E.; Carlini, C.; Pieroni, O.; Salvadori, P.; Menicagli, R. *J. Polym. Sci., Polym. Symp.* **1978**, No. 62, 143.
- (17) Chen, A. K.; Woody, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 29.

Synthesis of Poly(*p*-hydroxy- α -methylstyrene) by Cationic Polymerization and Chemical Modification

Hiroshi Ito* and C. Grant Willson

IBM Research Laboratory, San Jose, California 95193

Jean M. J. Fréchet,* M. Jean Farrall, and Eva Eichler

Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 9B4 Canada.

Received June 21, 1982

ABSTRACT: High molecular weight, soluble poly(*p*-hydroxy- α -methylstyrene) has been synthesized for the first time by cationic polymerization of *p*-[(*tert*-butoxycarbonyl)oxy]- α -methylstyrene with boron trifluoride etherate as an initiator in liquid sulfur dioxide followed by thermolytic deprotection. Cationic polymerization of *p*-acetoxy- α -methylstyrene in dichloromethane followed by hydrazinolysis afforded the title compound, but the polymerization was accompanied by partial cleavage of the protecting group. Conventional cationic polymerization of *p*-[(*tert*-butoxycarbonyl)oxy]- α -methylstyrene in dichloromethane resulted in formation of low molecular weight polymer accompanied by partial cleavage of the protecting group. Ether monomers, such as *p*-methoxy- and *p*-(ethoxymethoxy)- α -methylstyrenes, readily underwent cationic polymerization, while the *p*-(2-methoxyethoxy)methyl derivative suffered from partial deprotection and cross-linking. Removal of the ether protecting group was, in all cases, accompanied by chain degradation and/or cross-linking. Chemical modification of poly(α -methylstyrene) and poly(*p*-bromo- α -methylstyrene) by lithiation followed by hydroxylation produced cross-linked materials.

Introduction

The preparation of linear polymers containing phenolic functional groups has attracted a great deal of attention recently due to the potential use of these materials as antioxidants, resist resins for microlithography, etc. While high molecular weight poly(*p*-hydroxystyrene) has been successfully prepared,^{1,2} the synthesis of the corresponding poly(α -methylstyrene) analogue, namely, poly(*p*-hydroxy- α -methylstyrene) (poly[*p*-(1-methylethenyl)phenol] (VIII)), has remained very elusive and only low molecular weight oligomers have been reported in the literature.^{3,4} Thus, Kamagami and Hamashima³ obtained short oligomers of degree of polymerization (DP) 4-5 by UV or γ -ray irradiation of the solid monomer, *p*-hydroxy- α -methylstyrene ((1-methylethenyl)phenol (I)), at room temperature. However, no polymerization of I whatsoever was observed in solution. The cationic polymerization of I produced mostly dimers and trimers, with a very small amount of oligomers of DP up to 17.⁴ Similar results, characterized by the formation of only 1-3% yields of higher oligomers (DP up to 16), were obtained by Braun and Meier in the cationic polymerization of 2,6-di-*tert*-butyl-4-(1-methylethenyl)phenol.⁵ Better results were obtained in the radical copolymerization of I with vinyl comonomers.^{3,6,7} Thus, copolymerization with acrylonitrile produced a highly alternating copolymer with number-average molecular weight (M_n) \sim 50 000.³

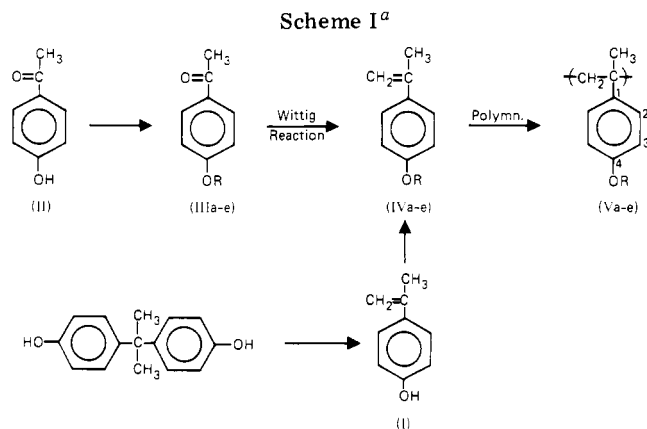
The successful synthesis of high molecular weight VIII is difficult mainly due to the fact that α -methylstyrenes are reluctant to undergo radical homopolymerization and

that the *p*-hydroxyl group reacts with cationic initiators and growing ends as a Lewis base and with anionic initiators and growing ends as a Brønsted acid. In consequence, our approach to the synthesis of VIII involves the polymerization of monomers with the hydroxyl group protected followed by removal of the protecting group to generate the free phenolic polymer. This paper reports the synthesis of VIII by cationic polymerization of several new protected monomers (IV) and subsequent chemical modification of the polymers (V) by deprotection. Attempts to prepare VIII directly by chemical modification of poly(α -methylstyrene) (VI) and its *p*-bromo derivative (VII) are also described.

Results and Discussion

Monomer Synthesis. A number of procedures have been reported for the preparation of I, including thermal⁸ or base-catalyzed⁹ cracking of 2,2-bis(*p*-hydroxyphenyl)propane and catalytic dehydrogenation of *p*-(1-methylethenyl)phenol,¹⁰ but few polymerizations of the derivatives of I have been reported. Aliev and co-workers prepared the allyl and glycidyl ethers of I and succeeded in their copolymerization with styrene to yield cross-linked materials.¹¹

A. Ester: *p*-Acetoxy- α -methylstyrene (IVa). Following the successful work of Arshady et al.² describing the preparation of poly(*p*-hydroxystyrene), our first approach to the synthesis of VIII was based on the synthesis of esters of I followed by polymerization and then hydrolysis to provide the free phenolic polymer (VIII). We



^a a, R = acetyl; b, R = *tert*-butoxycarbonyl; c, R = ethoxymethyl; d, R = (2-methoxyethoxy)methyl; e, R = methyl.

found that the esters could be obtained by two routes, either by esterification of I or by a Wittig reaction on the appropriately substituted acetophenone.

A first approach to the synthesis of monomer IVa involved *p*-hydroxyacetophenone (II) as a starting material and introduction of the vinyl group by a Wittig reaction after acylation (Scheme I). The Wittig reaction on the O-acylated acetophenones gave low and variable yields regardless of the nature of the ester group (IIIa and benzoate). Typically, reaction of the acylated acetophenone with 1 molar equiv of Wittig reagent afforded 15–26% yields of the desired vinyl compounds (IV) while much of the starting ester was hydrolyzed to II and approximately 50% of the starting ester remained unchanged. Inverse addition did not improve the yield and reactions carried out with an excess of the Wittig reagent only produced a larger proportion of hydrolyzed material, a small amount of I, and low yields of the desired product (IVa).

A more attractive route to the synthesis of IVa involved the preparation of I by base-catalyzed cleavage of 2,2-bis(*p*-hydroxyphenyl)propane⁹ followed by esterification of the phenol with acetic anhydride (Scheme I). This procedure is the preferred route and provides large quantities of protected monomers in excellent yields.

B. Ethers: *p*-(Ethoxymethoxy)- α -methylstyrene (IVc), *p*-(2-Methoxyethoxy)methoxy]- α -methylstyrene (IVd), and *p*-Methoxy- α -methylstyrene (IVe). The methyl (IVe), ethoxymethyl (IVc), and (2-methoxyethoxy)methyl (IVd) ether derivatives of I were synthesized in yields greater than 85% by a Wittig reaction on the appropriately functionalized acetophenones (IIIc–e). The Wittig route to the ether-protected monomers is more efficient because the ether protecting groups are more resistant to base hydrolysis.

C. Carbonate: *p*-(*tert*-Butoxycarbonyl)oxy]- α -methylstyrene (IVb). In contrast to the corresponding acyl derivatives, the reaction of *p*-(*tert*-butoxycarbonyl)oxy]acetophenone (IIIb) with methylene Wittig reagent gave a satisfactory yield (66%) of the desired protected monomer (IVb), consistent with the fact that the *tert*-butoxycarbonyl (*t*-Boc) protecting group is much more resistant to base hydrolysis than the corresponding acetyl and benzoyl groups. As is the case with the synthesis of IVa, IVb can be obtained in excellent yield by reaction of di-*tert*-butyl dicarbonate with I.

Polymerization. Polymerizations of substituted α -methylstyrenes have been much less studied than those of the styrene analogues due to difficulty in the monomer synthesis, reluctance to undergo radical polymerization, crystallization of the monomer during low-temperature

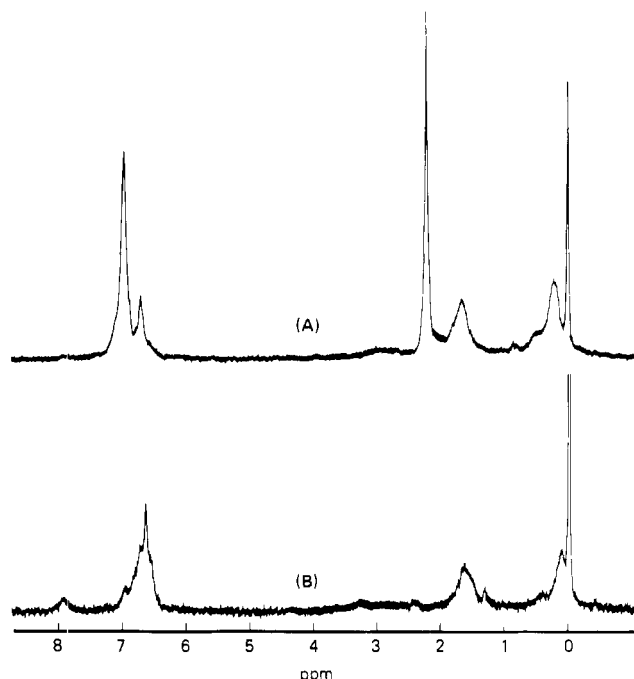


Figure 1. ¹H NMR spectra (in acetone-*d*₆) of (A) Va synthesized by BF₃·OEt₂ initiation in CH₂Cl₂ and (B) VIII obtained by hydrazinolysis of Va.

polymerization, and side reactions involving the substituents in both cationic and anionic polymerization. Cationic polymerizations of α -methylstyrenes bearing rather unreactive functionality such as *p*-alkyl-,^{12,13} *p*-methoxy-,¹² and *p*-halo- α -methylstyrenes¹² have been reported by Lenz and co-workers.

A. Polymerization of *p*-Acetoxy- α -methylstyrene (IVa). Cationic polymerization of IVa was carried out under an inert atmosphere in dichloromethane at low temperature using boron trifluoride etherate (BF₃·OEt₂) as an initiator (Table I). The polymers obtained were of relatively low molecular weight (*M*_n ~ 14 700). Infrared (IR) spectra of the polymers show a strong carbonyl absorption at 1760 cm⁻¹, indicating that the product is mainly poly(*p*-acetoxy- α -methylstyrene) (Va). However, a hydroxyl absorption of considerable intensity is observed in the IR spectra obtained both in a KBr pellet and as a film even though the polymer and the KBr powder were rigorously dried. The ¹H NMR spectrum of Va (Figure 1A) indicates that the acetyl methyl absorption is about 10% smaller than the theoretical value, suggesting that partial cleavage of the acetyl protecting group occurred during the cationic polymerization. The IR and ¹H NMR evidence was confirmed by a ¹³C NMR study. In Figure 2, the ¹³C NMR spectrum of the cationic polymerization product (A) is compared with that of VIII (B), the synthesis of which will be described later. Three of the four phenyl carbon signals due to the deprotected phenolic polymer (B) are clearly detected at 114.5, 141.0, and 153.6 ppm in the spectrum of the polymerization product (A). The phenolic units amount to about 10%, which is consistent with the ¹H NMR integration analysis. Thus, spectroscopic studies unequivocally reveal that the acetyl protecting group is partially removed under the cationic polymerization condition. Complications in the cationic polymerization of acetyl-bearing monomers^{14–16} and in the presence of carbonyl compounds^{17,18} have been reported by other workers.

B. Polymerization of Ether Monomers (IVc–e). We studied polymerization and chemical modification of ether derivatives, since monomers with ether protecting groups have been reported to undergo cationic polymerization

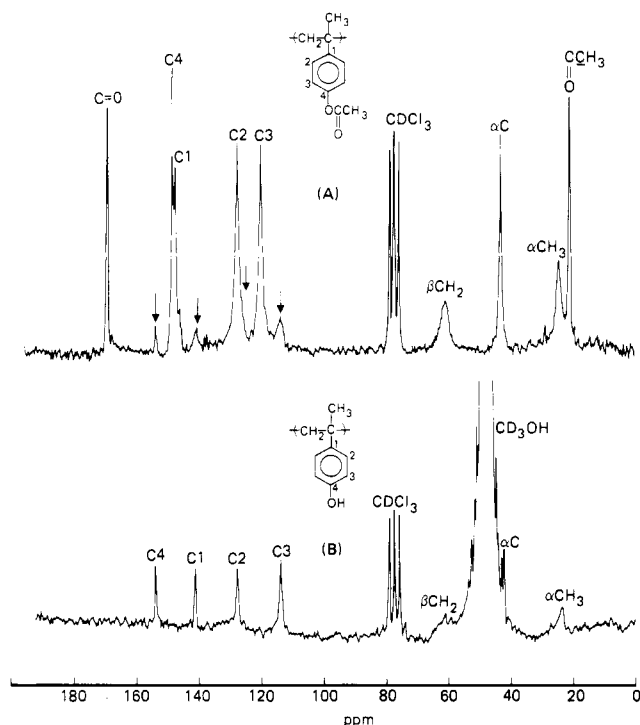


Figure 2. ^{13}C NMR spectra of (A) Va synthesized by $\text{BF}_3\cdot\text{OEt}_2$ initiation in CH_2Cl_2 (measured in CDCl_3) and (B) VIII obtained by hydrazinolysis of Va (measured in $\text{CD}_3\text{OH}/\text{CDCl}_3$). Arrows show resonances due to phenolic residues.

readily and without complication.^{14,15,19} The ethoxymethyl ether monomer (IVc) polymerized well under cationic conditions ($\text{BF}_3\cdot\text{OEt}_2$ initiation in dichloromethane) to yield a soluble polymer with M_n (membrane osmometry) = 19 700 while the polymerization of the (2-methoxyethoxy)methyl ether analogue (IVd) gave only a low yield of a soluble polymer with some loss of the protecting group and a considerable amount of insoluble (perhaps cross-linked) polymer.

Cationic polymerization of the methyl ether (IVe) with $\text{BF}_3\cdot\text{OEt}_2$ at -35°C in dichloromethane afforded a polymer with M_n (membrane osmometry) = 123 000. However, attempts to deprotect the resulting polymer were not successful and resulted in insoluble products.

C. Polymerization of *p*-(*tert*-Butoxycarbonyl)-oxy- α -methylstyrene (IVb). Polymerizations of IVb were carried out under high vacuum with use of a break-seal technique in order to establish scrupulously anhydrous conditions (Table I). The cationic polymerization with phosphorus pentafluoride (PF_5) generated in situ by thermolysis of *p*-chlorobenzene diazonium hexafluorophosphate produced a methanol-soluble polymer of low molecular weight. The IR spectrum of the product indicates that some of the carbonyl groups are still present, but the polymerization was accompanied by a significant amount of *t*-Boc cleavage. This is not surprising because the *t*-Boc group is known to be cleaved by reaction with trifluoroacetic acid²⁰ or a mixture of $\text{BF}_3\cdot\text{OEt}_2$ and acetic acid.²¹

Since the *t*-Boc group is quite stable toward base, anionic polymerization with α -methylstyrene tetramer dianion was attempted in the hope that the bulky initiator would not attack the *t*-Boc group. However, the red color of the initiator solution disappeared immediately upon mixing of the initiator and monomer solution, and no appreciable polymerization occurred. The resulting mixture was concentrated to dryness to yield the starting monomer, which was characterized by ^1H NMR. The initiator was

Table I
Polymerization of IVa and IVb

polymn no.	monomer (g)	initiator (mol %)	solvent (mL)	temp, $^\circ\text{C}$	time, h	yield, g (%)	$M_n^c \times 10^{-3}$	$M_w^c \times 10^{-3}$	$M_n^d \times 10^{-3}$
B75 ^a	IVa (13.5)	$\text{BF}_3\cdot\text{OEt}_2$	CH_2Cl_2 (100)	-30	3.0	3.0 (22)	9.5	19.0	14.7
E78 ^a	IVa (1.40)	$\text{BF}_3\cdot\text{OEt}_2$	CH_2Cl_2 (3)	-20	1.5	0.8 (57)			
2 ^b	IVb (0.267)	PF_5 (1.8)	CH_2Cl_2 (0.5)	0	16	0.088 (33) ^e			
3 ^{b,f}	IVb (0.473)	$^+\text{Na}(\alpha\text{-MeSt})_4^-\text{Na}^+$ (1.2)	THF (1.1)	-78	70	0 (0)			
29 ^b	IVb (0.940)	$\text{BF}_3\cdot\text{OEt}_2$	liq SO_2 (10.0)	0	48	0.014 (1.5)	4.9	9.3	
35 ^b	IVb (0.933)	$\text{BF}_3\cdot\text{OEt}_2$	liq SO_2 (3.0)	-65	26	0.761 (82)	23.7	44.6	
41 ^b	IVb (3.000)	$\text{BF}_3\cdot\text{OEt}_2$	liq SO_2 (10.0)	-65	26	2.614 (87)	22.5	51.3	46.9

^a Polymerization was carried out under inert atmosphere. ^b Polymerization was carried out under high vacuum. ^c Value determined by GPC with THF as a solvent (relative to polystyrene). ^d Value determined by membrane osmometry in DMF. ^e Low molecular weight polymer containing free phenolic hydroxyl groups. ^f Monomer crystallized out at -78°C .

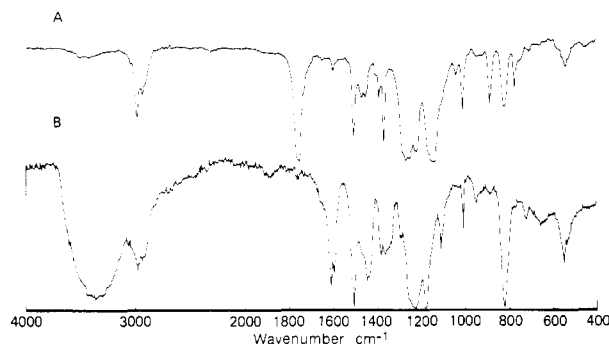


Figure 3. IR spectra (KBr) of (A) Vb synthesized by $\text{BF}_3 \cdot \text{OEt}_2$ initiation in liquid SO_2 and (B) VIII obtained by thermolysis of Vb.

quenched by a reaction with the *t*-Boc group.

Since Matsuda et al.²² have reported that methyl acrylate can be copolymerized with styrene by $\text{BF}_3 \cdot \text{OEt}_2$ initiation in liquid sulfur dioxide, we were prompted to employ this unique solvent. A preliminary polymerization at high dilution produced a methanol-insoluble polymer with the *t*-Boc group intact though the yield and molecular weight were low. However, the polymerization was greatly improved simply by increasing the monomer concentration. Polymers with molecular weight as high as 47 000 were obtained in excellent yields (>82%). Upon mixing of the initiator with the monomer solution at -65°C , the system clouded, and after 1 h, a phase separation occurred followed by solidification of almost the entire reaction mixture. This phenomenon was reported by Asami et al. in the cationic polymerization of styrene derivatives in liquid sulfur dioxide.²³

Tokura et al.^{24,25} claimed that cationic polymerization of α -methylstyrene occurred spontaneously upon mixing of the monomer with liquid sulfur dioxide. However, Akcelrud and Gomes²⁶ report that liquid sulfur dioxide is not capable of polymerizing α -methylstyrene. We observed that liquid sulfur dioxide dried by passing the gas through concentrated sulfuric acid followed by drying over phosphorus pentoxide (P_2O_5) causes spontaneous polymerization of α -methylstyrene.²⁷ However, when liquid sulfur dioxide is dried with 3-Å molecular sieves and P_2O_5 or with P_2O_5 alone, *p*-methoxy-, *p*-chloro-, and *p*-[(*tert*-butoxycarbonyl)oxy]- α -methylstyrenes do not spontaneously polymerize.²⁷ As has been well-known,^{24,25} no evidence of polysulfone formation was detected by NMR or IR spectroscopy.

Gel permeation chromatography (GPC) of the polymer Vb prepared in liquid sulfur dioxide indicates a relatively low dispersity (1.9–2.3). This is consistent with the work of Matsuda et al.,²⁸ who obtained almost monodisperse polymers ($M_w/M_n = 1.05$ –1.17) by cationic polymerization of styrene with $\text{BF}_3 \cdot \text{OEt}_2$ in liquid sulfur dioxide. Calibration of the GPC data by membrane osmometry revealed that the actual value of M_n (46 900) was more than twice as high as the value determined by GPC (22 500) using μ -Styragel columns calibrated with standard polystyrene samples.

The IR spectrum of high molecular weight polymer (Vb) prepared in liquid sulfur dioxide (Figure 3A) presents a striking contrast to that of the low molecular weight polymer prepared with PF_5 at 0°C in dichloromethane. The cationic polymerization in liquid sulfur dioxide affords a product in which all of the *t*-Boc protecting group is intact, as evidenced by the complete absence of the phenolic hydroxyl absorption and the presence of a large carbonyl absorption. In addition, the ^1H NMR (Figure 4) and ^{13}C NMR (Figure 5A) spectra do not show any evi-

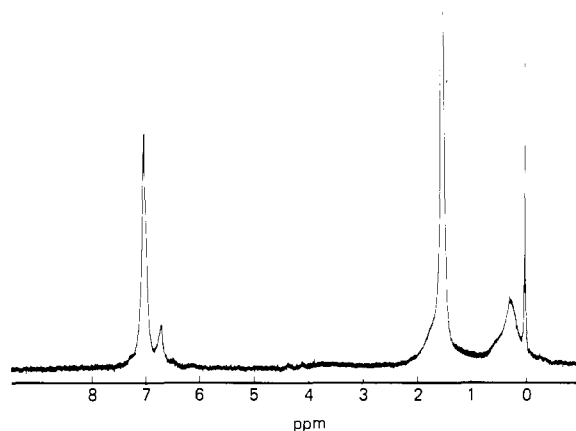


Figure 4. ^1H NMR spectrum (in acetone- d_6) of Vb synthesized by $\text{BF}_3 \cdot \text{OEt}_2$ initiation in liquid SO_2 .

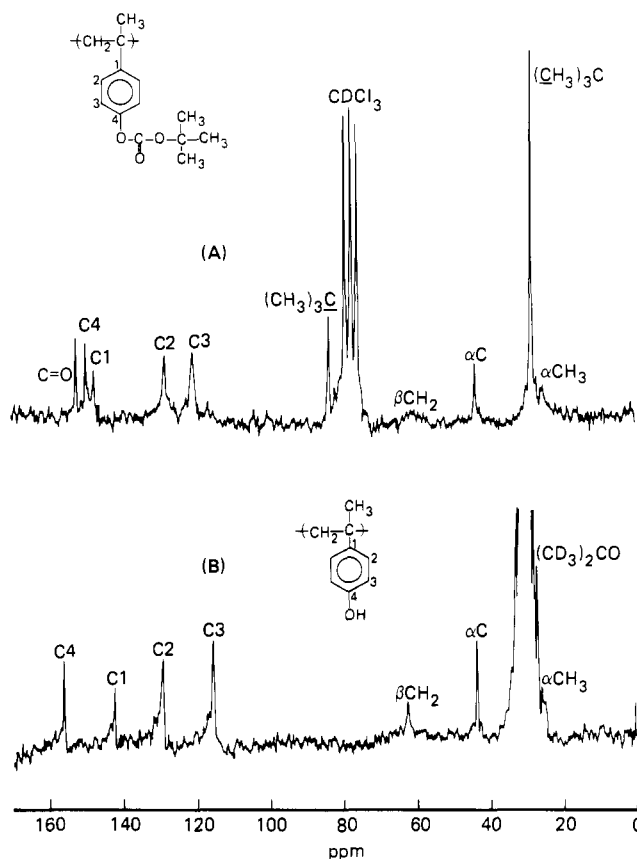
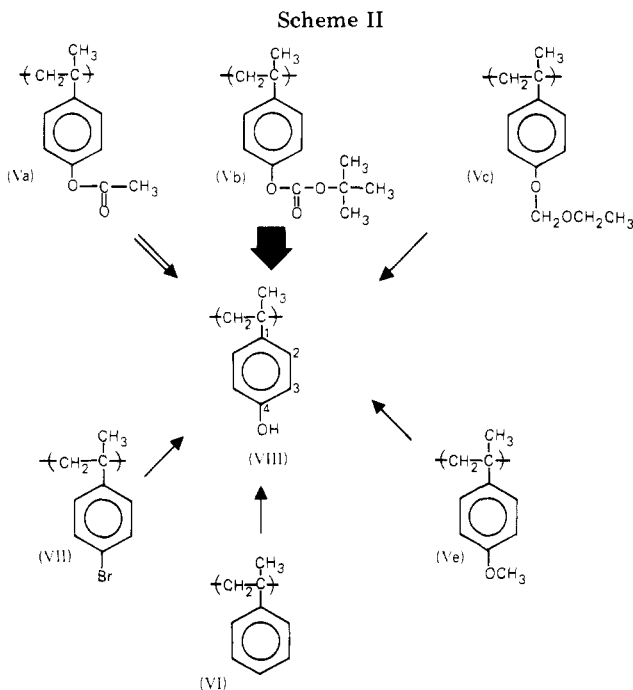


Figure 5. ^{13}C NMR spectra of (A) Vb synthesized by $\text{BF}_3 \cdot \text{OEt}_2$ initiation in liquid SO_2 (measured in CDCl_3) and (B) VIII obtained by thermolysis of Vb (measured in acetone- d_6).

dence of deprotection. Although the mechanism by which liquid sulfur dioxide affords stability to acidolysis of the *t*-Boc group is not well understood at present, clearly sulfur dioxide is the solvent of choice for cationic polymerization of monomers bearing carbonyl functionality. Strong solvation of the carbonyl group by sulfur dioxide may explain the protection.

Deprotection. A. Poly(*p*-acetoxy- α -methylstyrene) (Va). Removal of the acetyl protecting group of Va (Scheme II) was carried out by treatment with anhydrous hydrazine at room temperature.²⁹ The hydrazinolysis occurs instantly to provide the hydrazine salt of the polymer VIII. The free phenolic polymer is obtained from its salt by simple addition of water. In a representative experiment, the isolated phenolic polymer amounted to 97.8% of the theoretical value and quantitative removal



of the acetyl group was confirmed by IR, ^1H NMR (Figure 1B), and ^{13}C NMR (Figure 2B).

B. Removal of Ether Protecting Groups. Removal of the ethoxymethyl protecting group from Vc was easily accomplished by brief treatment of polymer Vc with 2 N sulfuric acid in acetic acid. The reaction is, however, accompanied by chain degradation as evidence by measurement of M_n before and after deprotection.

Deprotection of the methoxy polymer Ve was carried out by using boron tribromide as described in the literature.³⁰ Unfortunately, this reaction was not clean and, in addition to being incomplete, was accompanied by cross-linking, which resulted in the formation of a gelatinous, partially hydroxylated polymer that swelled extensively when suspended in aqueous base but did not dissolve.

C. Poly[(*tert*-butoxycarbonyl)oxy]- α -methylstyrene (Vb). The *t*-Boc group has been reported to cleave upon reaction with trifluoroacetic acid²⁰ or a mixture of $\text{BF}_3 \cdot \text{OEt}_2$ and acetic acid.²¹ Treatment of Vb with trifluoroacetic acid was accompanied by immediate development of a red color and evolution of gas (carbon dioxide and isobutene). Polymer VIII was isolated in 86% yield by precipitation in water. GPC examination of the deprotected polymer shows a bimodal distribution with a large peak corresponding to oligomers. Removal of the *t*-Boc group by reaction with trifluoroacetic acid was accompanied by significant main-chain degradation. This is in striking contrast with the polystyrene analogue, which can be deprotected by treatment with trifluoroacetic acid without chain degradation.³¹ Thus, the deprotection of Vb with trifluoroacetic acid is unsuitable for preparation of VIII. Acid hydrolysis of Va with aqueous hydrochloric acid also resulted in extensive degradation of high molecular weight acetylated polymer.

Our earlier thermogravimetric (TGA) study of poly(*p*-(*tert*-butoxycarbonyl)oxy)styrene showed that the polymer cleanly loses carbon dioxide and isobutene at about 200 °C with liberation of the phenolic hydroxyl group.³¹ The TGA curve of Vb (Figure 6) shows that a sharp 43% weight loss occurs at 200 °C, corresponding to the quantitative evolution of carbon dioxide and isobutene through thermolysis of the *t*-Boc group. Accordingly, VIII was prepared quantitatively by heating Vb at 200 °C on

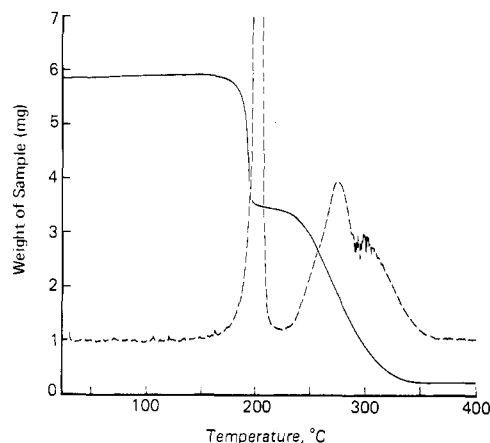


Figure 6. TGA of Vb synthesized by $\text{BF}_3 \cdot \text{OEt}_2$ initiation in liquid SO_2 .

a hot plate. The IR (Figure 3) and ^{13}C NMR (Figure 5) spectra before and after heating revealed that the deprotection reaction was quantitative. GPC analysis of the thermally deprotected polymer gave values of M_n (23 000) and M_w (44 500) that were disturbingly close to those of the starting polymer (Table I). However, more reliable data were obtained by membrane osmometry, which showed that the deprotection was accompanied by a change in M_n from 46 900 (DP = 200) to 28 000 (DP = 208), confirming the absence of main-chain cleavage.

Chemical Modification by Lithiation-Hydroxylation. A. Poly(α -methylstyrene) (VI). Since our previous work^{32,33} on the chemical modification of cross-linked polystyrene has shown that it is possible to introduce hydroxyl groups onto some of the aromatic rings by using a sequential lithiation-oxygen-quenching technique, the lithiation-hydroxylation procedure was attempted with a solution of poly(α -methylstyrene) (VI) in cyclohexane. Treatment of the polymer with tetramethylethylenediamine (TMEDA)-*n*-butyllithium complex³⁴⁻³⁶ followed by reaction with oxygen and workup gave two distinct fractions. One was a partially hydroxylated soluble polymer (VI and VIII) while the other was an insoluble polymer containing hydroxyl groups, which swelled extensively in aqueous base. The cross-linking side reaction can be explained on the basis of the tendency of phenyllithium or tolyllithium species to undergo oxidative coupling through a radical mechanism.³⁷

B. Poly(*p*-bromo- α -methylstyrene) (VII). In a parallel series of experiments polymer VI was brominated by using the catalytic procedure developed for polystyrene³² until 65% of the aromatic rings were para-substituted. Lithiation of the brominated polymer VII, followed by quenching with oxygen, yielded a hydroxylated but cross-linked product. As expected, similar results were obtained in the hydroxylation of a fully para-brominated polymer prepared by cationic polymerization of *p*-bromo- α -methylstyrene.

NMR Studies

A. ^{13}C NMR Assignments. The assignment of ^{13}C resonances of the α -methyl, main-chain carbons and substituent carbons of the poly(α -methylstyrene) derivatives can be made by comparing the spectra of Va, Vb, VIII, and poly(α -methylstyrene). The chemical shifts of the aromatic carbons of Va and VIII were calculated from the substituent effect on aryl carbon shielding in simple monosubstituted-benzene systems. According to the literature,³⁸ introduction of an acetyl group in the benzene ring induces a shift of the aryl carbon shieldings such that C1 moves

Table II
Aromatic ^{13}C Chemical Shifts of Va^a

carbon ^b	calcd			obsd ^f
	A ^c	B ^d	C ^e	
C1	147.5	146.1	147.3	147.4
C2	128.6	126.5	128.2	127.4
C3	120.4	119.4	121.3	120.1
C4	147.9	149.3	151.6	148.1

^a ppm downfield from Me₄Si. ^b Refer to Scheme I.

^c Calculated based on the reported chemical shifts of VI.

^d Calculated based on the chemical shifts of VIII measured in CD₃OH/CDCl₃. ^e Calculated based on the chemical shifts of VIII measured in (CD₃)₂CO. ^f Measured in CDCl₃.

Table III
Aromatic ^{13}C Chemical Shifts of VIII^a

carbon ^b	calcd ^c	obsd	
		A ^d	B ^e
C1	141.9	140.5	141.7
C2	129.1	127.0	128.7
C3	114.2	113.2	115.1
C4	151.8	153.2	155.5

^a ppm downfield from Me₄Si. ^b Refer to Scheme II.

^c Calculated based on the reported chemical shifts of VI.

^d Measured in CD₃OH/CDCl₃. ^e Measured in (CD₃)₂CO.

to lower field by 23 ppm, C2 to higher field by 6.4 ppm, C3 to lower field by 1.3 ppm, and C4 to higher field by 2.3 ppm. Using the reported chemical shift values of poly(α -methylstyrene) and the substituent parameters above, one can calculate the aromatic carbon shieldings of Va and compare these values with the observed chemical shifts (Table II). In a similar manner, the aromatic carbon chemical shifts of VIII can be calculated by employing the parameters of the hydroxyl substituent effect reported in the same literature³⁸ (Table III). It is also possible to calculate the aromatic carbon chemical shifts of Va based on the observed chemical shifts of VIII by applying the esterification effect on the aromatic carbon shieldings, as summarized in Table II. In spite of differences in the solvents used for the ^{13}C NMR measurements, the agreement between the calculated and observed chemical shift values is very good. The aromatic carbon resonances of Vb were assigned by comparing the spectrum with that of Va. The carbonyl carbon of the *t*-Boc group (Figure 5A) resonates at much higher field (151.6 ppm) than that of the acetyl group (168.9 ppm, Figure 2A).³⁹

B. Stereochemistry. As demonstrated in Figure 2A, the α -methyl protons of Va absorb at very high field due to ring currents,⁴⁰ and splitting due to triad tacticity is observed. According to the reported assignments of the α -methyl resonances of unsubstituted^{40,41} and para-substituted¹² poly(α -methylstyrenes), the three triad peaks were assigned to mm (0.83 ppm), mr (0.50 ppm), and rr (0.21 ppm) with increasing field strength. However, a quantitative determination of the tacticity is difficult at present due to the poor resolution of the heterotactic and syndiotactic peaks and the presence of small amounts of the phenolic polymer that results, as discussed earlier, from deprotection during polymerization.

The aromatic ^1H absorptions of Va are of interest. The resonance is composed of two main peaks at 7.00 and 6.72 ppm and a small third peak at 6.57 ppm. By comparing the spectrum of Va (Figure 1A) with that of the fully deprotected phenolic polymer (VIII) (Figure 1B), one might suspect that the peak at 6.72 ppm (Figure 1A) is due to a residue of partially deprotected polymer. However, since Vb synthesized by BF₃·OEt₂ initiation in liquid sulfur dioxide with the *t*-Boc group intact shows very similar

aromatic resonances, we assume that the aromatic ^1H resonances of Figure 1 are indicative of the tacticity and that the phenolic polymer absorptions are not resolved. Lenz et al.¹² have reported that the shape of the aromatic ^1H resonances of para-substituted poly(α -methylstyrenes) depends strongly on the nature of the para substituent: *p*-isopropyl, -methoxy, and -fluoro derivatives exhibited broad singlet aromatic absorptions, while *p*-*tert*-butyl- and chloro-substituted poly(α -methylstyrenes) show AAB aromatic absorptions. The aromatic proton resonances of Va do not show splittings due to either AAB spin systems or higher order tacticity at 80 MHz under our measurement conditions. Thus, the three resonances observed can be adequately explained on the basis of triad sequence analysis.

The α -methyl and aromatic proton resonances of Vb (Figure 4) are very similar to those of Va (Figure 1A). The aromatic proton absorptions at 7.01, 6.70, and 6.48 ppm may be assigned to triad sequences, as discussed earlier. The tacticity of Vb prepared in liquid sulfur dioxide appears to be very similar to that of Va, with the syndiotactic sequence predominating.

The ^1H NMR spectrum of the phenolic polymer VIII obtained by the hydrazinolysis of the acetate polymer Va is very similar to that of the low molecular weight oligomer obtained by the solid-state polymerization of I reported by Kamagami and Hamashima.³ The α -methyl proton resonances are split into triads (mm, hidden; mr, 0.43 ppm; rr, 0.10 ppm). The aromatic resonance in VIII is a complicated multiplet centered at 6.65 ppm.

Experimental Section

Measurements. NMR spectra were recorded in deuteriochloroform (CDCl₃) unless otherwise indicated on Varian EM-360, HA-100, CFT-20, or CFT-80 spectrometers. IR spectra were recorded on Perkin-Elmer 283 or Nicolet MX-1 spectrometers. The melting points reported are uncorrected. Chromatographic separations were performed on a Waters Model Prep-500 preparative high-pressure liquid chromatograph with silica gel columns. Molecular weight determinations were made with a Wescan recording membrane osmometer with toluene or dimethylformamide (DMF) as a solvent while GPC measurements were performed on a Waters Model 150 chromatograph equipped with six μ -Styragel columns at 30 or 40 °C in tetrahydrofuran (THF). TGA measurements were performed on a DuPont 951 at a heating rate of 10 °C/min. Thin-layer chromatography (TLC) was performed on silica gel plates with ethyl acetate/hexane as a developer.

Materials. THF used in Wittig reactions was distilled from LiAlH₄. Dichloromethane was dried over P₂O₅ and distilled from CaH₂ prior to use. BF₃·OEt₂ was purified by distillation or, in the case of the high-vacuum polymerizations, distilled three times in vacuo with the center cut taken each time and distributed by distillation in vacuo to calibrated capillary tubes connected to a break-seal.⁴² *p*-Chlorobenzenediazonium hexafluorophosphate (Aldrich Chemical Co.) was purified by recrystallization from methanol.¹⁴⁻¹⁶ Sulfur dioxide (Matheson) was dried by passing the gas through a column packed with 3-Å molecular sieves, condensed in a cooled flask, and distilled under nitrogen flow into an ampule connected to a break-seal, followed by drying the liquid over granular P₂O₅ in the ampule under high vacuum. All reactions were carried out under dry nitrogen unless otherwise stated.

Monomer Synthesis. Synthesis of *p*-Acetoxy- α -methylstyrene (IVa). To a cooled and stirred suspension of 35.7 g of methyltriphenylphosphonium bromide in 180 mL of THF was slowly added 42 mL of 2.4 M *n*-butyllithium in hexane. After 1 h the solution was treated with 17.8 g of IIIa¹⁰ in 150 mL of THF. After standing at room temperature overnight, the reaction mixture was filtered and worked up. Purification was accomplished on a preparative high-pressure liquid chromatograph (HPLC) using ethyl acetate/hexane as eluent to yield 4.6 g (26%) of pure IVa as a solid melting near room temperature. Alternately, IVa was obtained by direct acylation of *p*-hydroxy- α -methyl-

styrene⁹ under classical conditions. ¹H NMR δ 2.12 (s, 3 H, α -CH₃), 2.26 (s, 3 H, CH₃CO), 4.99 and 5.23 (d, 2 H, β -CH₂), 6.82–7.46 (m, 4 H, para-substituted aromatic). Anal. Calcd for C₁₁H₁₂O₂: C, 75.01; H, 6.81. Found: C, 74.83; H, 6.72.

Synthesis of *p*-[(*tert*-Butoxycarbonyl)oxy]- α -methylstyrene (IVb). A. Wittig Reaction on IIIb. A solution of 5.44 g of II in 150 mL of THF was treated with 4.48 g of potassium *tert*-butoxide. To the mixture was then added 10.02 g (15% excess) of di-*tert*-butyl dicarbonate in THF. After stirring for 1 h at room temperature, the reaction was poured into cold water, and the resulting mixture was extracted with ethyl acetate. After a standard work-up procedure, the solution was worked up to yield 9.2 g (97% yield) of a product with mp 56 °C: IR no hydroxyl; C=O at 1683 cm⁻¹, O—CO—O at 1755 cm⁻¹; ¹H NMR δ 1.59 (s, 9 H, *tert*-butyl), 2.60 (s, 3 H, CH₃CO), 7.22, 7.30, 7.94, 8.02 (q, 4 H, para-substituted aromatic).

A suspension of 3.57 g of methyltriphenylphosphonium bromide in 50 mL of THF was treated with 1.12 g of potassium *tert*-butoxide. After the solution was stirred for 30 min, 2.36 g of IIIb in 20 mL of THF was added. TLC showed the reaction to be complete immediately after the addition. After workup viscous material was obtained, which was purified by HPLC to give 1.55 g (66%) of pure IVb: mp 32–33 °C; IR C=C at 1630 cm⁻¹, O—CO—O at 1755 cm⁻¹; ¹H NMR δ 1.50 (s, 9 H, *tert*-butyl), 2.07 (s, 3 H, α -CH₃), 4.97 and 5.26 (m, 2 H, β -CH₂), 6.97, 7.09, 7.30, 7.69 (q, 4 H, para-substituted aromatic); ¹³C NMR δ 21.9 (CH₃), 27.8 (*tert*-butyl CH₃), 83.4 (quaternary C), 112.7 (β -CH₂), 121.0 and 126.6 (aromatic C2 and C3), 139.1 (aromatic C1), 142.6 (α -C), 150.6 (aromatic C4), 152.0 (C=O). Anal. Calcd for C₁₄H₁₈O₃: C, 71.81; H, 7.69. Found: C, 72.13; H, 7.58.

B. Reaction of I with Di-*tert*-butyl Dicarbonate. A mixture of 5.64 g of I and 6.5 g of potassium *tert*-butoxide in 50 mL of THF was stirred for 10 min, then a THF solution of 12.7 g of di-*tert*-butyl dicarbonate was added. The resulting gelatinous mixture was mechanically stirred for 20 min and then poured into cold water. After workup and HPLC purification 8.03 g (81%) of IVb was obtained.

Synthesis of *p*-(Ethoxymethoxy)- α -methylstyrene (IVc). To a solution of 68 g of II in 0.6 L of toluene was added sodium ethoxide (0.5 mol of sodium in 0.15 L of absolute ethanol). The resulting mixture was distilled under nitrogen to remove ethanol. After cooling to 0 °C, the residue was treated with 43.7 g of chloromethyl ethyl ether and stirred overnight at room temperature. After workup, the crude material was distilled at 2 mmHg and then further purified by HPLC to give 40.8 g (43%) of pure *p*-acetylphenyl ethoxymethyl ether (IIIc). ¹H NMR δ 1.2 (t, 3 H, CH₂CH₃, J = 7 Hz), 2.54 (s, 3 H, CH₃CO), 3.74 (q, 2 H, CH₂CH₃, J = 7 Hz), 5.26 (s, 2 H, OCH₂O), 7.00, 7.18, 7.96, 8.04 (q, 4 H, para-substituted aromatic).

A suspension of 71.4 g of methyltriphenylphosphonium bromide in 0.5 L of dry THF was treated with 22.4 g of potassium *tert*-butoxide. After addition of 38.8 g of IIIc in 0.1 L of THF and workup, the product was purified by HPLC to yield 32.9 g (85.6%) of IVc. IR CH₂= at 3065 cm⁻¹, C=C at 1625 cm⁻¹, para-disubstitution at 835 cm⁻¹; ¹H NMR δ 1.17 (t, 3 H, CH₂CH₃, J = 7 Hz), 2.09 (s, 3 H, α -CH₃), 3.67 (q, 2 H, CH₂CH₃, J = 7 Hz), 5.16 (s, 2 H, OCH₂O), 4.95 and 5.26 (m, 2 H, β -CH₂), 6.96 (d, 2 H, aromatic, J = 9 Hz), 7.36 (d, 2 H, aromatic, J = 9 Hz). Anal. Calcd for C₁₂H₁₆O₂: C, 74.82; H, 8.30. Found: C, 74.96; H, 8.38.

Synthesis of *p*-[(2-Methoxyethoxy)methoxy]- α -methylstyrene. To a suspension of 4.23 g of sodium hydroxide in 0.2 L of THF was added 20 g of II. After the mixture was cooled to 0 °C, 22 g of (2-methoxyethoxy)methyl chloride was added and the mixture was stirred for 20 min and allowed to stand at 0 °C overnight. The product was isolated as described for IIIc to give 29.1 g (88.5%) of IIId. ¹H NMR δ 2.52 (s, 3 H, CH₃CO), 3.37 (s, 3 H, CH₃), 3.67 (m, 4 H, CH₂CH₂), 5.31 (s, 2 H, OCH₂), 6.9–8.0 (m, 4 H, para-substituted aromatic).

IVd was prepared from 44.6 g of methyltriphenylphosphonium bromide, 14 g of potassium *tert*-butoxide, and 28 g of IIId in THF as described above. After chromatographic purification, 22 g (68%) of IVd was obtained. Mass spectrum, M⁺ at m/e 222; IR C=C at 1628 cm⁻¹; ¹H NMR δ 2.12 (s, 3 H, α -CH₃), 3.36 (s, 3 H, CH₃), 3.56 and 3.80 (m, 4 H, CH₂CH₂), 4.98 (m, 1 H, β -CH₂), 5.26 (bs, 1 H, β -CH₂ and CH₂), 6.36 and 6.98 (q, 4 H, para-substituted aromatic).

Synthesis of *p*-Methoxy- α -methylstyrene (IVe). IVE was prepared from 95 g of methyltriphenylphosphonium bromide, 29.9 g of potassium *tert*-butoxide, and 40 g of *p*-methoxyacetophenone in THF as described above. After HPLC purification, 32.6 g (82.6%) of IVE was obtained. Mass spectrum, M⁺ at m/e 148; ¹H NMR δ 2.18 (s, 3 H, α -CH₃), 3.84 (s, 3 H, OCH₃), 5.04 and 5.36 (m, 2 H, β -CH₂), 6.98–7.54 (q, 4 H, para-substituted aromatic).

Polymerization Reactions. The polymerization reactions were carried out as described in Table I. In the case of IVb, polymerizations were carried out under high vacuum in a break-seal-equipped apparatus, as described in the literature.^{14–16,19,42} For reactions involving PF₅ as initiator, the catalyst was introduced into the polymerization ampule by in situ pyrolysis of *p*-chlorobenzenediazonium hexafluorophosphate. The α -methylstyrene tetramer dianion was prepared as reported previously.⁴³ In all cases the polymers were recovered by precipitation in methanol. The cationic polymerization of IVb with BF₃·OEt₂ in liquid sulfur dioxide was carried out as follows. The monomer IVb (3.000 g) was dried under high vacuum overnight and dissolved in 10.0 mL of liquid sulfur dioxide distilled in vacuo into the polymerization ampule to give a yellow solution. With the monomer solution frozen at liquid nitrogen temperature, BF₃·OEt₂ (0.020 mL, 1.2 mol % to the monomer) was introduced by distillation in vacuo. Upon thawing at –65 °C, the mixture became turbid, and after 1 h at –65 °C, a phase separation was observed followed shortly by almost complete solidification of the contents of the ampule. After 26 h, the ampule was cut open and cold methanol was added at –65 °C to provide the polymer as a white precipitate. The polymer was dissolved in dichloromethane, precipitated and reprecipitated in methanol, and then dried in vacuo at 38 °C to provide 2.614 g (87.1%) of product with M_n (GPC) = 22 500, M_n (membrane osmometry) = 46 900, and M_w (GPC) = 51 300. IR, ¹H NMR, and ¹³C NMR spectra of the product did not show any evidence of cleavage of the *t*-Boc group as was the case in the PF₅-catalyzed polymerization in CH₂Cl₂. A similar reaction that was stopped after 2 h at –65 °C only gave a low yield of polymer.

The ethoxymethyl ether monomer IVc (5.2 g) was polymerized with BF₃·OEt₂ in dichloromethane as described for IVa to yield 2.7 g (52%) of a polymer with M_n (osmometry) = 19 700.

The methyl ether monomer IVe (12.8 g) was polymerized as described for IVa by using 1.5 mol % of BF₃·OEt₂ at –35 °C in dichloromethane to yield 8.7 g (68%) of a polymer with M_n (osmometry) = 123 000.

Chemical Modification: Deprotection. Hydrazinolysis of Poly(*p*-acetoxy- α -methylstyrene) (Va). Polymer Va (0.309 g) dissolved in 25 mL of dioxane was treated with anhydrous hydrazine (1.5 mL). Within 1 min, the solution became turbid and a white precipitate formed. After 4 h at room temperature, the precipitated polymer was isolated, redissolved in wet dioxane, and then reprecipitated in water. After the solution was dried in vacuo at 60 °C, 0.230 g (97.8%) of product was obtained. IR, ¹H NMR, and ¹³C NMR revealed that the deprotection reaction was complete.

Reaction of Poly(*p*-[(*tert*-butoxycarbonyl)oxy]- α -methylstyrene) (Vb) with Trifluoroacetic Acid.²⁰ Trifluoroacetic acid (2 mL) was added at room temperature to 0.202 g of the *t*-Boc polymer Vb. An instantaneous gas evolution and red color development were observed and the solution soon became cloudy. After 15 min, water was added to discharge the color and precipitate a white polymer, which was isolated by filtration, washed with water, and dried to provide 99 mg (86%) of product: IR, large hydroxy absorption near 3350 cm⁻¹, no remaining C=O. GPC analysis shows two peaks, a small amount of a polymer and a much larger amount of low-DP oligomers, clearly revealing that main-chain scission occurred. When the product was precipitated in diethyl ether after the same treatment as described above, the recovery was only 7% and the molecular weight of the product was much lower than predicted, again indicating chain degradation.

Thermal Deprotection of Poly(*p*-[(*tert*-butoxycarbonyl)oxy]- α -methylstyrene) (Vb). The polymer powder (60 mg) was heated in an aluminum pan on a hot plate at 200 °C for 1 h to give a quantitative yield (33 mg) of the phenolic polymer VIII. The thermolysis was confirmed to be complete by IR, ¹H NMR, and ¹³C NMR. Molecular weight determination

by membrane osmometry after the thermolysis ($M_n = 28000$) clearly indicates that main-chain degradation did not occur.

Reaction of Poly(*p*-(ethoxymethoxy)- α -methylstyrene) (Vc) with Sulfuric Acid. To a solution of 1 g of Vc in 80 mL of refluxing glacial acetic acid was added 0.5 mL of 2 N H_2SO_4 . The resulting mixture was added to water to produce a precipitate, which was washed with water and dried in vacuo to provide 0.645 g (92%) of the phenolic polymer VIII. The polymer shows a large hydroxyl IR absorption, is soluble in aqueous base, and has M_n (osmometry) = 9200.

Reaction of Poly(*p*-methoxy- α -methylstyrene) (Ve) with Boron Tribromide. A solution of 1 g of Ve in 40 mL of toluene was treated with excess BBr_3 at $-35^\circ C$ as described in the literature.²⁸ The reaction produced a gelatinous material that shows a large hydroxyl IR absorption and is insoluble in both organic solvents and aqueous base.

Chemical Modification by Lithiation-Hydroxylation. **Poly(α -methylstyrene) (VI).** A solution of 2 g of VI with M_n (osmometry) = 163000 in 0.15 L of cyclohexane was lithiated³³⁻³⁶ by treatment with 13 mL of 1.3 N *sec*-butyllithium in hexane. The precipitated polymer was filtered under an inert atmosphere, washed with cyclohexane, suspended in 50 mL of THF, cooled to $-78^\circ C$, and treated with a rapid flow of O_2 . After workup, extraction with THF afforded 1.1 g of a partially hydroxylated polymer containing hydroxyl groups on approximately 20% of the aromatic rings. A second fraction (0.7 g), insoluble in organic solvents and aqueous base, also contains hydroxyl groups and swells extensively when treated with aqueous base.

Poly(*p*-bromo- α -methylstyrene) (VII). A solution of 7 g of VI in 175 mL of CCl_4 containing 3.2 mL of Br_2 and 0.1 g of thallium triacetate was heated to reflux in the dark for 1 h until all the Br_2 disappeared. The polymer was then precipitated in methanol, dissolved in $CHCl_3$, filtered, reprecipitated twice in methanol, and dried to provide 7.9 g of product. Analysis shows that 65% of the aromatic rings are substituted. An NMR study of the polymer confirms the degree of functionalization and that the substitution occurred in the para positions exclusively.

The polymer VII prepared above was dissolved in toluene and lithiated with 2.4 M *n*-butyllithium in hexane as described in the literature.³³ The product obtained after quenching with oxygen was gelatinous and could not be dissolved. Analysis indicated that 52% of the aromatic rings were hydroxylated. Similar results were obtained with a fully brominated polymer.

Acknowledgment. Synthesis of *p*-[(*tert*-butoxycarbonyl)oxy]- α -methylstyrene was carried out in part by E. Gipstein, who is gratefully acknowledged. We thank J. Carothers for TGA and ^{13}C NMR measurements, D. Mathias for GPC analysis, and D. Roberto for osmometry measurements.

Registry No. I, 4286-23-1; II, 99-93-4; IIIa, 13031-43-1; IIIb, 84775-28-0; IIIc, 84775-30-4; IIId, 84775-31-5; IVa, 2759-56-0; IVb, 84775-27-9; IVc, 84775-29-1; IVe, 1712-69-2; Va, 84775-32-6; Vb, 84775-35-9; Vc, 84775-36-0; Vd, 84775-34-8; Ve, 55186-73-7; di-*tert*-butyl dicarbonate, 24424-99-5; chloromethyl ethyl ether, 3188-13-4; (2-methoxyethoxy)methyl chloride, 3970-21-6; *p*-methoxyacetophenone, 100-06-1; trifluoroacetic acid, 76-05-1; sulfuric acid, 7664-93-9.

References and Notes

- (1) Kato, M. *J. Polym. Sci., Part A-1* **1969**, *7*, 2405.
- (2) Arshady, R.; Kenner, G. W.; Ledwith, A. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2017.
- (3) Kamagami, S.; Hamashima, M. *Kobunshi Ronbunshu* **1977**, *34*, 179.
- (4) Kamagami, S.; Yamaji, I. *Kobunshi Ronbunshu* **1978**, *35*, 665.
- (5) Braun, D.; Meier, B. *Makromol. Chem.* **1974**, *175*, 791.
- (6) Aliev, S. M.; Ismailov, R. G.; Bairamov, M. R. *Azerb. Khim. Zh.* **1967**, *56*; *Chem. Abstr.* **1968**, *69*, 67031d.
- (7) Ismailov, R. G.; Aliev, S. M.; Bairamov, M. R.; Allakhverdiev, I. K. *Azerb. Khim. Zh.* **1969**, *8*; *Chem. Abstr.* **1970**, *72*, 67617m.
- (8) Scherring-Kahlbaum, French Patent 657122, 1928; U.S. Patent 1798813, 1931. Krizan, H.; Schnell, H. British Patent 905994, 1962.
- (9) Kahovec, J.; Pivcová, H.; Pospisil, J. *Collect. Czech. Chem. Commun.* **1971**, *36*, 1986.
- (10) Corson, B. B.; Heintzelman, W. J.; Schwartzman, L. H.; Tiefenthal, H. E.; Lokken, R. J.; Nickels, J. E.; Atwood, G. R.; Pavlik, F. J. *J. Org. Chem.* **1958**, *23*, 544.
- (11) Aliev, S. M.; Bairamov, M. R.; Ibragimova, M. D. *Vysokomol. Soedin., Ser. A* **1979**, *21*, 1368. Aliev, S. M.; Bairamov, M. R.; Aliev, S. A.; Abbasov, M. A. *Zh. Org. Khim.* **1972**, *8*, 561.
- (12) Lenz, R. W.; Regel, W.; Westfelt, L. *Makromol. Chem.* **1975**, *176*, 781.
- (13) Lenz, R. W.; Sutherland, J. E.; Westfelt, L. C. *Makromol. Chem.* **1976**, *177*, 653.
- (14) Ruckel, E. R.; Schuerch, C. *J. Org. Chem.* **1966**, *31*, 2233.
- (15) Zachoval, J.; Schuerch, C. *J. Am. Chem. Soc.* **1969**, *91*, 1165.
- (16) Zachoval, J.; Schuerch, C. *J. Polym. Sci., Part C* **1959**, *187*.
- (17) Dzhavadyan, E. A.; Rozenberg, B. A.; Yenikolopyan, N. S. *Polym. Sci. USSR (Engl. Transl.)* **1969**, *11*, 2650.
- (18) Dzhavadyan, E. A.; Rozenberg, B. A.; Yenikolopyan, N. S. *Polym. Sci. USSR (Engl. Transl.)* **1971**, *13*, 1841.
- (19) Ito, H.; Schuerch, C. *J. Am. Chem. Soc.* **1979**, *101*, 5797.
- (20) Kappeler, H.; Schwyzer, R. *Helv. Chim. Acta* **1960**, *43*, 1453.
- (21) Hiskey, R. G.; Beacham, L. M.; Matl, V. G.; Smith, J. N.; Williams, E. B., Jr.; Thomas, A. M.; Wolters, E. T. *J. Org. Chem.* **1971**, *36*, 488.
- (22) Matsuda, M.; Ohshima, K.; Tokura, N. *J. Polym. Sci., Part A* **1964**, *2*, 4271.
- (23) Asami, R.; Tokura, N. *J. Polym. Sci.* **1950**, *42*, 545.
- (24) Tokura, N.; Matsuda, M.; Shirai, I.; Shiina, K.; Ogawa, Y.; Kondo, Y. *Bull. Chem. Soc. Jpn* **1962**, *35*, 1043.
- (25) Tokura, N.; Matsuda, M.; Ogawa, Y. *J. Polym. Sci., Part A* **1963**, *1*, 2965.
- (26) Akcelrud, L.; Gomes, A. S. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2423.
- (27) Ito, H., unpublished results.
- (28) Matsuda, M.; Iino, M.; Nakagawa, Y.; Yamazaki, T.; Tokura, N. *Kogyo Kagaku Zasshi* **1966**, *69*, 115.
- (29) Ledwith, A.; Rahnama, M.; Sen Gupta, P. K. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2239.
- (30) Williams, R. E. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2123.
- (31) Fréchet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer*, in press.
- (32) Fréchet, J. M. J.; Farrall, M. J. In "Chemistry and Properties of Crosslinked Resins"; Labana, S. S., Ed.; Academic Press: New York, 1977; pp 59-83. Farrall, M. J.; Fréchet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877.
- (33) Fréchet, J. M. J.; de Smet, M.; Farrall, M. J. *Polymer* **1979**, *20*, 675.
- (34) Chalk, A. J. *J. Polym. Sci., Part B* **1968**, *6*, 649.
- (35) Evans, D. C.; George, M. H.; Barrie, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 247.
- (36) Farrall, M. J.; Fréchet, J. M. J. *Macromolecules*, **1979**, *12*, 426.
- (37) Muller, E.; Topel, T. *Ber. Dtsch. Chem. Ges.* **1939**, *72*, 273.
- (38) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York and London, 1972; p 197.
- (39) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, London, Sydney, and Toronto, 1972; pp 119, 126.
- (40) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York and London, 1972; p 84.
- (41) Brownstein, S.; Bywater, S.; Worsfold, D. J. *Makromol. Chem.* **1961**, *48*, 127.
- (42) Ito, H.; Schuerch, C. *Macromolecules* **1981**, *14*, 246.
- (43) Ito, H.; Miller, D. C.; Willson, C. G. *Macromolecules* **1982**, *15*, 915.