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Syntheses of Acetophenone Enol Ester Polymers and Their Conversion to Poly(phenylacetylenes)

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ABSTRACT: α-Acetoxystyrene (ACOST), 4-methylene-4*H*-1,3-benzodioxin-2-one (MBDOON), and 3-methylenephthalide (MP) readily undergo radical polymerization although they are α-substituted styrene derivatives. While poly(α-acetoxystyrene) (PACOST) is syndiotactic-rich due to the severe steric hindrance, the α,α-cyclic analogues are almost perfectly atactic (heterotactic-rich), indicating that the cyclization reduces the steric hindrance. PACOST and poly(4-methylene-4*H*-1,3-benzodioxin-2-one) (PMBDOON) release acetic acid and carbon dioxide upon heating to 200 °C, being converted to poly(phenylacetylene) (PPA) and poly((*o*-hydroxyphenyl)acetylene) (PHOPA), respectively. PPA thus obtained has a trans structure. The thermolysis temperature can be lowered to ca. 100 °C by generating a strong acid in the PACOST film through photolysis of a sulfonium salt cationic photoinitiator. PPA produced by acidolysis at the lower temperature contains a significant amount of cis sequences. PMBDOON can be also converted to PHOPA by heating the polymer powder with an acid at ca. 100 °C. However, thermolysis and acidolysis of PACOST and PMBDOON are accompanied by depolymerization. In contrast, poly(3-methylenephthalide) (PMP) is very stable toward thermolysis and acidolysis.

Introduction

We have been interested in reactions of radiochemically generated acids with polymer matrices especially for lithographic applications. Acid-catalyzed cross-linking, depolymerization, and deprotection reactions were first utilized in 1982 in the design of sensitive resist systems incorporating "chemical amplification",[2-4] and many publications have followed.[5-7] One such example is acid-catalyzed deprotection reactions (A_{AL}-1 acidolysis[8]) involving polymer pendant groups.[2-5,9-11] In this scheme, conversion of lipophilic polymers to hydrophilic phenol or carboxylic acid polymers allows either positive imaging with a polar developer or negative imaging with use of a nonpolar organic developer without swelling (Scheme I). Triarylsulfonium salts are typical radiochemical acid generators,[12] and nitrobenzyl esters[13,14] have been also used recently in resist applications.

Poly(α,α-dimethylbenzyl methacrylate) (PDMBZMA) (Scheme I) bearing a tertiary benzyl group in the ester side chain is thermolyzed or acidolyzed to form poly(methacrylic acid) and α-methylstyrene.[10,11,15] Hence, poly(α-acetoxystyrene) (PACOST) with a tertiary benzylic carbon adjacent to ester oxygen in the polymer backbone is expected to release acetic acid to form poly(phenylacetylene) (PPA) upon thermolysis or acidolysis (Scheme I). Thus, we have extended our research on thermal and acid-catalyzed deprotection of polymer pendant groups to the cases where the backbone α-carbon participates in the reaction. In Chart I are presented some polymers bearing tertiary ester functionalities and their mutual structural relationships. PACOST is structurally similar to cyclic benzoate or carbonate as shown in Chart I, which may be considered to be cyclic analogues of poly(((*tert*-butoxycarbonyl)oxy)styrene) (PBOCST)[2-5,16] and poly(*tert*-butyl vinylbenzoate) (PTBVB).[9] As Scheme I indicates, PBOCST and PTBVB undergo thermolysis or acidolysis to form poly(hydroxystyrene) (PHOST) and poly(vinylbenzoic acid) (PVBA), releasing isobutene/carbon dioxide and isobutene, respectively. Thus, poly((*o*-hydroxyphenyl)acetylene) (PHOPA) and poly(*o*-ethynylbenzoic acid) are expected to be produced through thermolysis or acidolysis of poly(4-methylene-4*H*-1,3-benzodioxin-2-one) (PMBDOON) and poly(3-methylenephthalide) (PMP), respectively. While polyacetylenes are typically synthesized by polymerization of acetylene monomers,[17,18] use of processable polymers as precursors to highly conjugated conducting polymers has attracted much attention recently.[19,20] Formation of acetylenic structures by treating PACOST with acid has been mentioned in the literature[21] but no detailed studies on the subject are available to our best knowledge. We have been also interested in lithographic imaging of polyacetylene films by photochemically induced acidolysis of precursor polymers.

In addition to the polymer reactions mentioned above, we have been engaged in investigations of the polymerization behavior of α-substituted styrene derivatives[22,23]

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Scheme I
Radiochemically Induced Acid-Catalyzed Deesterification

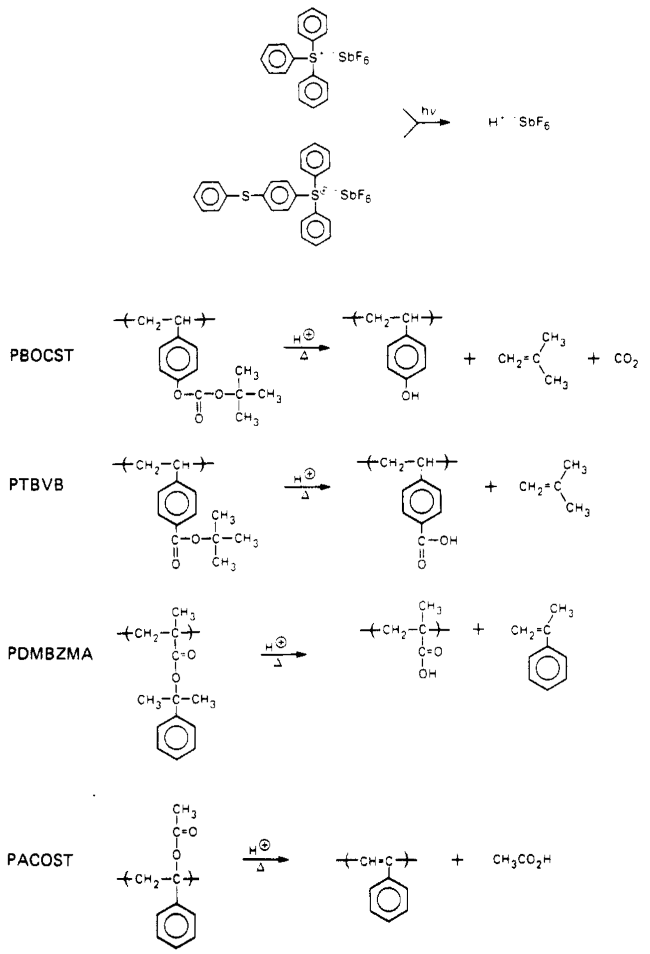
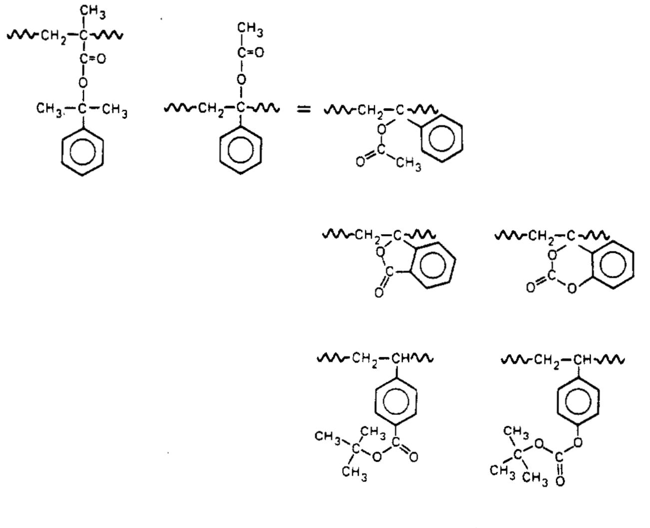
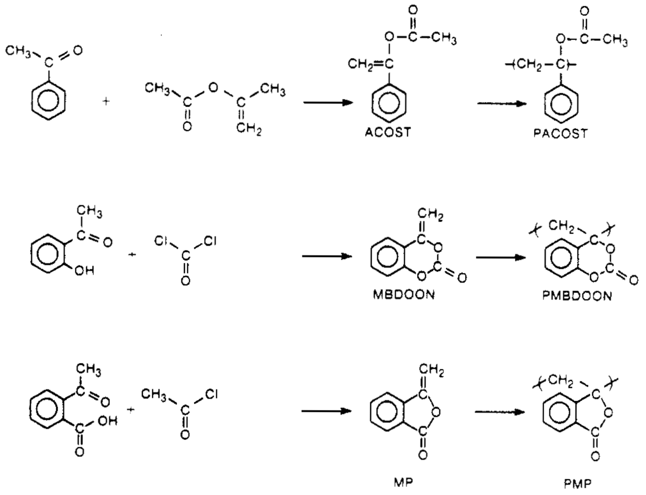


Chart I
Polymers Bearing Tertiary Ester Functionalities



and exo-methylene α,α-cyclic monomers.[24-27] Although radical polymerizations of α-acetoxystyrene (ACOST)[28-32] and 3-methylenephthalide (MP)[33] have been reported in the literature, the cyclic carbonate MBDOON is a new monomer. Radical polymerization of these monomers and the structure of the polymers are briefly discussed in this paper while detailed kinetics, thermodynamics, and reactivities in radical polymerization of ACOST are described elsewhere[23] and the polymerization behavior of the cyclic monomers is currently being investigated.

Scheme II
Synthesis of ACOST, MBDOON, and MP



Experimental Section

Measurements. NMR spectra were recorded on an IBM NR-250/AF, a Varian EM-390, a Bruker AM-500, or a Hitachi R-24B spectrometer in CDCl$_3$ or dimethyl-d_6 sulfoxide (DMSO-d_6). DEPT, COSY, and ^{1}H–^{13}C 2D techniques were utilized for assignment of NMR spectra of monomers as well as ^{1}H-coupled ^{13}C NMR. In the case of the polymer samples, the inverse-gated decoupling technique was applied to minimize the nuclear Overhauser effect (NOE) for better quantitative analysis. IR spectra were measured on an IBM IR/32 FT spectrometer. UV spectra were recorded on a Hewlett-Packard Model 8450A UV–vis spectrometer using thin films cast on quartz plates. Molecular weight determination was made by gel permeation chromatography (GPC) using a Waters Model 150 chromatograph equipped with 6 μStyragel columns at 30 °C in tetrahydrofuran (THF) or in *N*-methylpyrrolidinone (NMP). Thus, the molecular weights reported in this paper are polystyrene equivalent. Thermal analyses were performed on a Du Pont 1090 thermal analyzer at a heating rate of 5 °C/min for thermogravimetric analysis (TGA) and 10 °C/min for differential scanning calorimetry (DSC) under an inert atmosphere. GC/MS analysis was carried out with a Hewlett-Packard 5995A gas chromatograph/mass spectrometer. Film thickness was measured on a Tencor Alpha-Step 200. Combustion analysis was performed by Galbraith Laboratories, Knoxville, TN.

Materials. α,α'-Azobis(isobutyronitrile) (AIBN) was purified by the conventional method. Acetophenone, 2-hydroxyacetophenone, and 2-acetylbenzoic acid were purchased from Aldrich. Triphenylsulfonium hexafluoroantimonate was synthesized according to the literature.[34]

Synthesis of α-Acetoxystyrene. ACOST was prepared according to Scheme II[35] in 34% yield: bp 62–63 °C/0.2 mmHg (lit.[36] bp 120–122 °C/20 mmHg); IR (NaCl) 1765 (C=O), 1645 cm^{-1} (C=C). ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.5 (m, 2 H, aromatic H3), 7.4 (m, 3 H, aromatic H2 and H4), 5.52 (d, 1 H, β-CH cis to phenyl, J = 2.1 Hz), 5.07 (d, 1 H, β-CH trans to phenyl, J = 2.1 Hz), 2.27 (s, 3 H, CH$_3$); ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 168.73 (C=O), 152.71 (α-C), 134.03 (C1), 128.56 (C4), 128.25 (C2), 124.60 (C3), 101.81 (β-CH$_2$), 20.58 (CH$_3$).

Synthesis of 4-Methylene-4*H*-1,3-benzodioxin-2-one. MBDOON was prepared by condensation of *o*-hydroxyacetophenone with phosgene as shown in Scheme II.[37] To an ice-cooled phosgene solution (80 mL, 20% in toluene) was dropwise added with stirring a solution of 16 g (130 mmol) of *N,N*-dimethylaniline and 17.5 g (130 mmol) of *o*-hydroxyacetophenone. After 20 h of stirring, the ammonium chloride salt was removed by filtration, and the mixture was concentrated. The oily residue was distilled on a Kugelrohr apparatus under vacuum (<0.1 mmHg). Unreacted *N,N*-dimethylaniline and *o*-hydroxyacetophenone were first distilled out at 70–100 °C followed by the product boiling at 100–110 °C. The white solid thus obtained (14 g, 67% yield) was purified by crystallization from *n*-hexane: mp 64–65 °C (lit.[37] mp 64–65 °C); IR (KBr) 1776 cm^{-1}

(C=O); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.45 (dd, 1 H, aromatic H3, J = 7.85, 1.52 Hz), 7.34 (td, 1 H, aromatic H5, J = 7.84, 1.59 Hz), 7.16 (td, 1 H, aromatic H4, J = 7.63, 1.15 Hz), 6.98 (dd, 1 H, aromatic H6, J = 8.24, 1.12 Hz), 5.02 (d, 1 H, β-CH cis to phenyl, J = 3.37 Hz), 4.88 (d, 1 H, β-CH trans to phenyl, J = 3.38 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 149.16 (C2), 147.70 (α-C), 142.51 (C=O), 131.62 (C5), 125.62 (C4), 123.37 (C3), 116.06 (C6), 113.70 (C1), 91.86 (β-CH_2).

Synthesis of 3-Methylenephthalide. This monomer (MP) was synthesized in 10% yield according to the reported procedure (Scheme II).[38] In addition, MP was prepared by dehydration of 2-acetylbenzoic acid with *p*-toluenesulfonic acid in benzene, using a Dean–Stark apparatus, and isolated by column chromatography. This synthetic procedure is now under optimization. Mp 55.2–56.5 °C (lit.[38] mp 57 °C); IR (KBr) 1776 (C=O), 1662 cm^{-1} (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.84 (m, 1 H, aromatic H3), 7.67 (m, 2 H, aromatic H5, H6), 7.55 (m, 1 H, aromatic C4), 5.183 (d, 1 H, β-CH cis to phenyl, J = 3.06 Hz), 5.180 (d, 1 H, β-CH trans to phenyl, J = 3.06 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 166.68 (C=O), 151.72 (α-C), 138.87 (C1), 134.40 (C5), 130.37 (C4), 125.10 (C3), 124.95 (C2), 120.53 (C6), 91.13 (β-CH_2).

Radical Polymerization. All the polymerization were carried out in glass ampules sealed under vacuum after repeated freeze–thaw cycles, and the polymers were precipitated in excess methanol, filtered, and dried under vacuum. ACOST was polymerized in bulk with AIBN at 65 °C for 7–16 days to provide ca. 50% yield: IR (KBr) 1741 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.6–5.7 (phenyl), 4.0–2.0 (β-CH_2), 2.0–0 (CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 170.0 (C=O), 140.6 (C1), 126.2 (C2, C3, C4), 85.5 (α-C), 44.6 (β-CH_2), 22.0 (CH_3).

MBDOON was polymerized with AIBN in dioxane at 70–85 °C or in NMP at 60 °C for 24–48 h, providing 60–100% yield: IR (KBr) 1788 cm^{-1} (C=O); ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.5–5.9 (phenyl), 3.5–2.2 (β-CH_2); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 145.7 (C2), 141.4 (C=O), 129.7 (C5), 126.1 (C4), 124.2 (C1), 116.5 (C3), 115.2 (C6), 85.7 (α-C), 53.0 (β-CH_2). Anal. Calcd for $C_9H_6O_3$: C, 66.67; H, 3.73. Found: C, 66.10; H, 3.99.

MP was polymerized with AIBN in NMP at 80 °C for 18 h, providing 89% yield. A high initiator concentration of 11 mol % was employed in an attempt to increase the solubility of the polymer by reducing its molecular weight. IR (KBr) 1772 cm^{-1}; ^{13}C NMR (125.76 MHz, DMSO-d_6) δ 166.5 (C=O), 148.3 (C1), 133.0 (C5), 128.2 (C4), 124 (C2, C3, C6), 85.0 (α-C), 46 (β-CH_2).

UV Exposure of Polymer Films. PACOST was dissolved in cyclohexanone and PMBDOON and PMP were dissolved in NMP at ca. 17 wt %, to which was added triphenylsulfonium hexafluoroantimonate (9.5 wt % of the total solid). Films, spin-cast on NaCl plates, quartz disks, or Si wafers, were prebaked at 100–135 °C for 10 min and exposed through a 254-nm band-pass filter to radiation from an Optical Associates, Inc., exposure system. Imagewise exposure was carried out in a contact mode. Exposed films were postbaked at 100–130 °C for 5 min and subjected to IR or UV analysis. The PACOST system was developed in xylenes, providing positive tone images of the mask.

Results and Discussion

Chemical Shift Assignment of Monomers. Since assignment of monomer NMR spectra provides a basis for interpretation of polymer spectra, we carefully studied the chemical shifts of the monomers using DEPT, COSY, and ^{1}H–^{13}C 2D techniques as well as ^{1}H-coupled ^{13}C NMR in addition to the regular ^{1}H and ^{1}H-decoupled ^{13}C NMR. The assignments of the ACOST resonances are given in the Experimental Section, which is based in part on a coupling between β-CH_2 with the aromatic H2. ^{1}H NMR spectra (250 MHz) of MBDOON and MP in $CDCl_3$ are presented in Figure 1. MBDOON exhibits a β-CH_2 AB quartet at ca. 5 ppm and four sets of well-separated aromatic CH resonances. The outermost doublets in the aromatic region with further splittings must be assigned to the aromatic H3 and H6 and the inner triplets with additional fine splittings to H4 and H5. The COSY experiment shows a stronger coupling between the β-CH cis to the phenyl ring and the aromatic CH at the highest field, which can be assigned to H6. The highest and the lowest field doublets couple on the COSY plot with the lower and higher field triplets, respectively, allowing the aromatic proton assignment shown in Figure 1a. The β-protons of MP are accidentally almost equivalent with only 0.003 ppm resonance separation, exhibiting an AB quartet almost degenerated to a singlet (Figure 1b). The assignment of the aromatic CH proton resonances shown in Figure 1b is also based on the COSY experiment and integration.

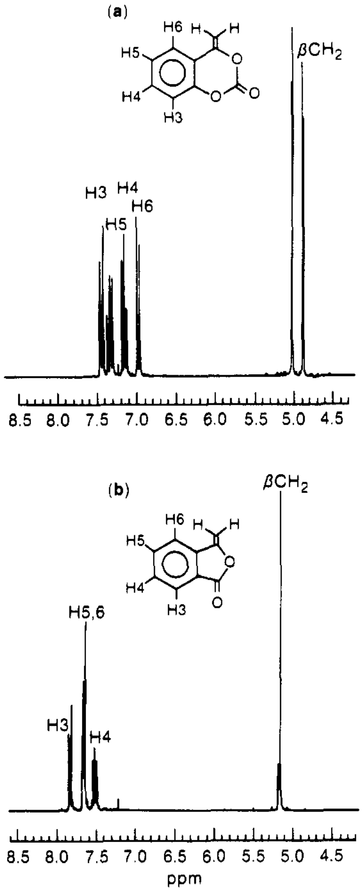


Figure 1. ^{1}H NMR spectra (250 MHz) of MBDOON (a) and MP (b) in $CDCl_3$.

^{1}H-decoupled ^{13}C NMR spectra with NOE (62.9 MHz) of MBDOON and MP in $CDCl_3$ are presented in Figure 2. The assignment of CH_2 and CH resonances are based on the ^{1}H–^{13}C 2D experiments. We investigated long-range ^{13}C–^{1}H couplings for assignment of the quaternary carbon resonances. The ^{1}H-coupled ^{13}C resonance of the peak at 142.5 ppm is a doublet with a very small coupling of 2.19 Hz and can be assigned to the carbonyl carbon coupling with H3 (four bonds away) (Figure 3). This is rather surprising since carbonate carbonyls typically absorb at 150–160 ppm according to the literature.[39] This carbonate carbonyl group resonates at a higher field than any other organic carbonyl groups. The carbon resonance at 147.7 ppm basically splits into a triplet by coupling with the β-protons ($J_{C\text{-}C\text{-}H}$ = 9.9 Hz), also exhibiting longer range couplings of $J_{C\text{-}C\text{-}C\text{-}H}$ = 4.0 Hz and $J_{C\text{-}C\text{-}C\text{-}C\text{-}H}$ = 1.6 Hz, and can be assigned to the α-carbon. The aromatic carbon resonance at 149.16 ppm (Figure 3) shows fewer couplings than the resonance at 113.70 ppm (not shown), and therefore these resonances are assigned to C2 and C1, respectively, as C1 can couple with the β-CH_2. The β-methylene carbon exhibits a quartet resonance due to coupling with the magnetically non-

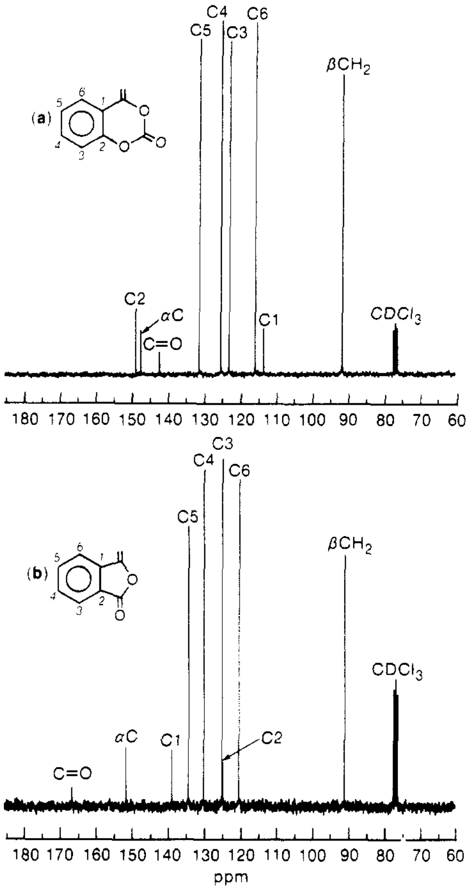


Figure 2. ^{13}C NMR spectra (62.9 MHz) of MBDOON (a) and MP (b) in CDCl$_3$.

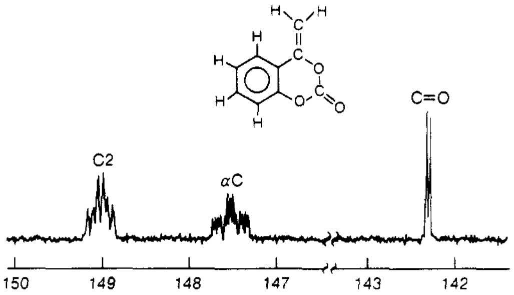


Figure 3. ^{1}H-coupled ^{13}C NMR spectrum (62.9 MHz) of MBDOON in CDCl$_3$.

equivalent geminal protons (J_{C-H} = 164.74 and 163.17 Hz). The H-coupled aromatic CH resonances are doublets of doublets with additional fine splittings (J_{C-H} = 140–165 Hz, J_{C-C-H} = 7.7–9.2 Hz, $J_{C-C-C-H}$ = 0.85–2.2 Hz). The C6 resonance at 120.53 ppm is more complicated due to interaction with the β-methylene protons.

In a similar fashion, the assignment of the ^{13}C resonances of MP has been achieved as shown in Figure 2b. The order of the aromatic CH resonances is the same as that of MBDOON but C1 and C2 are reversed. The carbonyl group of MP resonates in the same range as benzoate derivatives but at a higher field than alicyclic esters.

The β-carbon of these α-substituted styrene derivatives resonates at much higher fields than that of styrene (112.5 ppm) and α-methylstyrene (111.5 ppm), indicating that these monomers are electron rich. The cyclic monomers (91.9 and 91.1 ppm) appear to have a higher electron density on the β-carbon than ACOST (101.8 ppm) and seems to be as electron rich as vinyl acetate (96.5 ppm) and methyl vinyl ether (85.5 ppm) judging from their β-carbon chemical shifts.

Radical Polymerization and Tacticity. The conditions and results of radical polymerization of ACOST, MBDOON, and MP are summarized in Table I. These α-substituted styrene derivatives readily undergo radical homopolymerization in contrast to α-methylstyrene. However, whereas the cyclic monomers provide high yield in a short period of time in solution, ACOST is much slower to polymerize even in bulk. These observations are consistent with what we have reported for other exomethylene cyclic monomers.[24-27] Detailed kinetics, thermodynamics, and reactivity studies of these monomers will be reported elsewhere.

While ^{1}H resonances of the polymers were simply too broad, ^{13}C NMR has provided tacticity information. The inverse-gated ^{13}C NMR spectrum (62.9 MHz) of PACOST in CDCl$_3$ is presented in Figure 4. Monthéard et al.[30] reported radical polymerization of ACOST and concluded that PACOST was predominantly heterotactic based on their poorly resolved aromatic C1 resonance (25.2 MHz, CDCl$_3$). We do not observe any sign of splittings due to tacticity in the C1 resonance but the α-carbon exhibits splittings due to triad tacticity with some pentad information as the expanded spectrum in Figure 4 demonstrates. We believe that PACOST is rich in the syndiotactic sequence as sterically hindered monomers such as α-methylstyrene tend to give syndiotactic polymers. The triad tacticity of PACOST is estimated as follows: rr = 54, mr = 39, and mm = 7%.

Polymerization of MBDOON has never been reported before to our best knowledge. The inverse-gated ^{13}C NMR spectrum (62.9 MHz) of PMBDOON in DMSO-d_6 is presented in Figure 5. The assignment is based on the comparison with the monomer spectrum. The carbonyl resonance exhibits three well-resolved peaks due to triad tacticity. The C1 resonance almost overlapping with C4 appears to be indicative of stereoregularity. It is clear that PMBDOON is predominantly heterotactic and almost perfectly atactic (rr = 35, mr = 46, and mm = 19%). The ^{13}C spectrum (125 MHz) of PMP in DMSO-d_6 shown in Figure 6 is even more interesting. Almost all the carbons that are remote from the chiral center provide tacticity information rather than the backbone carbons. Even the C4 resonance (four bonds away from the α-position) nicely splits, perhaps reflecting pentad sequences. The carbonyl and C5 resonances resemble each other. In spite of the heavy overlapping, the resonances due to C2, C3, and C6 are also indicative of tacticity. The C5 resonance is cleanly separated into three peaks, indicating that PMP is highly atactic (rr = 32, mr = 50, and mm = 18%) as is the case with PMBDOON.

It is interesting to compare the stereoregularity of PACOST and its cyclized analogues. The cyclization of the α-position reduces the stereoregulation due to the reduced steric hindrance, which complements very well with the increased reactivity of the cyclic monomers. It has been reported that radical polymerization of α-methylene-γ-butyrolactone, a cyclic analogue of methyl methacrylate (MMA), gives a heterotactic polymer, while MMA polymerizes to a syndiotactic polymer by radical initiation.[40]

Thermolysis of PACOST, PMBDOON, and PMP. TGA curves of PACOST and PDMBZMA are compared in Figure 7. While the polymethacrylate is converted to poly(methacrylic acid), losing α-methylstyrene at ca. 210 °C,[8] PACOST loses ca. 40% of its weight at 200–240 °C. GC/MS analysis of gaseous products generated upon heating the PACOST powder clearly reveals that the first-

Table I
Radical Polymerization of ACOST, MBDOON, and MP

monomer, g	AIBN, mol %	solvent (mL)	temp, °C	time, days	yield, %	M_n	M_w
ACOST							
3.1	0.5		60	6	27	10 700	22 500
1.0	0.5		65	7	51		
2.0	0.2		65	16	50	24 600	58 900
2.0	0.2		65	16	50	25 000	59 000
MBDOON							
0.39	1.0	dioxane (2.6)	70–85	1	89		
0.30	3.3	NMP (0.5)	60	1	60		
0.30	3.3	NMP (0.5)	60	2	100		
0.47	1.1	NMP (1.0)	60	2	94	23 700	38 500
1.62	1.0	NMP (3.5)	60	2	94		
MP							
0.9	11.4	NMP (5.0)	80	0.75	89	6 600	11 400

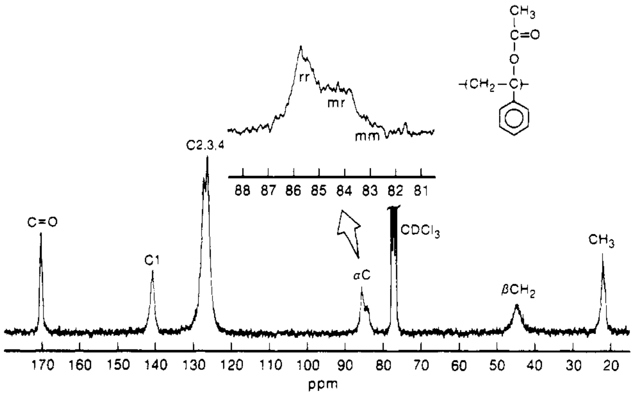


Figure 4. Inverse-gated ^{13}C NMR spectrum (62.9 MHz) of PACOST in $CDCl_3$.

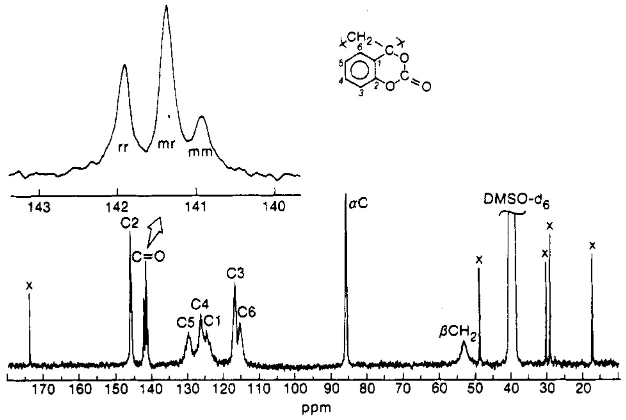


Figure 5. Inverse-gated ^{13}C NMR spectrum (62.9 MHz) of PMBDOON in DMSO-d_6. (×) NMP used in polymerization.

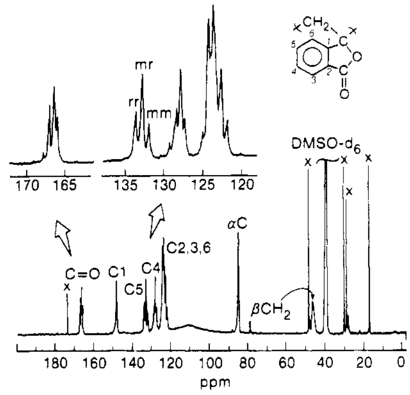


Figure 6. Inverse-gated ^{13}C NMR spectrum (125 MHz) of PMP in DMSO-d_6. (×) NMP used in polymerization.

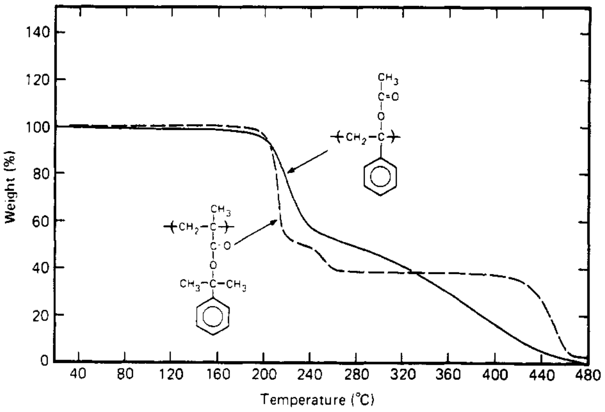


Figure 7. TGA of PACOST and PDMBZMA (5 °C/min).

stage weight loss is due to liberation of acetic acid (the quantitative loss would be 37%). Thus, PACOST is converted at ca. 240 °C to PPA without showing a glass transition. The degradation behavior above 240 °C is similar to that of PPA's reported in the literature.[41] Monthéard et al.[30] and Sahraoui et al.[29,42] have reported the thermal degradation behavior of PACOST.

In Figures 8 and 9 are presented IR and UV spectra of PACOST films heated at 220 °C. PACOST (M_n = 24 600 and M_w = 58 900) was dissolved in cyclohexanone at 16.3 wt %. Films cast onto a NaCl or quartz disk were heated at 135 °C to remove the casting solvent. After heating at 220 °C for 30 min, the strong carbonyl absorption of PACOST at 1740 cm^{-1} almost completely disappears, and the IR spectrum of the heated sample is similar to that of PPA made by polymerization of phenylacetylene.[43] As Figure 9 indicates, the PACOST film does not absorb above 300 nm and is similar to a polystyrene film in the wavelength range below 300 nm. Upon heating at 220 °C, the film becomes thinner due to loss of acetic acid and becomes darker in color, with drastically increased absorption at 200–250 nm. The UV absorption of the heated film is extended to 500 nm. Thermolysis of PACOST results in formation of highly conjugated PPA.

A PACOST powder (M_n = 10 700 and M_w = 22 500) was heated at 200 °C with 32% weight loss, and the resulting brown powder was subjected to GPC analysis after washing with water and drying. The molecular weight of PPA was much lower (M_n = 2100 and M_w = 4300) than the theoretical loss of acetic acid can account for, suggesting occurrence of backbone scission. Since we did not observe the ACOST monomer or its fragments by GC/MS, the degradation is likely to occur on PPA.

In Figure 10 are compared TGA curves of PMBDOON with PBOCST and of PMP with PTBVB. PBOCST releases a quantitative amount (45.5%) of carbon dioxide and isobutene at ca. 190 °C and is converted to PHOST. Similarly, PMBDOON loses ca. 30% of its

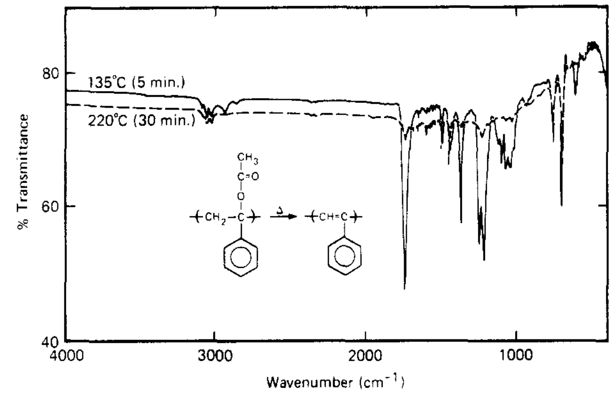


Figure 8. IR spectra of PACOST film before and after heating at 220 °C for 30 min.

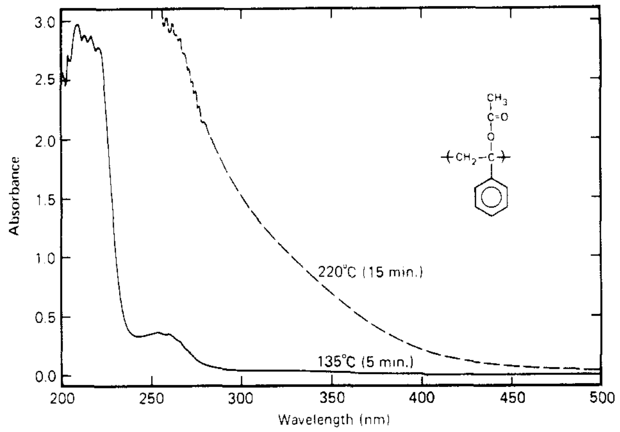


Figure 9. UV spectra of PACOST film before and after heating at 220 °C for 15 min.

mass due to liberation of carbon dioxide (27.2%) in a slightly higher temperature range, below which no glass transition is observed. In contrast, while PTBVB is converted to PVBA at ca. 230 °C, releasing isobutene quantitatively (27.5%), PMP does not exhibit any degradation up to 340 °C, with only a minor weight loss below 200 °C due to evaporation of NMP used as a polymerization solvent.

PMBDOON, insoluble in common organic solvents, was dissolved in NMP, spin-coated on a NaCl plate, and prebaked at 135 °C for 5 min. As the IR spectra shown in Figure 11 demonstrate, the carbonate carbonyl absorption at 1788 cm^{-1} almost completely disappears upon heating the film at 200 °C for 20 min, which is accompanied by appearance of a phenolic OH at ca. 3500 cm^{-1}. The PMBDOON film was heated at 200 °C for 10 min after prebake at 120 °C and was subjected to UV analysis as shown in Figure 12. Upon the high-temperature bake, the optical density (OD) of the film increases from 0.415 to 2.90 at 248 nm in spite of film shrinkage, and the UV absorption is extended to 800 nm, indicating that PMBDOON is converted to PHOPA. It has been reported that ortho-substituted PPA's extend their UV absorption to longer wavelengths.[44] The thermolysis of PMBDOON at 200 °C also results in main-chain degradation. A PMBDOON powder (M_n = 23 700 and M_w = 38 500) was heated at 200 °C for 15 min and converted with 31% weight loss to a grayish brown powder with a bimodal molecular weight distribution (40% of M_n = 2900 and M_w = 2400 and 60% of M_n = 790 and M_w = 900). Carbon and hydrogen analyses of PHOPA thus obtained were a little lower than the theoretical values (76.28 vs 81.36 and 4.79 vs 5.08, respectively) presumably due to the residual carbonate. In an attempt to increase the solubility of PMBDOON, MBDOON was copolymerized with styrene (feed ratio = 43/57) in bulk with AIBN at 60 °C for 6 h, providing a copolymer containing 48% of the styrene units in 77% yield. However, the copolymer was not soluble in common casting solvents. A copolymer film spin-cast from NMP exhibited much reduced UV absorption when heated at 200 °C for 15 min due to interrupted conjugation.

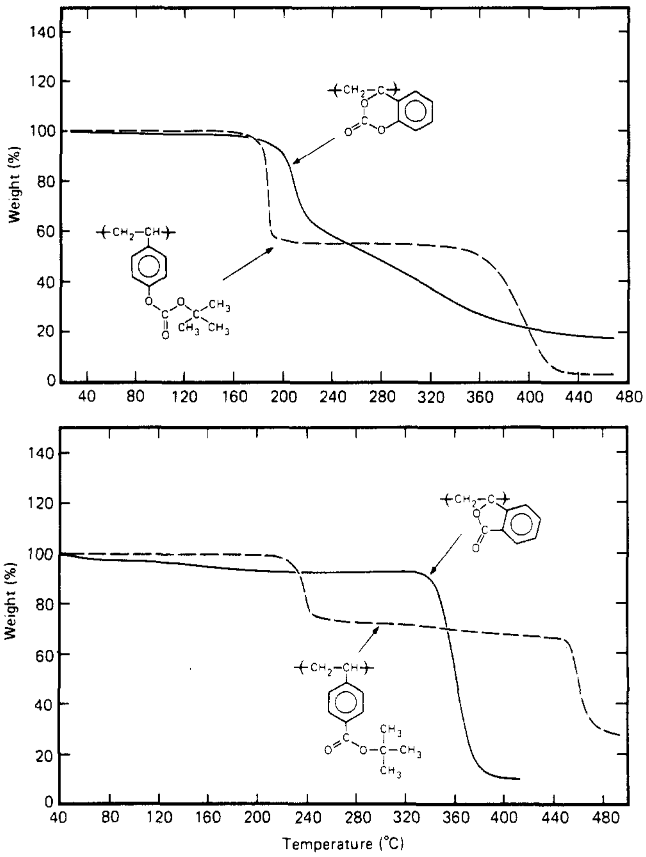


Figure 10. TGA of PMBDOON–PBOCST and PMP–PTBVB (5 °C/min).

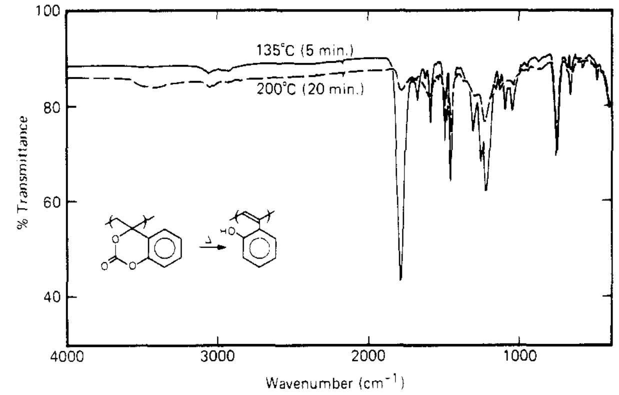


Figure 11. IR spectra of PMBDOON film before and after heating at 200 °C for 20 min.

In contrast to PACOST and the cyclic carbonate, PMP does not exhibit any spectral change when heated to 240 °C. The lactone carbonyl IR absorption at 1773 cm^{-1} remains unchanged without appearance of carboxylic acid C=O or OH. Thus, PMP cannot be converted to poly(*o*-ethynylbenzoic acid) by heating. PMP exhibits its glass transition at ca. 230 °C upon the second DSC run after heating to 310 °C.

Thermolysis of tertiary esters is believed to proceed via six-membered cyclic intermediates as shown in Scheme

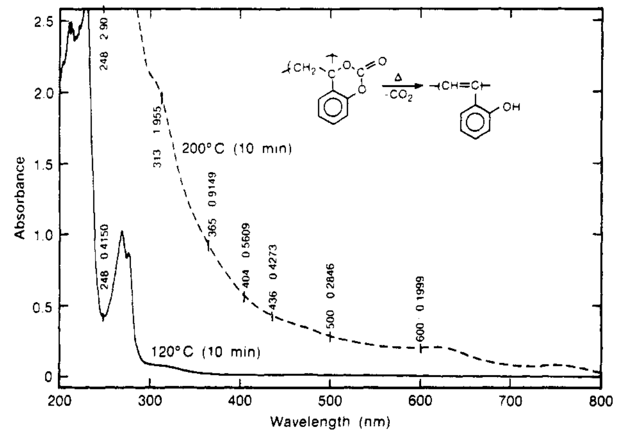


Figure 12. UV spectra of PMBDOON film before and after heating at 200 °C for 10 min.

Scheme III
Thermolysis of PACOST

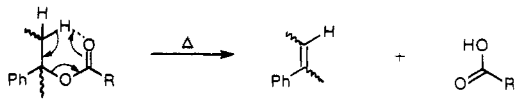
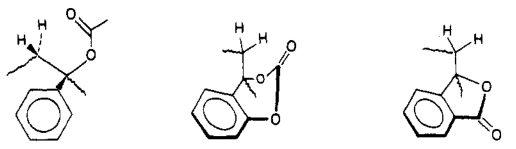


Chart II
Conformation of PACOST, PMBDOON, and PMP



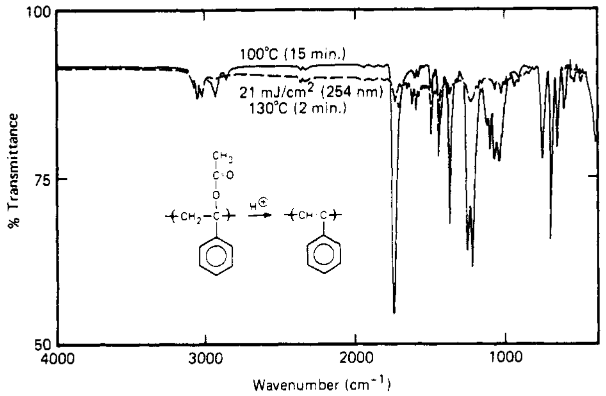


Figure 13. IR spectra of 1.2-μm-thick film of PACOST containing 9.5 wt % of $Ph_3S^+\ ^-SbF_6$ after prebake at 100 °C and after UV exposure (21 mJ/cm²) followed by postbake at 130 °C.

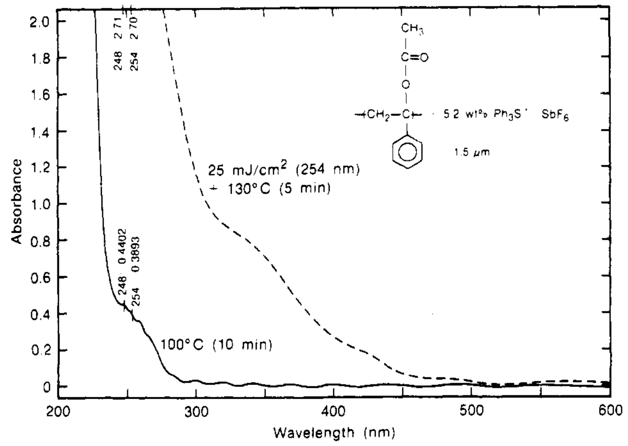
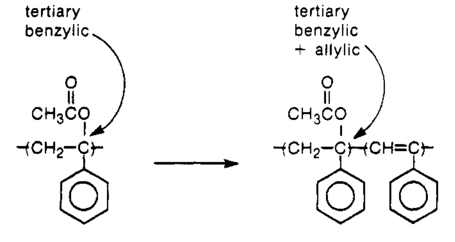
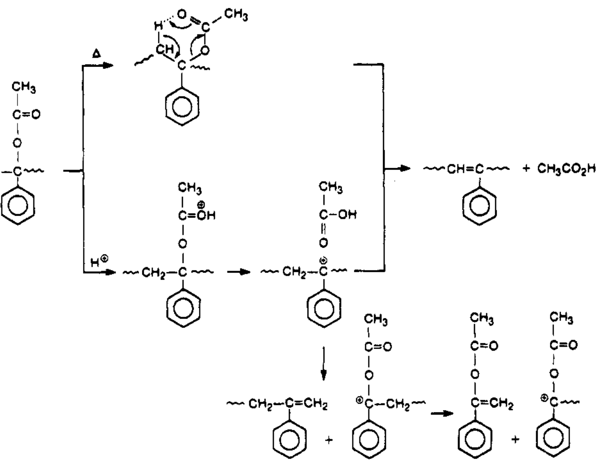


Figure 14. UV spectra of 1.5-μm-thick film of PACOST containing 5.2 wt % of $Ph_3S^+\ ^-SbF_6$ after prebake at 100 °C and after UV exposure (25 mJ/cm²) followed by postbake at 130 °C.

Scheme IV
Chain Reaction in Elimination of Acetic Acid from PACOST



Scheme V
Acid-Catalyzed Deesterification and Depolymerization in PACOST



III. The carbonyl oxygen atom must find a hydrogen atom in close proximity for elimination. PACOST satisfies the requirement readily and so does PMBDOON with a slight difficulty owing to the envelope conformation of the 1,3-dioxane ring as shown in Chart II. In contrast, PMP cannot assume the cyclic intermediate due to the planar five-membered-ring structure (Chart II).

Acidolysis of PACOST, PMBDOON, and PMP. The thermolysis reaction is acid catalyzed; that is, the thermolysis temperature can be significantly lowered by adding an acid. We used triphenylsulfonium hexafluoroantimonate to photochemically generate $HSbF_6$ in the polymer matrices. In Figure 13 are shown IR spectra of the PACOST film containing 9.5 wt % of the sulfonium salt before and after UV exposure/postbake. The carbonyl absorption at 1738 cm^{-1} almost disappears upon postbake at 130 °C for 2 min after exposure to 21 mJ/cm² of 254-nm radiation. A PACOST film (1.5 μm thick) containing 5.2 wt % of the sulfonium salt has an OD of ca. 0.4 in the 250-nm region, which increases with ca. 24% thickness loss to about 2.7 upon exposure to 25 mJ/cm² followed by postbake at 130 °C for 5 min, as UV spectra in Figure 14 demonstrate. The film thus obtained is black and absorbs UV light up to 500 nm. Acidolysis of PACOST is very facile owing to the high stability of the tertiary benzylic carbenium ion generated. Elimination of acetic acid adds another stabilization factor (allylic) to the adjacent α-carbon, rendering acidolysis even more facile, which is expected to result in highly extended conjugation through a chain reaction mechanism (Scheme IV).

However, as shown in Scheme V, acid-catalyzed depolymerization may compete with elimination of β-proton. In fact, radical polymerization of ACOST is an equilibrium process with a ceiling temperature of 47 °C.[23] When PACOST was treated in solution with trifluoromethane-

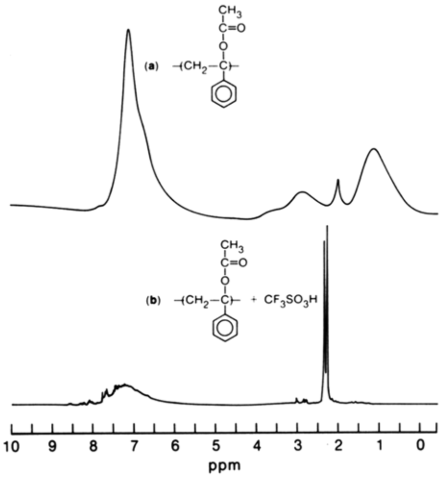


Figure 15. ^{1}H NMR spectra (250 MHz) of PACOST before (a) and after (b) addition of triflic acid in CDCl$_3$.

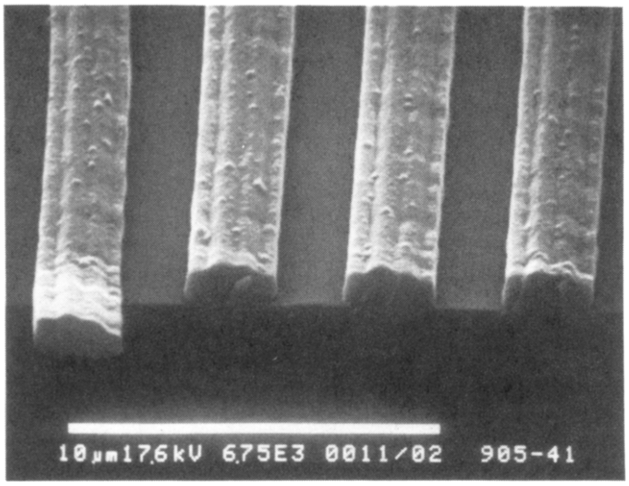
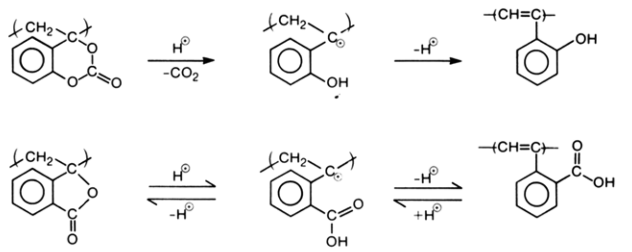


Figure 16. Scanning electron micrograph of positive images contact-printed in the PACOST resist containing 5.2 wt % of Ph$_3$S$^+$ $^-$SbF$_6$ (13 mJ/cm^2).

Scheme VI
Acidolysis of PMBDOON and PMP



sulfonic (triflic) acid, the product was highly soluble in methanol and the black powdery polymer isolated by precipitation in hexanes amounted to only 11.3%, indicating occurrence of depolymerization. Treatment of PACOST with triflic acid in CDCl$_3$ resulted in a total change in the ^{1}H NMR spectrum as demonstrated in Figure 15 with appearance of two sharp methyl resonances, which are due to acetic acid and acetophenone. It is known that acidolysis of ACOST produces acetic acid and acetophenone.[35] The degree of depolymerization in solution is estimated to be 80% based on the relative intensity of the two methyl proton resonances, agreeing well with the amount of polymer isolated from a similar solution. Trifluoroacetic acid did not induce any degradation in dichloromethane at room temperature for at least 9 h. PACOST (M_n = 21 300 and M_w = 33 700) and 10 mol % of *p*-toluenesulfonic acid monohydrate were freeze-dried from dioxane, heated at 100 °C for 5 min, and washed with water, resulting in dramatic reduction of molecular weights to M_n = 1800 and M_w = 3400.

PACOST containing the sulfonium salt photochemical acid generator functions as a *positive* resist as the scanning electron micrograph in Figure 16 demonstrates. PACOST mixed with 5.2 wt % of the sulfonium salt was spin-cast from cyclohexanone, exposed to 13 mJ/cm^2 of 254-nm radiation, postbaked at 120 °C for 5 min, and then developed with xylenes, providing positive images of the mask with full retention of thickness in the unexposed regions. Reexposure/postbake of the imaged film converts the PACOST lines in Figure 16 to PPA lines. While PPA prepared by thermolysis or acidolysis is highly soluble in a variety of organic solvents, the precursor PACOST is more resistant to solvents due to its stiffness. The positive-imaging behavior of the PACOST resist presumably results from combination of the solubility change and molecular weight reduction by depolymerization.

As mentioned earlier, PMBDOON and PMP are not soluble in common organic solvents. Therefore, we used NMP as a casting solvent for the photochemical acidolysis studies of the cyclic polymers. However, primarily due to the low volatility and slight basicity of NMP, acid-catalyzed thermolysis did not take place much in the polymer films postbaked at ca. 130 °C. We next mechanically mixed the PMBDOON powder with ca. 10 wt % of *p*-toluenesulfonic acid monohydrate and heated the solid mixture on a Kugelrohr apparatus at 100 °C for 1 h under vacuum. The dark brown powder thus obtained was washed with water and dried to a dark green powder. According to NMR spectra of the dark green solution in DMSO-d_6, the conversion was <10% and racemization did not take place in the solid-state acidolysis. PMBDOON can be converted to PHOPA by reaction with an acid in the solid state. In spite of the low conversion, presumably due to a poor mixing, the powder and solution are darkly colored, suggesting a high degree of conjugation. As discussed earlier with PACOST, acidolysis appears to propagate by a chain mechanism rather than in a random fashion, resulting in an extended conjugation. The solid-state acidolysis product is most likely to be a blend of PHOPA with a high degree of extended conjugation and the unreacted PACOST.

In contrast, a mechanical mixture of PMP with 10 wt % of *p*-toluenesulfonic acid monohydrate did not exhibit any appreciable color change when heated even to 200 °C. The heated polymer was again washed with water, dried, and subjected to NMR analysis. An inverse-gated ^{13}C NMR spectrum of the slightly yellow solution in DMSO-d_6 did not show any evidence of the lactone ring opening or racemization. The cyclic benzoate is very stable toward acid.

In the case of the cyclic carbonate, elimination of carbon dioxide renders the acidolysis reaction irreversible as shown in Scheme VI. However, since no small molecules would leave from the lactone even if acidolysis took place, the reaction of the cyclic benzoate should be in equilibrium as Scheme VI illustrates. The left-side equilibrium could result in racemization, which was not observed by NMR spectroscopy. However, since PMP is already almost completely atactic, racemization might not be observed spectroscopically. It is not clear at the moment whether or not the C–O bond of the lactone ring is cleaved by acid at all.

Microstructure of PPA. The microstructure of polyacetylenes has been studied by IR and then by NMR

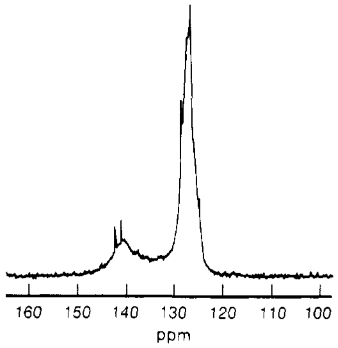


Figure 17. Inverse-gated ^{13}C NMR spectrum (62.9 MHz, $CDCl_3$) of PPA obtained by heating PACOST at 200 °C.

extensively for PPA,[45-52] which is soluble in organic solvents. ^1H NMR spectra of PPA obtained by thermolysis or acidolysis exhibit only a very broad resonance without any fine details and are very similar to those of PPA prepared by polymerization of phenylacetylene with WCl_6.[50,51] An inverse-gated ^{13}C NMR spectrum of PPA in $CDCl_3$ obtained by heating the PACOST powder at 200 °C for 2.5 h under vacuum is shown in Figure 17, which resembles the spectrum of *trans*-PPA made with WCl_6[49] or of a cis isomer heat treated at a temperature >120 °C.[48] Such a heat treatment has been known to lead to cis → trans isomerization. Assuming the cyclic intermediate in the elimination of acetic acid and formation of polyacetylene, the microstructure of the thermally obtained PPA would be very much dependent on the conformation of the precursor PACOST, which is in turn a function of the stereoregularity of PACOST. As described earlier, PACOST is syndiotactic-rich and presumably assumes a trans zigzag conformation, which then leads to formation of a trans-transoid isomer from the beginning. However, the cis isomer, if produced at all from other conformers of PACOST, would undergo thermal isomerization to the trans isomer at the thermolysis temperature of >120 °C.

IR has provided information on the microstructure of PPA.[45-47,51] The bands at 920 and 890 cm^{-1} have been reported to be characteristic to trans and cis isomers, respectively. In Figure 18 are presented IR spectra of films of PPA prepared by heating a PACOST powder at 200 °C and of PPA made by heating a PACOST film containing photochemically generated $HSbF_6$. PPA obtained by the high-temperature treatment is predominantly trans, agreeing well with its NMR analysis. While the PACOST film does not have any IR absorptions in the 890-nm region (a), the film exposed to 50 mJ/cm^2 and postbaked at 130 °C for 2 min shows a presence of a significant amount of cis sequences (b). When the exposed film is heated at 200 °C, the cis content becomes smaller (c). A mixture of PACOST and *p*-toluenesulfonic acid monohydrate, freeze-dried from dioxane and then heated at 100 °C for 5 min, exhibited IR bands at 920 and 890 cm^{-1} of almost equal intensity. In the solid state below T_g, the microstructure of PPA is expected to be determined by conformation/configuration of the precursor PACOST, provided that the temperature is low enough to prevent randomization, which will be a subject of a future publication.

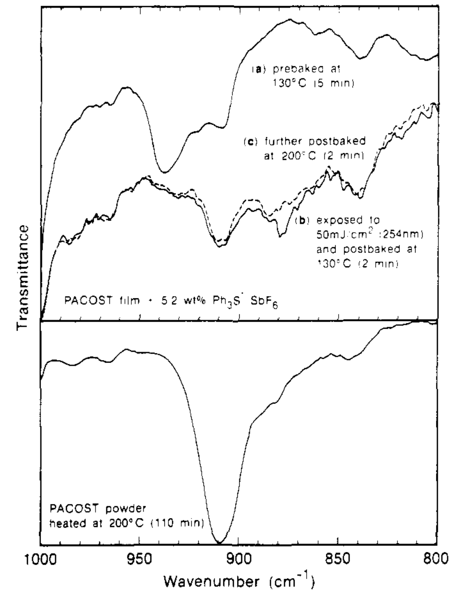


Figure 18. IR spectra of PACOST film containing 5.2 wt % of Ph_3S^+ $^-SbF_6$ (a), PPA film obtained by photochemical acidolysis of PACOST resist film (b), PPA film further postbaked at 200 °C (c), and PPA film obtained by heating PACOST film at 200 °C (bottom).

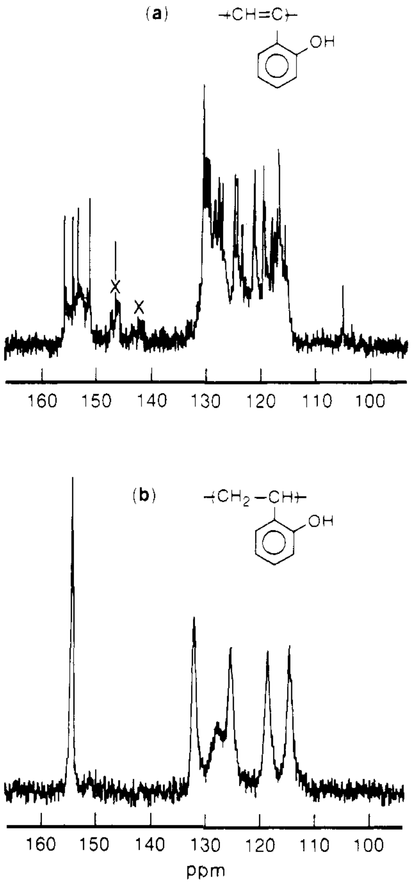


Figure 19. Inverse-gated ^{13}C NMR spectra (62.9 MHz, DMSO-d_6) of PHOPA (a) and poly(*o*-hydroxystyrene) (b).

In Figure 19 is presented an inverse-gated ^{13}C NMR spectrum of PHOPA in DMSO-d_6 together with that of poly(*o*-hydroxystyrene) as a reference. PHOPA was prepared by heating a PMBDOON powder at 200 °C and the polystyrene derivative by hydrazinolysis of poly(*o*-acetoxystyrene). The spectrum of PHOPA is similar to that of the saturated counterpart but is very much complex and shows some resonances (×) due to the starting PMBDOON. Although ortho-substituted PPA's have been reported by Higashimura et al.[44] and functional PPA's para-substituted with CO_2CH_3, CH_2OH, and CHO by Iwamura et al.,[53] detailed NMR analysis of such polymers is not available and preparation of PHOPA has not been reported before to our knowledge. We are currently investigating the microstructure of PHOPA. PHOPA shows two distinct IR bands at 940 and 890 cm^{-1}.

Summary

1. ACOST, MBDOON, and MP readily undergo radical homopolymerization although they are α-substituted styrene derivatives.

2. While ACOST gives a highly syndiotactic polymer, PMBDOON and PMP are almost completely atactic, suggesting that the cyclization of the α-position reduces a steric hindrance and therefore stereoregulation.

3. PACOST and PMBDOON can be converted to PPA and PHOPA, respectively, by heating a powder or film at ca. 200 °C. The thermal treatment is accompanied by depolymerization. PMP is thermally stable and remains unchanged after the high-temperature treatment. PPA obtained by thermolysis of PACOST at 200 °C has a trans structure.

4. PACOST can be converted to PPA by generating a strong acid through photolysis of triarylsulfonium salts and subsequent postbake at ca. 100 °C. Depolymerization also takes place in acidolysis. PPA thus obtained contains a significant amount of the cis sequences.

5. PACOST containing a few percent of a sulfonium salt acid generator functions as a positive resist.

6. While PMBDOON can be converted to PHOPA by acidolysis, PMP is inert to acid treatment.

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