Macromolecules **1990,** *23,* 2589–2598

Thermal and Acid-Catalyzed Deesterification and Rearrangement of Poly(2-cyclopropyl-2-propyl 4-vinylbenzoate) and Their Application to Lithographic Imaging

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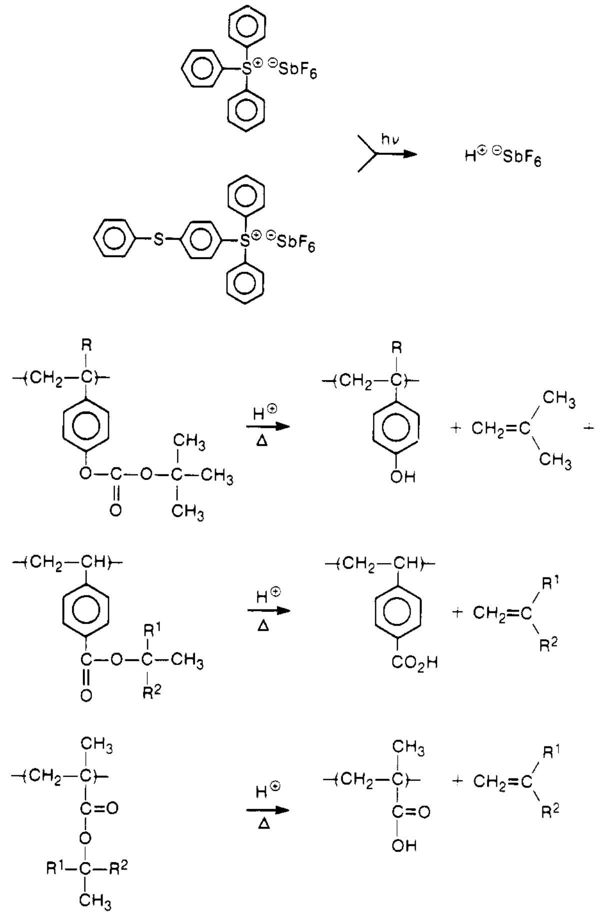
Revised Manuscript Received November 28, 1989

ABSTRACT: Poly(2-cyclopropyl-2-propyl 4-vinylbenzoate) releases 2-cyclopropylpropene at about 160 °C. Although the thermal deprotection temperature is about 80 and 30 °C lower than that of the corresponding *tert*-butyl ester and poly(4-(*tert*-butoxycarbonyloxy)styrene), respectively, a minor concomitant rearrangement to the 4-methyl-3-pentenyl ester occurs in the case of the cyclopropyl carbinol ester (about 10%). The temperature of deprotection that converts the ester polymer to poly(4-vinylbenzoic acid) can be lowered by photochemically generating a strong acid in the solid state. However, the acid-catalyzed thermolysis favors rearrangement (about 66%) over deprotection. The thermal and acid-catalyzed deesterification and rearrangement can be exploited in the design of new resist materials that are developed in a negative mode either with nonpolar organic solvents or with aqueous base, depending on the postexposure bake temperature. Cross-linking through the 4-methyl-3-pentenyl group is also discussed.

Introduction

The design of sensitive resist systems incorporating "chemical amplification" was proposed in 1982,[2-4] which utilized acid-catalyzed cross-linking, depolymerization, and deprotection reactions. In this scheme, radiochemically generated acids induce a cascade of subsequent chemical transformations, providing a gain mechanism. Although cross-linking through radical polymerization has been long known in the imaging technology, the use of radiochemical acid generators has offered opportunities to incorporate a variety of new imaging mechanisms into the resist design for semiconductor manufacturing.[5-8] *tert*-Butyl esters and carbonates readily undergo $A_{AL}1$-type acid-catalyzed deesterification in a reaction that does not require a stoichiometric amount of water to produce isobutene/acid and isobutene/carbon dioxide/alcohol, respectively. Acid-catalyzed deprotection of polymers with such pendant groups results in a large change of the polarity of repeating units and consequently of solubility, allowing positive imaging (exposed regions are selectively removed) with a polar developer such as alcohol or aqueous base or negative imaging (unexposed areas are selectively removed) with use of a nonpolar organic solvent (Scheme I). The first examples of the dual tone resist systems are poly(*p*-(*tert*-butoxycarbonyloxy)styrene) (PBOCST)[2,3,5] and its α-methyl analogue,[2] which are converted upon postexposure bake to phenolic polymers by reaction with a strong Brønsted acid generated by irradiation of onium salts. Diazonium, iodonium, and sulfonium metal halides originally developed for photochemical epoxy curing[9,10] have been employed as photochemical acid generators for chemical amplification resist systems along with iodonium and sulfonium trifluoromethanesulfonates as non-metallic salts.[11-13] Nonionic cationic photoinitiators such as nitrobenzyl esters[14,15] have also attracted attention recently. Ito et al.[16,17] have studied the effect of the structure of the ester groups of poly(*p*-vinylbenzoates) and polymethacrylates on their photochemical sensitivity and found that the thermal deprotection temperature of these ester polymers is a good measure of the sensitivity.

Scheme I
Radiation-Induced Acid-Catalyzed Deesterification



However, the dimethyl cyclopropyl carbinol ester of poly(methacrylic acid) behaves differently in its thermolysis from other polymethacrylates studied.[17] Replacement of one of the methyl groups of poly(*tert*-butyl methacrylate) (PTBMA) with a cyclopropyl group results in a dramatic decrease in the thermal deprotection temperature by 80 °C but in a reduced sensitivity toward acid-catalyzed deprotection. The primary pathway of the thermal deesterification is believed to be via a cyclic intermediate to split an olefin (Scheme II). The cyclopropyl carbinol ester may undergo heterolysis of C–O bond to

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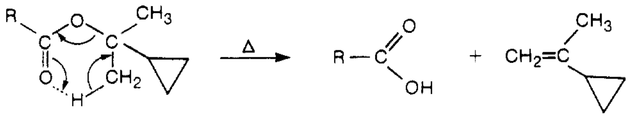
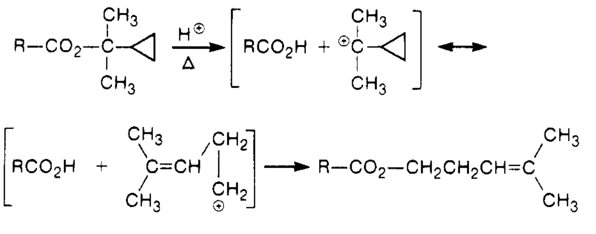
Scheme II
Thermolysis of Cyclopropyl Carbinol Ester



Scheme III
Acid-Catalyzed Rearrangement of Cyclopropyl Carbinol Ester



generate the dimethyl cyclopropyl carbenium ion which tends to rearrange itself to the primary cation and recombine with the carboxylate to form a primary ester (Scheme III). The thermal rearrangement is much more pronounced in the presence of acid.

In this paper are reported detailed thermolysis and acidolysis studies of poly(2-cyclopropyl-2-propyl 4-vinylbenzoate) (PCPPVB) as well as its lithographic application.

Experimental Section

Measurements. NMR spectra were recorded on an IBM Instrument NR-250/AF, a Varian EM-390, or a Hitachi R-24B spectrometer in $CDCl_3$ or tetrahydrofuran (THF-d_8). 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 Instrument 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 THF. 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 inert atmosphere. Film thickness was measured on a Tencor alpha-step 200. Combustion analysis was performed by Galbraith Laboratory, Knoxville, TN.

Materials. α,α-Azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) were purified by the conventional methods. 4-Vinylbenzoic acid (VBA), 4-chlorostyrene, and styrene (ST) were purchased from Aldrich. Diphenyl(4-(thiophenoxy)phenyl]sulfonium hexafluoroantimonate was synthesized by the previously reported procedure.[18] Propylene glycol monomethyl ether acetate (PM Acetate) was obtained from Arco Chemical Co.

Synthesis of 4-Vinylbenzoates. Synthetic routes to the 4-vinylbenzoate monomers are shown in Scheme IV, which are basically similar to the procedures for methacrylates.[17] VBA was converted with thionyl chloride or oxalyl chloride to 4-vinylbenzoyl chloride, which was then reacted with corresponding alkoxides in THF. Lithium alkoxides were obtained by treating with *n*-butyllithium (BuLi), *tert*-butyl alcohol, and cyclopropyl dimethyl carbinol which was in turn made by reacting cyclopropyl methyl ketone (Aldrich) with methylmagnesium bromide. The synthetic procedure for 2-cyclopropyl-2-propyl (dimethyl cyclopropyl carbinyl) 4-vinylbenzoate (CPPVB) was as follows. To a solution of dimethyl cyclopropyl carbinol in 40 mL of dry THF was added under N_2 13 mL of BuLi (2.5 M in hexane). A solution of 4.5 g (27 mmol) of 4-vinylbenzoyl chloride in 20 mL of anhydrous THF was added to the resulting mixture after 30 min. The dark red solution was refluxed for 1 h, cooled to 0 °C, and hydrolyzed by adding 70 mL of water. The aqueous phase was extracted with three 30-mL portions of ether and combined with the organic phase. After being dried over magnesium sulfate, the solution was concentrated to give 5.9 g of the crude product, which was then purified by chromatography. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.55; H, 7.98. IR (KBr): 1715 (C═O) and 1608 cm^{-1} (C═C). ^1H NMR (90 MHz, $CDCl_3$): δ 7.92 (d, 2 H, aromatic H3, $J = 9$ Hz), 7.36 (d, 2 H, aromatic H2, $J = 9$ Hz), 6.67 (dd, 1 H, α-CH, $J = 10.8, 18$ Hz), 5.75 (d, 1 H, β-CH trans to α-CH, $J = 18$ Hz), 5.28 (d, 1 H, β-CH cis to α-CH, $J = 10.8$ Hz), 1.55 (s, 6 H, CH_3), 0.77–1.0 (m, 1 H, cyclopropyl CH), 0.37–0.55 (m, 4 H, cyclopropyl CH_2). ^{13}C NMR (15 MHz, $CDCl_3$): δ 164.57 (C═O), 141.06 (C1), 135.78 (α-CH), 131.06 (C4), 129.26 (C3), 125.57 (C2), 115.48 (β-CH_2), 81.79 (C—O), 24.62 (CH_3), 20.90 (cyclopropyl CH), 1.54 (cyclopropyl CH_2).

Preparation of 4-methyl-3-pentenyl 4-vinylbenzoate (MPVB) was carried out as described below. To a mixture of VBA (5 g, 33.7 mmol) in 50 mL of benzene was added oxalyl chloride (3.4 mL, 4.95 g, 38.9 mmol) and a drop of *N*,*N*-dimethylformamide (DMF). After 1.2 h, two more drops of DMF were added and after another hour the mixture was concentrated to a yellow oil. Distillation provided 4-vinylbenzoyl chloride (5 g, 30.0 mmol) in 89% yield. 4-Methyl-3-penten-1-ol (3.0 g, 34.0 mmol, Aldrich) was added to NaH (1.44 g of 60% NaH, 3.6 mmol, washed twice with hexanes) in 50 mL of THF and refluxed for 2 h, to which was added 4-vinylbenzoyl chloride (5 g, 30.0 mmol). After 3 h, water was added and the product extracted with a mixture of hexanes and ether (7:1). The organic layer was dried over magnesium sulfate and concentrated. Flash chromatography (230–400 mesh SiO_2, hexanes) provided the desired ester in 96.2% yield (6.3 g). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.94; H, 7.91. IR (neat); 1718 (C═O) and 1609 cm^{-1} (C═C). The pentenyl ester was subjected to DEPT, COSY, and ^1H–^{13}C 2D NMR analyses. ^1H NMR (250 MHz, $CDCl_3$): δ 7.95 (d, 2 H, aromatic H3, $J = 8.4$ Hz), 7.4 (d, 2 H, aromatic H2, $J = 8.4$ Hz), 6.7 (dd, 1 H, α-CH, $J = 17.6, 10.9$ Hz), 5.83 (dd, 1 H, β-CH trans to α-CH, $J = 17.6, 0.7$ Hz), 5.3 (dd, 1 H, β-CH cis to α-CH, $J = 10.9, 0.7$ Hz), 5.15 (m, 1 H, CH═), 4.25 (t, 2 H, OCH_2, $J = 8.7$ Hz), 2.43 (dt, 2 H, CH_2, $J = 7.07, 7.08$ Hz), 1.69 (d, 3 H, cisoid CH_3, $J = 1.0$ Hz), 1.63 (s, 3 H, transoid CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 166.0 (C═O), 141.6 (C1), 135.8 (α-CH), 134.3 (═CMe_2), 129.6 (C3), 129.45 (C4), 125.8 (C2), 119.1 (CH═), 116.0 (β-CH_2), 64.3 (OCH_2), 27.6 (CH_2), 25.5 (cisoid CH_3), 17.5 (transoid CH_3).

tert-Butyl 4-vinylbenzoate (TBVB) was prepared by reacting (4-vinylphenyl)magnesium chloride with di-*tert*-butyl dicarbonate (Aldrich). Magnesium (8.88 g, 370 mmol) was placed in a dry three-necked flask equipped with a condenser, a mechanical stirrer, and an addition funnel. The reaciton apparatus was flame-dried with nitrogen purging. 4-Chlorostyrene (34.8 g, 25 mmol, distilled from CaH_2) in THF (dried over sodium ketyl and distilled) was added dropwise to maintain the temperature just under reflux. The reaction mixture was stirred at room temperature for 1.5 h and then heated for 30 min. Di-*tert*-butyl dicarbonate (65 g, 297 mmol) was placed in a round-bottom flask and dissolved in dry THF (300 mL), to which was added at 0 °C (4-vinylphenyl)magnesium chloride in THF via needle stock. The reaction was quenched after 1.5 h at 0 °C with water (300 mL) and 5% HCl. After extraction with hexanes/ether, combined organic layers were dried over magnesium sulfate and concentrated. Column chromatography (230–400 mesh SiO_2, ether/hexanes = 1.1/10) followed by distillation from *tert*-butyl catechol (60 °C/5 μmHg) provided the desired pure TBVB in 60.1% yield based on 4-chlorostyrene. IR (neat); 1712 (C═O) and 1609 cm^{-1} (C═C). ^1H NMR (250 MHz, $CDCl_3$): δ 7.89 (d, 2 H, aromatic H3, $J = 8.3$ Hz), 7.36 (d, aromatic H2, $J = 8.3$ Hz), 6.67 (dd, 1 H, α-CH, $J = 17.9, 10.8$ Hz), 5.77 (dd, 1 H, β-CH trans to α-CH, J 17.9, 0.58 Hz), 5.28 (dd, 1 H, β-CH cis to α-CH, $J = 10.8, 0.58$ Hz), 1.54 (s, 9 H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 165.5 (C═O), 141.4 (C1), 136.1 (α-CH), 131.2 (C4), 129.7 (C3), 125.9 (C2), 116.1 (β-CH_2), 80.9 (C—O), 28.2 (CH_3).

Radical Polymerization. Radical homo- and copolymerization of the benzoate monomers were carried out in toluene

Scheme IV
Synthesis of 4-Vinylbenzoate Monomers

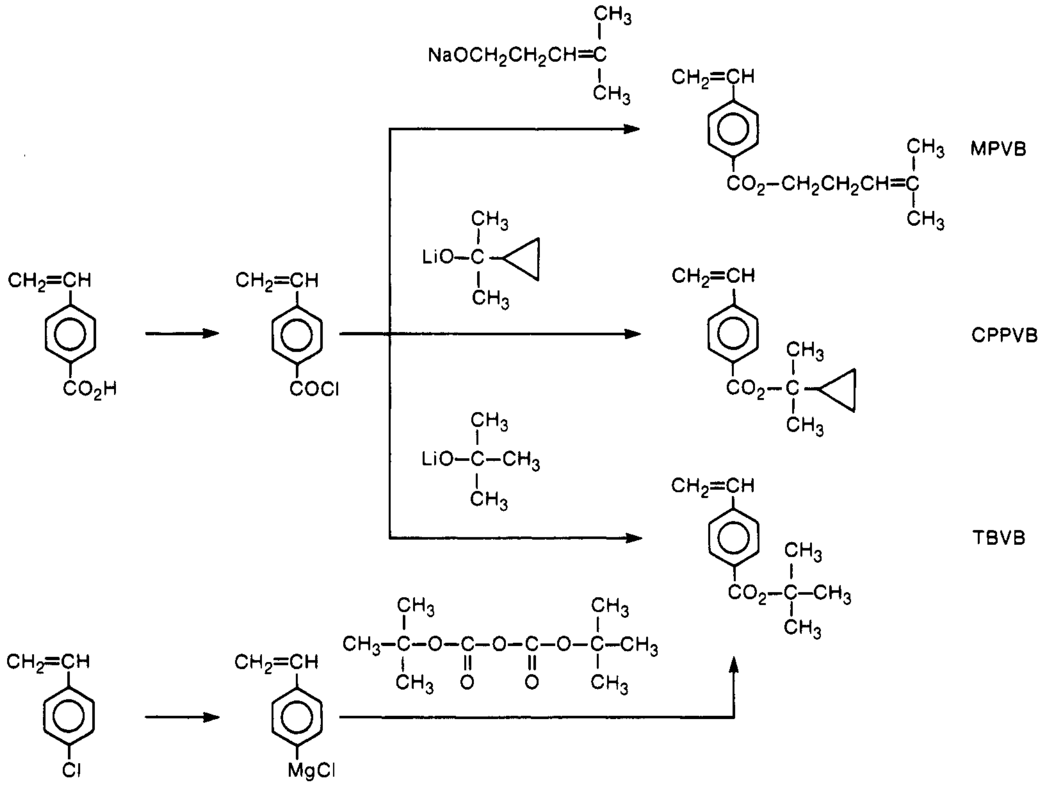


Table I
Radical Polymerization of 4-Vinylbenzoates at 60 °C

monomer (g)	initiator (mol %)	solvent (mL)	time, h	yield, %	M_n	M_w
CPPVB (0.95)	AIBN (0.74)	toluene (4.0)	24.0	72	57 400	98 700
CPPVB (0.95)	AIBN (0.59)	cyclohexanone (10.0)	10.2	55	52 200	173 000
CPPVB (1.01)	AIBN (0.69)	cyclohexanone (10.0)	10.2	59	52 600	153 400
CPPVB (1.01)	AIBN (0.67)	cyclohexanone (10.0)	9.0	56	54 000	170 000
TBVB (5.1)	BPO (0.5)	toluene (5.1)	168.0	91	144 000	344 600
TBVB (5.0)	BPO (5.0)	toluene (17.0)	15.5	68	20 000	49 300
MPVB (0.5)	BPO (1.0)	toluene (0.4)	16.0	insoluble gel		
MPVB (4.0)	AIBN (1.0)	THF (6.0)	8.0	30	97 000	206 000
MPVB (4.0)	AIBN (1.0)	toluene (8.0)	8.0	23	64 800	144 700

at 60 °C with AIBN or BPO as the initiator. The polymers were purified by precipitation in methanol and dried. MPVB was also copolymerized with VBA in THF at 60 °C using BPO as the initiator, and the resulting copolymers were precipitated in hexanes. Copolymer compositions were determined by NMR. PCPPVB—Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.10; H, 7.67. ^1H NMR (250 MHz, $CDCl_3$): δ 7.6 (b s, 2 H, aromatic H3), 6.43 (b s, 2 H, aromatic H2), 1.7–0.9 (β-CH_2, α-CH, cyclopropyl CH), 1.46 (CH_3), 0.44 (s, 4 H, cyclopropyl CH_2). PTBVB—^1H NMR (250 MHz, $CDCl_3$): δ 7.62 (b s, 2 H, aromatic H3), 6.41 (b s, 2 H, aromatic H2), 2.0–1.0 (β-CH_2, α-CH), 1.50 (s, CH_3). PMPVB—Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.94; H, 7.91. ^1H NMR (250 MHz, $CDCl_3$): δ 7.68 (b s, 2 H, aromatic H3), 6.42 (t, 2 H, aromatic H2), 5.19 (s, 1 H, CH=), 4.25 (s, 2 H, OCH_2), 2.46 (s, 2 H, CH_2), 2.0–1.2 (β-CH_2, α-CH), 1.72 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3).

UV Exposure of Poly(vinylbenzoate) Films. Poly(vinylbenzoates) were dissolved at about 17 wt % in PM Acetate, to which was added diphenyl(4-(thiophenoxy)phenyl)sulfonium hexafluoroantimonate (9.2–10.4 wt % of the total solid). Films spin-cast on NaCl plates, quartz disks, or Si wafers were prebaked at 100 °C for 10 min and exposed through a 313-nm band-pass filter to radiation from an Oriel illuminator. Imagewise exposure was carried out in a contact mode. Exposed films were postbaked at 100–160 °C for 5 min and subjected to IR or UV analysis or developed with anisole or aqueous KOH solution (American Hoechst 400 K/H_2O = 1/4).

Results and Discussion

Monomer Synthesis and Polymerization. Alkyl 4-vinylbenzoates can be conveniently prepared in >90% yield by reacting the corresponding alkoxides with 4-vinylbenzoyl chloride which can be readily obtained in 85–90% yield from commercially available VBA. In the case of the *tert*-butyl ester, we have also explored an alternative synthetic approach, which involves reaction of di-*tert*-butyl dicarbonate with (4-vinylphenyl)magnesium chloride made from 4-chlorostyrene. The reaction was contaminated with styrene produced by quenching of the unreacted styrenic Grignard reagent and 4-chlorostyrene left unreacted in the metalation reaction. Although there are some other minor side products, this procedure has turned out to be quite useful in the preparation of TBVB, providing a 60% purified yield based on 4-chlorostyrene.

The 4-vinylbenzoate monomers readily undergo radical homopolymerization as indicated in Table I. The radical polymerization of VBA and its methyl ester was reported by Marvel and Overberger in 1945.[19] Vinylbenzoates are reactive styrenic monomers, possessing higher Q and e values than those of styrene due to the resonance stabilization by and the electron-withdrawing effect of the COO group.[20,21] The lower electron density on

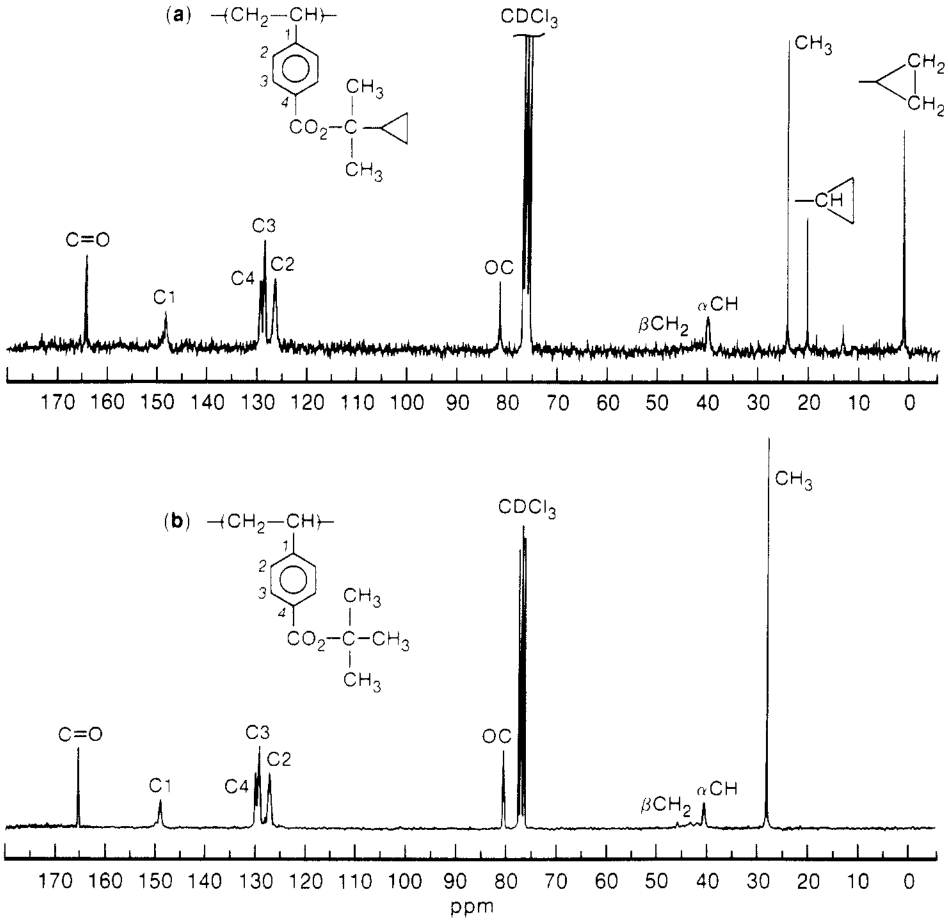


Figure 1. Inverse gated ^{13}C NMR spectra (62.9 MHz) of PCPPVB (a) and PTBVB (b) in $CDCl_3$.

the β-carbon of CPPVB, TBVB, and MPVB are reflected by the β-CH_2 ^{13}C and ^1H resonances absorbing at lower fields compared with those of styrene. Radical and living anionic polymerizations of TBVB have been reported by Yamamoto et al.[22] and by Nakahama et al.,[23] respectively. Ito et al.[16] reported use of several poly(4-vinylbenzoates) as resist materials. TBVB behaves normally to high conversion in radical polymerization, providing polymers with monomodal molecular weight distribution. However, CPPVB and MPVB tend to give a gel when the polymerization is brought to high conversion. In order to avoid gelation, the polymerization of CPPVB was run at a high dilution and terminated at low conversion (ca. 50%). Radical polymerization of 2-cyclopropylethyl methacrylate suffered from serious gelation,[17] which is clearly due to facile abstraction of hydrogen on the carbon next to the cyclopropyl ring. In the case of the dimethyl cyclopropyl carbinol ester, the cyclopropyl CH appears to be prone to chain transfer. MPVB possesses eight allylic hydrogens, which are readily abstracted by radicals, giving rise to gelation or bimodal molecular weight distribution upon prolonged polymerization. The yield of PMPVB was again kept low by high dilution and short reaction time to avoid gelation.

Inverse gated decoupled ^{13}C NMR spectra of PCPPVB and PTBVB are compared in Figure 1. The cyclopropyl carbons resonate at very high fields (1.8 and 20.9 ppm). While the cyclopropyl methylene protons of PCPPVB resonate as a broad singlet in $CDCl_3$, the resonance exhibits a significant splitting of 0.06 ppm or 16.2 Hz in THF-d_8 (see Figure 13a). The aromatic C1 resonances of PCPPVB and PTBVB at about 150 ppm are indicative of tacticity, but only two of three triad sequences are clearly visible. The inverse gated decoupled ^{13}C NMR spectrum of PMPVB is shown in Figure 2. While aromatic C4 of the tertiary esters (Figure 1) resonates at a lower field than C3, C4 of the primary ester absorbs between C2 and C3. As the expanded ^{13}C NMR spectrum in Figure 2 clearly indicates, the aromatic C1 resonance exhibits three peaks due to tacticity. The triad tacticity of the polymer is estimated to be rr, 56%, mr, 35%, and mm, 9%. Although ^1H NMR spectra of the tertiary ester polymers do not clearly provide tacticity information, the aromatic H2 of PMPVB exhibits a resonance very similar to the aromatic C1 resonance (see Figure 13c).

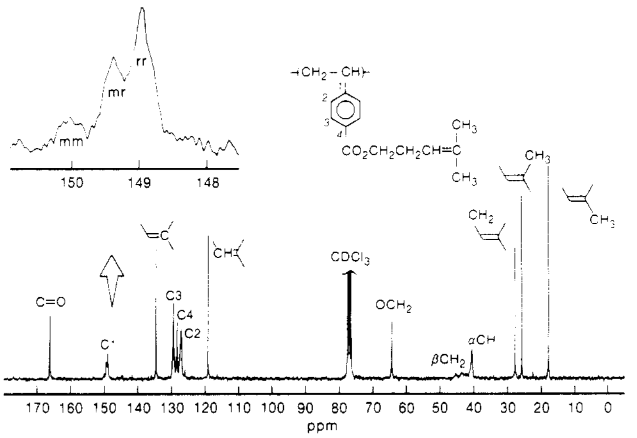


Figure 2. Inverse gated ^{13}C NMR spectrum (62.9 MHz) of PMPVB in $CDCl_3$.

PTBVB has a glass transition temperature (T_g) of about 170 °C. The T_g of PCPPVB is obscured by a deprotection endotherm but estimated to be about 160 °C by DSC. Because of the flexible alkyl chain, PMPVB exhibits T_g

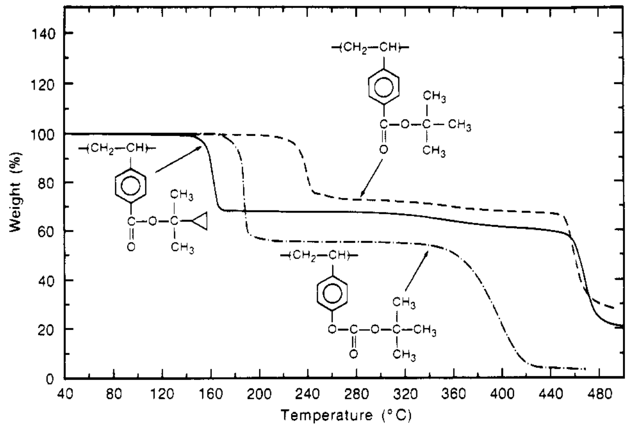


Figure 3. TGA of PCPPVB, PTBVB, and PBOCST (5 °C/min).

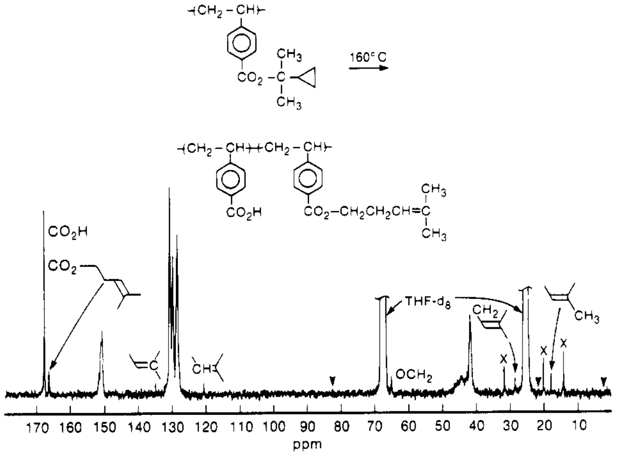


Figure 4. Inverse gated ^{13}C NMR spectrum (62.9 MHz, THF-d_8) of PCPPVB heated at 160 °C. Arrowheads indicate positions of resonances due to PCPPVB.

at about 80 °C.

Thermolysis of PCPPVB. In Figure 3 is presented a TGA curve of PCPPVB together with those of PTBVB and PBOCST. The *tert*-butyl carbonate releases a quantitative amount (45.5 wt %) of carbon dioxide and isobutene at about 190 °C upon heating (5 °C/min) while the *tert*-butyl benzoate is quantitatively converted to PVBA losing isobutene (27.5 wt %) at about 240 °C. Replacement of one of the methyl groups of the *tert*-butyl ester with a cyclopropyl group results in dramatic reduction in the deprotection temperature by ca. 80 °C. Thus, the dimethyl cyclopropyl carbinol ester is even more thermally labile than the tBOC group. The second small weight loss observed at about 340 °C in the heated benzoate polymers is due to intermolecular dehydration of PVBA. DSC of PVBA or the benzoate polymers exhibits T_g at about 250 °C.

Although the deprotection temperature of PCPPVB is much lower than those of PTBVB and PBOCST, the weight loss (ca. 32%) that occurs at 160 °C is smaller than expected for quantitative loss of 2-cyclopropylpropene (35.7 wt %). This is presumably due to concomitant rearrangement to a thermally stable 4-methyl-3-pentenyl ester. The PCPPVB powder was heated at 160 °C for 30 min on a Kugelrohr apparatus under vacuum, resulting in 31% weight loss. The resulting powder, highly soluble in THF-d_8, was subjected to ^{1}H and ^{13}C NMR analyses. The inverse gated decoupled ^{13}C NMR spectrum is shown in Figure 4, which clearly indicates the absence of the cyclopropyl group and the presence of the 4-methyl-3-pentenyl group by comparison with Figures 1 and 2. We also measured NMR spectra of PVBA made by radical polymerization of VBA as a reference. The polymer obtained by heating PCPPVB is primarily PVBA containing about 10 mol % of the pentenyl ester according to the ^{13}C NMR spectrum, which agrees well with our ^{1}H NMR integration and the TGA weight loss.

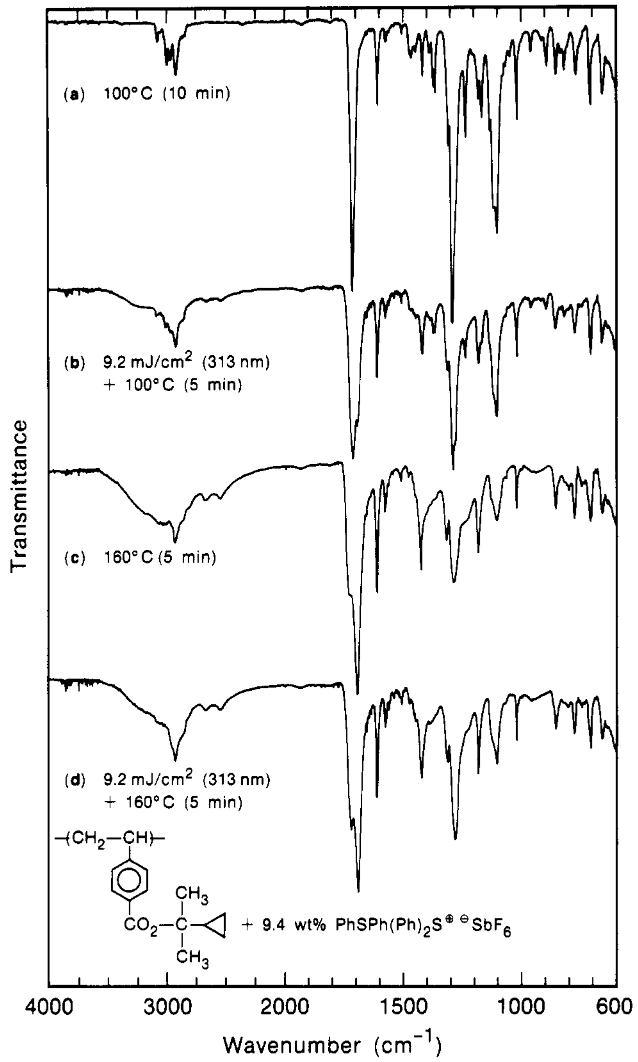


Figure 5. IR spectra of PCPPVB film containing 9.4 wt % of PhSPh(Ph)$_2$S^{+-}SbF$_6$ after prebake (a), after UV exposure (9.2 mJ/cm^2) followed by postbake at 100 °C (b), after high temperature treatment at 160 °C without UV exposure (c), and after UV exposure (9.2 mJ/cm^2) followed by postbake at 160 °C (d).

Acid-Catalyzed Deprotection and Rearrangement of PCPPVB. Acid-catalyzed deprotection and rearrangement of PCPPVB were carried out by generating HSbF$_6$ in the polymer film by photolysis of a triarylsulfonium salt. Since poly(vinylbenzoates) and PVBA have a strong UV absorption below 300 nm with an optical density (OD) of ca. 1/μm and ca. 3.1/μm in the 250-nm region,[16] diphenyl(4-(thiophenoxy)phenyl)sulfonium hexafluoroantimonate which extends its absorption to 350 nm[24] was used as the photochemical acid generator. Addition of the sulfonium salt at 3.83 mol % (to the polymer repeating unit) to the polymer results in an OD of 0.35/μm (45% transmission) at the exposing wavelength of 313 nm. An IR spectrum of the PCPPVB film (ca. 1.0 μm thick, M_n = 54 000, M_w = 170 700) containing 9.4 wt % of the sulfonium salt is shown in Figure 5a. Figure 5b clearly indicates that PCPPVB is significantly converted to PVBA upon exposure to 9.2 mJ/cm^2 of 313-nm radiation followed by postbake at 100 °C, as evidenced by the strong absorptions due to carboxylic OH at about 3200 cm^{-1} and carboxylic acid C=O at 1700 cm^{-1}. The

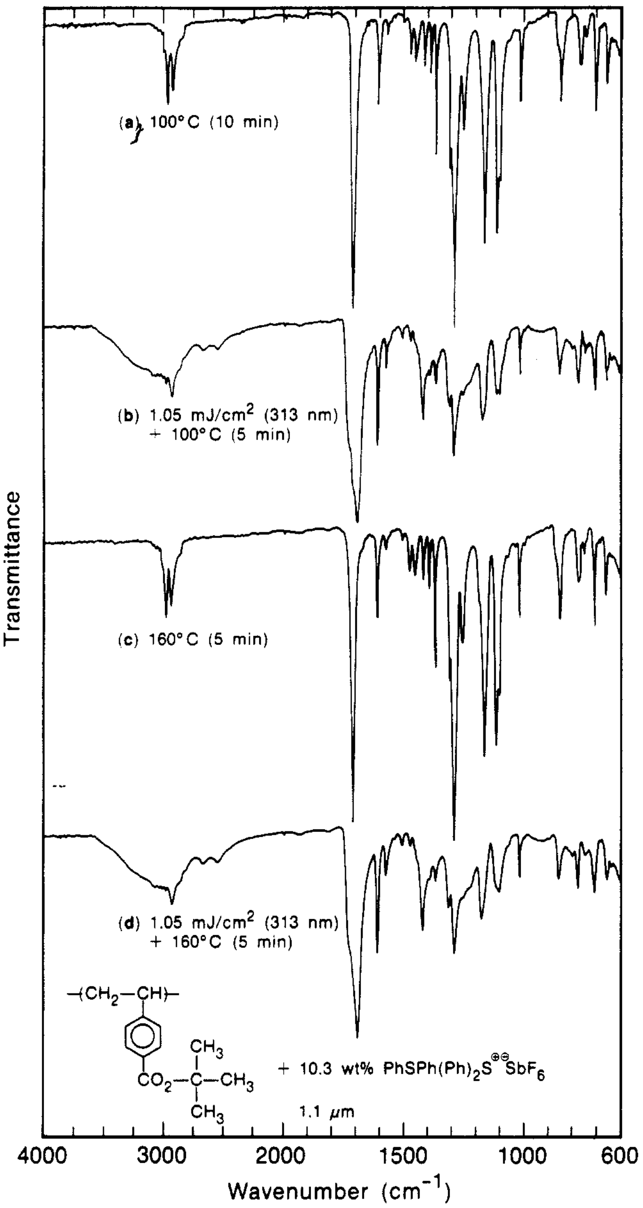


Figure 6. IR spectra of PTBVB film containing 10.3 wt % of PhSPh(Ph)$_2$S$^+$ $^-$SbF$_6$ after prebake (a), after UV exposure (1.05 mJ/cm^2) followed by postbake at 100 °C (b), after high temperature treatment at 160 °C without UV exposure (c), and after UV exposure (1.05 mJ/cm^2) followed by postbake at 160 °C (d).

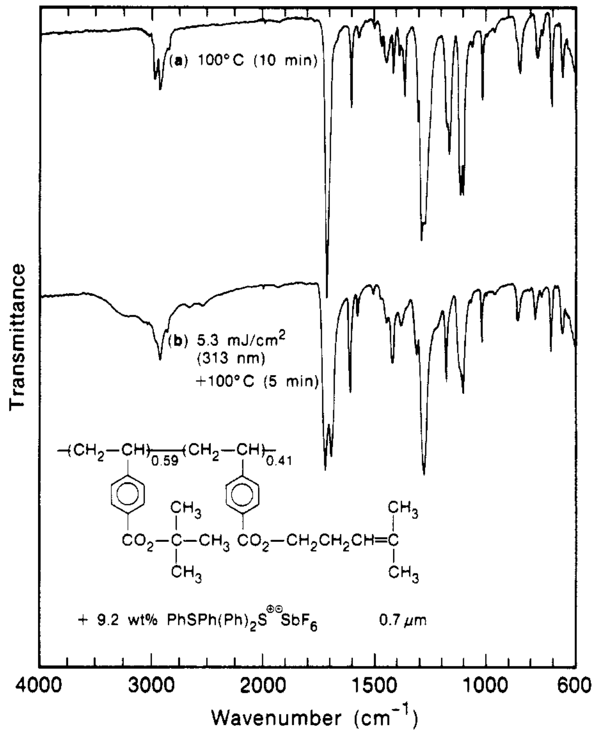


Figure 7. IR spectra of P(TBVB-*co*-MPVB) film containing 9.2 wt % of PhSPh(Ph)$_2$S$^+$ $^-$SbF$_6$ before (a) and after (b) UV exposure (5.3 mJ/cm^2) followed by postbake at 100 °C.

concentration of the VBA units in the exposed film is estimated to be about 40%, which is in contrast with the higher conversion (ca. 60%) obtained with the PTBVB film (M_n = 25 300, M_w = 73 300) at a much lower dose of 1.05 mJ/cm^2 (Figure 6b). The film thickness and the sulfonium salt loading on a molar basis were kept constant in the two cases. Thus, the cyclopropyl carbinol ester appears to be less susceptible than the *tert*-butyl ester to acid-catalyzed deesterification in spite of its much lower thermal deprotection temperature, which is in accord with the polymethacrylate case previously published.[17] When heated at 160 °C in the absence of acid, PCPPVB undergoes a significant deprotection (Figures 5c) whereas PTBVB remains unchanged (Figure 6c), as TGA in Figure 3 indicates. Heating the exposed films at 160 °C results in higher conversion than at 100 °C in both cases (Figures 5 and 6d). What is interesting is that the 160 °C bake gives a higher conversion in the absence of acid for PCPPVB (compare parts c and d of Figure 5).

In order to confirm that the cyclopropyl carbinol ester undergoes acid-catalyzed rearrangement, we prepared a copolymer of TBVB with MPVB (copolymer composition = 59/41, M_n = 64 300, M_w = 193 400, monomodal) (Table II). IR spectra of the copolymer film containing 9.2 wt % of the sulfonium salt before and after exposure/postbake are shown in Figure 7. The tertiary and primary ester carbonyl groups absorb at the same wavenumber of 1730 cm^{-1}. After exposure and postbake, the copolymer is converted to a copolymer of VBA and MPVB. Comparison of parts b, c, and d of Figure 5 with Figure 7b indicates that thermolysis and acidolysis of PCPPVB result in formation of a copolymer of VBA and MPVB.

Film shrinkage after exposure and postbake is a good measure of conversion of these deprotection reactions. The effects of exposure dose and postbake temperature on conversion in terms of remaining film thickness are presented in Figure 8. The PCPPVB film containing 9.2 wt % of the sulfonium salt is stable when heated at 100 or 130 °C for 5 min without UV exposure and shrinks more upon postbake at higher doses due to loss of more olefin. The 130 °C bake provides a higher conversion than the 100 °C bake at the same dose but the degree of shrinkage saturates at approximately 12% at about 5 and 50 mJ/cm^2 when postbaked at 130 and 100 °C, respectively, without ever reaching the maximum value of 32% which is expected from TGA or 35.7% which is expected from the quantitative loss of 2-cyclopropylpropene. On the contrary, the 160 °C bake results in almost maximum shrinkage in the unexposed regions and the exposed film retains more thickness at higher doses, which is clearly due to more pronounced rearrangement in the presence of acid. The shrinkage saturates again at ca. 12% at about 20 mJ/cm^2 when postbake is carried out at 160 °C. Thus, the maximum degree of acid-catalyzed rearrangement is about 66% in the solid state, irrespective of postbake temperature.

Lithographic Imaging. The PCPPVB film (ca. 1.0 μm thick) containing 9.2 wt % of the sulfonium salt was exposed to 313-nm UV radiation, postbaked at 100, 130,

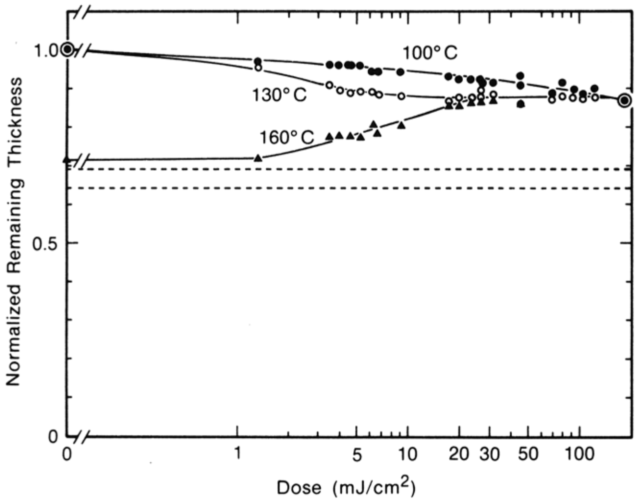


Figure 8. Shrinkage of PCPPVB film containing 9.4 wt % of $PhSPh(Ph)_2S^{+-}SbF_6$ as a function of UV dose and postbake temperature. The dotted lines represent the maximum deprotection based on TGA and the quantitative elimination of 2-cyclopropylpropene.

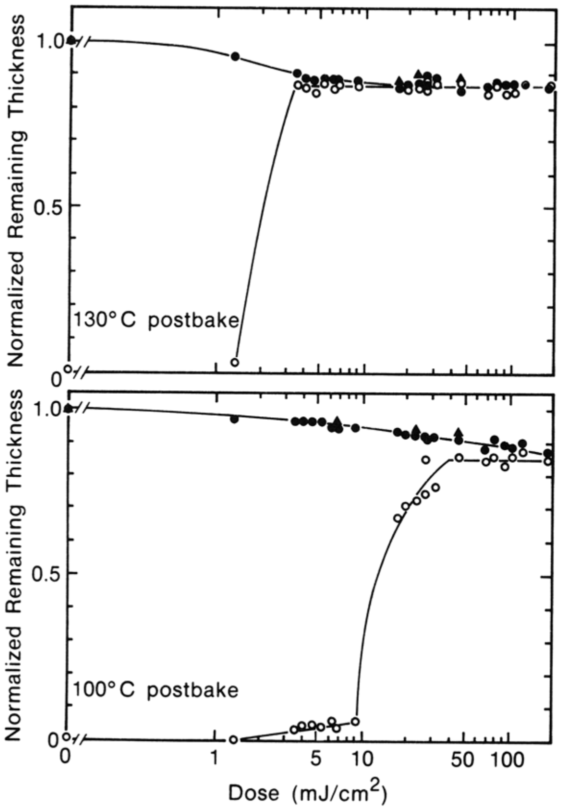


Figure 9. Thickness of PCPPVB film containing 9.4 wt % of $PhSPh(Ph)_2S^{+-}SbF_6$ as a function of UV dose; postbaked at 130 °C (top) and 100 °C (bottom); thickness measured after postbake (●) and after development with anisole (○) and with aqueous base (400 K/H_2O = 1/4) (▲).

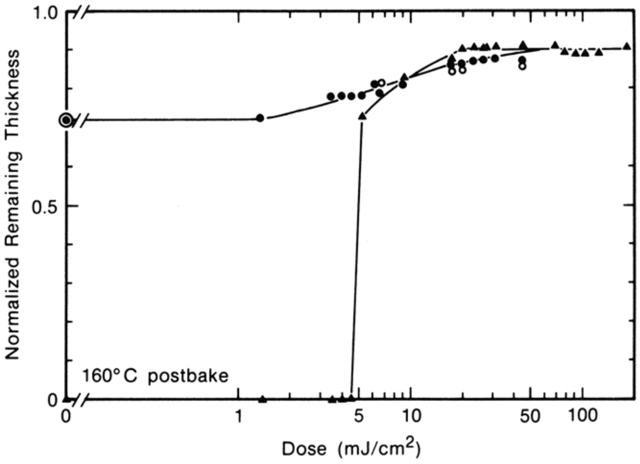
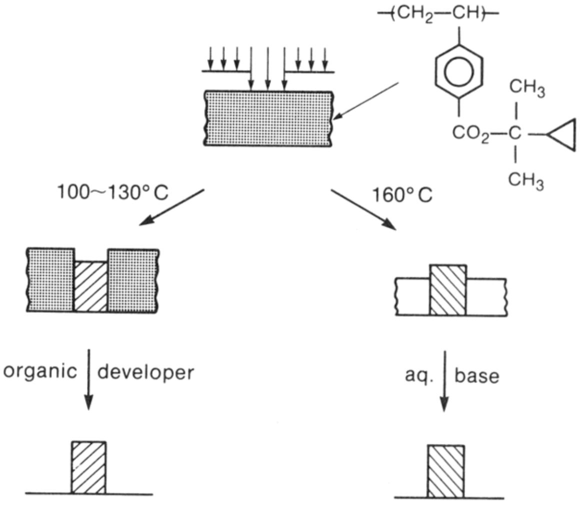


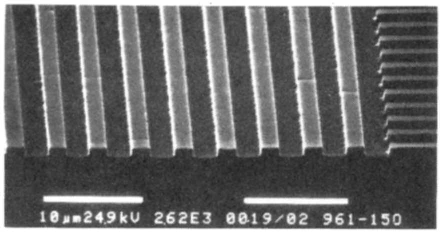
Figure 10. Thickness of PCPPVB film containing 9.4 wt % of $PhSPh(Ph)_2S^{+-}SbF_6$ as a function of UV dose; postbaked at 160 °C; thickness measured after postbake (●) and after development with anisole (○) and with aqueous base (400 K/H_2O = 1/4) (▲).

Scheme V
Negative Imaging of PCPPVB Resist

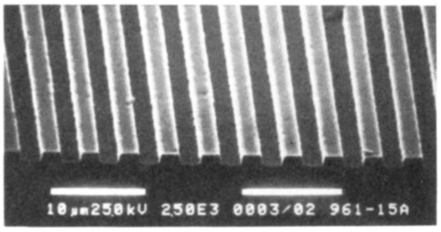


or 160 °C for 5 min, and developed with anisole or aqueous base. Film thickness measured after postbake (●), after development with anisole (○), and after development with aqueous base (▲) is shown as a function of exposure dose in Figures 9 and 10. Unexposed films are cleanly soluble in anisole but insoluble in aqueous base when heated below 130 °C because the film consists of lipophilic PCPPVB. As the film is exposed, more VBA units are generated upon postbake and the film becomes insoluble in anisole at about 3 and 40 mJ/cm^2 when postbaked at 130 and 100 °C, respectively. The dose at which the exposed film becomes insoluble in the nonpolar organic solvent corresponds to the dose at which maximum shrinkage (ca. 12%) and the maximum conversion (ca. 34%) are attained. The exposed films never become soluble in aqueous base presumably because the concentration of the VBA units formed (ca. 34%) is not high enough, failing to provide positive imaging. This behavior is totally different from the PTBVB system which provides positive images upon development with aqueous base.

When postbaked at 160 °C, the PCPPVB resist system behaves completely differently as Figure 10 indicates. The 160 °C postbake renders the unexposed film insoluble in anisole but soluble in aqueous base due to the predominant thermal deprotection to convert PCPVB to PVBA containing only about 10% of the MPVB units as described earlier. The exposed films are insoluble in anisole because of generation of the polar VBA units (90–34%) and become insoluble in aqueous base at about 5 mJ/cm^2 when postbaked at 160 °C because the exposed area mainly consists of the nonpolar MPVB units produced by acid-catalyzed rearrangement. Thus, the polarity is reversed by the high-temperature postbake, and as demonstrated in Scheme V, the PCPPVB resist system functions as a negative resist that can be developed either with a nonpolar organic solvent when postbaked below 130 °C or with aqueous base when postbaked above 160



(**a**) negative imaging with organic developer



(**b**) negative imaging with aqueous base

Figure 11. Scanning electron micrographs of negative images delineated in PCPPVB resist by development with anisole (a, 6.8 mJ/cm^2) and with aqueous base (b, 18 mJ/cm^2) after postbake at 130 and 160 °C, respectively.

°C. In contrast, the PBOCST and PTBVB systems can be developed in either a positive or a negative mode depending on the polarity of the developer solvent. We have demonstrated with the poly(*tert*-butyl methacrylate) (PTBMA) resist system a similar negative imaging with aqueous base by the polarity reversal in addition to the conventional dual tone imaging based on acid-catalyzed conversion of PTBMA to poly(methacrylic acid) (PMA). The negative imaging of the PTBMA resist with aqueous base is achieved in this case by thermally converting PMA (or a copolymer with TBMA) formed in the exposed regions to poly(methacrylic anhydride) and by subsequent flood UV exposure followed by postbake to convert PTBMA in the unexposed areas to PMA.[17] In Figure 11 are presented scanning electron micrographs of negative images printed in the PCPPVB resist by development with anisole after 130 °C postbake (6.8 mJ/cm^2 of 313-nm radiation) (a) and by development with aqueous base after postbake at 160 °C (17.5 mJ/cm^2) (b).

Cross-Linking of PMPVB. The mechanism of the negative imaging with the PCPPVB resist is believed to be based on the acid-catalyzed polarity change when the postbake is performed below 130 °C and on the polarity reversal that occurs at 160 °C. However, cross-linking may also cooperatively take place in the exposed regions as the photochemically generated acid could react with the double bond of the rearrangement product and as the triarylsulfonium salts are known to generate an aryl radical upon photolysis[25] which could abstract hydrogen radicals from the allylic structure of the rearranged product.

A copolymer of MPVB and ST containing 31 mol % of MPVB (M_n = 39 000, M_w = 86 000) was made with AIBN in THF in 44% yield (60 °C, 8 h) (Table II) and mixed with 9.4 wt % of the sulfonium salt. Exposure to 58 mJ/cm^2 of 313-nm radiation followed by postbake at 160 °C rendered the film insoluble in the casting solvent (PM Acetate), indicating that the 4-methyl-3-pentenyl group participates in acid- or radical-induced cross-linking. In addition, the PCPPVB resist was first heated at 160 °C and then exposed (43 mJ/cm^2) and postbaked at 160 °C, providing weakly negative images upon development with aqueous base.

Further evidence of cross-linking through the methylpentenyl group has been obtained spectroscopically. In Figure 12 are shown IR spectra of the PMPVB film containing 9.4 wt % of the sulfonium salt before and after UV exposure/postbake. The primary ester appears to be cleaved to a small extent by the photochemically generated acid. In addition to increase in the intensity of the peak at 2900 cm^{-1}, the IR absorption due to the trisubstituted ethylene at 828 cm^{-1} became smaller upon exposure and postbake. PCPPVB and PMPVB were treated with trifluoromethanesulfonic (triflic) acid in THF-d_8 in

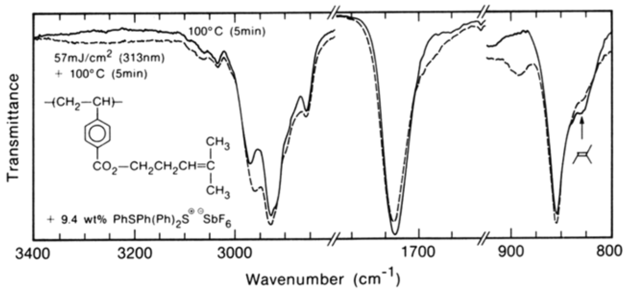


Figure 12. IR spectra of PMPVB film containing 9.4 wt % of PhSPh(Ph)$_2$S^{+-}SbF$_6$ before and after UV exposure and postbake.

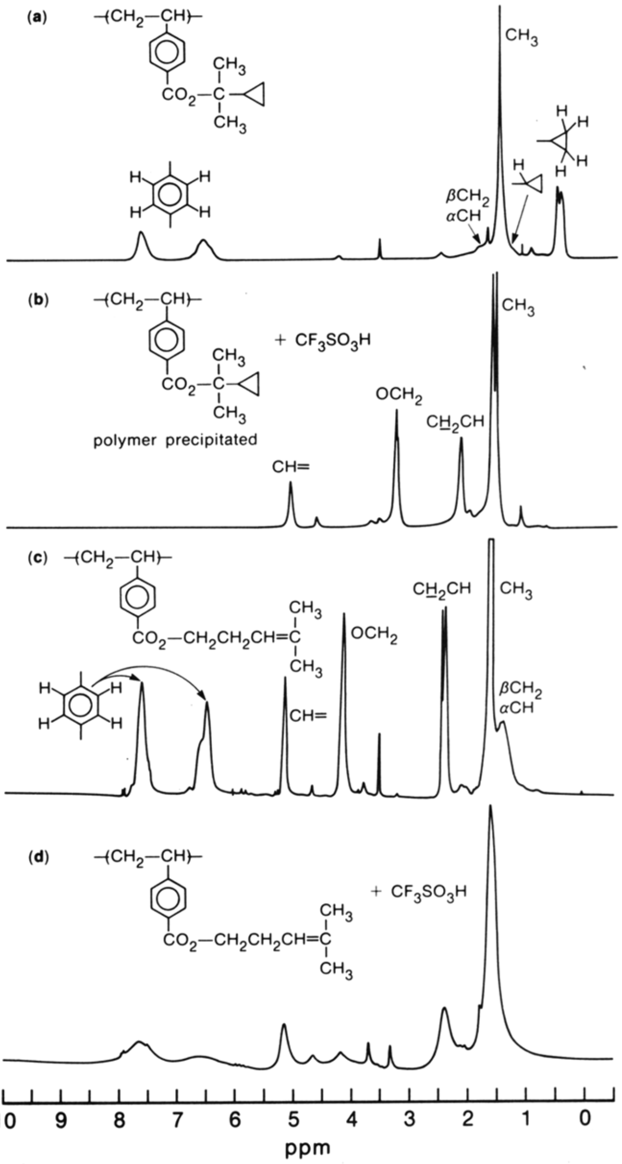


Figure 13. ^{1}H NMR spectra (250 MHz, THF-d_8) of PCPPVB before (a) and after (b) addition of triflic acid and of PMPVB before (c) and after (d) addition of triflic acid.

Table II
Radical Copolymerization of MPVB at 60 °C

comonomer (mol %)	initiator (mol %)	solvent, (mL/g of monomer)	time, h	yield, %	MPVB in copolymer, mol %	M_n	M_w
VBA (78.6)	AIBN (1.0)	THF (1.8)	8	48	15	59 600	116 700
VBA (33.8)	AIBN (1.0)	THF (3.0)	8	47	64	53 300	103 500
ST (78.0)	AIBN (0.6)	THF (2.0)	8	45	31	34 000	86 100
TBVB (53.0)	BPO (0.9)	toluene (2.2)	6	40	41	64 300	193 400

an NMR tube. Upon addition of triflic acid to PCPPVB, the polymer precipitated out of the solution although PCPPVB, PMPVB, and PVBA are all soluble in THF, and only the resonances due to 4-methyl-3-pentenyl ester (perhaps triflate) (Figure 13b) recorded. When PMPVB was treated with triflic acid in THF (Figure 13d), all the proton resonances became very broad. Treatment of 4-methyl-3-penten-1-ol with triflic acid resulted in total consumption of the olefinic double bond according to ^{1}H and ^{13}C NMR and in a higher field shift and collapse of the two methyl proton resonances.

We prepared copolymers of VBA with MPVB by radical initiation in THF at 60 °C (Table II). A copolymer containing 37 mol % of VBA (M_n = 53 300, M_w = 103 400), which represents the copolymer formed in the exposed areas of the PCPPVB resist, was cast into a film from THF and heated at 100 °C for 5 min. After the heat treatment, the copolymer film was still soluble in THF but insoluble in aqueous base and anisole, indicating that the VBA concentration is high enough to render the copolymer film insoluble in anisole but still too low to allow dissolution in aqueous base. Thus, the negative imaging with anisole and the insolubility of the exposed regions of the PCPPVB resist postbaked below 130 °C can be interpreted in terms of copolymer composition without considering cross-linking. Another copolymer of VBA with MPVB containing 85 mol % of VBA (M_n = 59 600, M_w = 116 800), representing a copolymer formed in the unexposed areas by heating the PCPPVB resist at 160 °C, was also dissolved in THF and cast into a film. When heated at 100 °C for 5 min, the film was still soluble in THF and aqueous base. However, 160 °C bake rendered the film insoluble in THF and in aqueous base, suggesting that cross-linking occurred upon the high temperature treatment, thus failing to explain the negative imaging with aqueous base. We stated earlier that the PCPPVB resist heated at 160 °C prior to UV exposure functioned as a negative resist upon aqueous base development. The VBA–MPVB copolymers containing 80–90 mol % of VBA made by thermolysis of PCPPVB and by direct copolymerization appear to behave differently. We prepared a copolymer by heating the PCPPVB powder at 160 °C for 30 min, which was highly soluble in THF as mentioned earlier. However, the copolymer film cast from THF became insoluble in THF and aqueous base upon heating at 160 °C. These observations indicate that the pentenyl group generated from the cyclopropyl dimethyl carbinyl group does not undergo cross-linking even at 160 °C presumably because the olefinic double bonds are not in close proximity in this case. However, upon dissolution and casting, the pentenyl groups rearrange themselves and perhaps aggregate to allow propagation of cross-linking. Another interesting observation is that the copolymer of MPVB with ST containing 31 mol % of MPVB remained soluble in the casting solvent even after 160 °C bake as mentioned earlier, suggesting that the 4-methyl-3-pentenyl groups are separated from each other in the nonpolar matrix. It appears that cross-linking through the 4-methyl-3-pentenyl group is very much affected by morphology.

The 4-methyl-3-pentenyl group undergoes cross-linking, which may be induced by heating, radical, or acid. The CPPVB homopolymer becomes insoluble upon long standing at room temperature whereas its copolymers are much more stable. However, in the lithographic imaging of the PCPVB resist, the major mechanism of the differential dissolution is based on the change in the VBA concentration. The cross-linking through the 4-methylpentenyl group may participate in the negative imaging mechanism cooperatively at high exposure doses.

Summary

PCPPVB undergoes thermal deprotection at about 160 °C and is converted to PVBA containing ca. 10 mol % of the MPVB units. Rearrangement of the CPPVB group to the MPVB group is much more pronounced in the presence of acid, and acidolysis of PCPPVB results in as much as 66% rearrangement. The thermal and acid-catalyzed deprotection and rearrangement reactions can be exploited in the design of a new type of chemical amplification resist systems that function as a negative resist which can be developed with an organic solvent or with aqueous base depending on the postexposure bake temperature. Although the 4-methyl-3-pentenyl group undergoes cross-linking, the major mechanism of the negative imaging is via alteration of the VBA unit concentration (polarity change and polarity reversal). The cross-linking through the 4-methyl-3-pentenyl group appears to be very much affected by morphology.

Acknowledgment. We thank E. Hadziioannou and C. Weidner for their analytical assistance.

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Notes

Effect of Microscopic Environment on Emission Quenching of Photoexcited Ruthenium Complex by Dialkylviologens

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Received September 27, 1989;
Revised Manuscript Received November 20, 1989

Introduction

Photochemistry in molecular assembly systems has been extensively investigated in relation to solar energy conversion.[1-3] Some interesting effects of the microheterogeneous environments formed by molecular assemblies on photochemical reactions, especially photoinduced electron-transfer reactions, have been found.[1-4] Micellar and microemulsion systems have been studied in detail.[4-9] Kinetic behavior of a reaction between substrates solubilized in a micelle is quite different from that in a homogeneous solution.[8,10-12] In a previous paper on the quenching of a photoexcited ruthenium complex by viologens having various alkyl substituents in SDS micellar solution,[6] we found that the intramicellar electron-transfer quenching rate constants decreased with increasing alkyl chain length of the viologen quenchers from methyl to hexyl. The difference in the reactivity results from the interaction between the viologen quenchers and the micelle.

In this note, we study the quenching of a photoexcited tris(2,2′-bipyridine)ruthenium complex ($\mathrm{Ru(bpy)_3}^{2+*}$) by viologen quenchers ($\mathrm{C}_n\mathrm{V}^{2+}$) in a polyelectrolyte (poly(styrenesulfonate)), in a polymer latex (polystyrene latex) and in a homogeneous solution (acetonitrile). It is found that the effect of hydrophobicity of the viologen quenchers (effect of alkyl chain length) on the quenching reactivity is changed drastically by the reaction environments (polyelectrolyte, polymer latex, and acetonitrile).

$$\mathrm{Ru(bpy)_3}^{2+*} + \mathrm{C}_n\mathrm{V}^{2+} \rightarrow \mathrm{Ru(bpy)_3}^{3+} + \mathrm{C}_n\mathrm{V}^{+} \qquad (1)$$

$$\mathrm{C}_n\text{: } (\mathrm{CH_3})_2,\ (\mathrm{C_2H_5})_2,\ (\mathrm{C_4H_9})_2,\ (\mathrm{C_6H_{13}})_2$$

Experimental Section

Poly(sodium styrenesulfonate) (PSS) was prepared by free radical polymerization of sodium *p*-styrenesulfonate with a potassium persulfate thermal initiator in water at 50 °C. The polymer was purified by ion exchanging with cation and anion exchange resins, followed by ultrafiltration. A polystyrene latex was prepared by polymerization of styrene (10 mL), methacrylic acid (1 mL), and divinylbenzene (0.1 mL) with a potassium persulfate thermal initiator in water at 70 °C. The latex solution was filtered with a 5-μm membrane to remove macroaggregates and purified by ultrafiltration (Toyo ultrafilter UK-200). The polymer latex particles were observed with a Hitachi H-300 electron microscope. The electron micrographs indicated that the latex particles were perfect spheres and almost monodisperse. The diameter of the particles was estimated to be 300 nm.

N,N′-Dialkyl-4,4′-bipyridinium halides were prepared from the reaction of 4,4′-bipyridine with the corresponding alkyl halides, and the crude products were purified by recrystallization.

All of the sample solutions were degassed by repeated freeze–pump–thaw cycles. The fluorescence intensity was measured with a Shimadzu RF 503A spectrofluorophotometer.

Results and Discussion

It is well-known that the photoexcited state of $\mathrm{Ru(bpy)_3}^{2+}$ is redox-active and is quenched by electron-acceptor and -donor quenchers.[13,14] The excited state of $\mathrm{Ru(bpy)_3}^{2+}$ is dynamically quenched by dialkylviologen compounds via an electron-transfer mechanism (eq 1). The relative ratios of the steady-state emission intensity of $\mathrm{Ru(bpy)_3}^{2+*}$ in the absence (I_0) and presence (I) of viologen quencher in acetonitrile are shown in Figure 1. The redox potential of the viologens, which indicates effectiveness as an electron acceptor, was unaffected by the alkyl substituents ($E_{1/2} = -0.45$ V vs SCE).[6] It is known that the rate constants for electron-transfer quenching in homogeneous solutions are determined by the redox potentials of quenchers.[15,16] As expected from the above equivalent redox potentials of the viologens, the quench-

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