Synthesis and Characterization of Statistical Copolymers of Styrene and 4-(1-hydroxyalkyl)Styrene

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ABSTRACT: A family of new polymers based on poly(4-(1-hydroxyalkyl)styrene), and its copolymers with styrene were synthesized and thoroughly characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR, and UV spectroscopies. The chemical modification reactions of polystyrene (PS) was used as a novel method of performing the synthesis of poly(4-(1-hydroxyethyl-*co*-styrene)), poly(4-(1-hydroxypropyl-*co*-styrene)), poly(4-(1-hydroxybutyl-*co*-styrene)), and poly(4-(1-hydroxyphenylmethyl-*co*-styrene)). The novelty of this method lies in the incorporation of the desired mol % of the functional groups in polystyrene chain, to obtain random copolymers of desired composition. In preliminary testing/evaluation studies the utility and versatility of the new copolymers, which have

the potential to be negative-tone photoresist materials, were studied. Thus a few photoresist formulations based on poly-(styrene-*co*-4-(1-hydroxyalkylstyrene)) were developed with 5 wt % of a photoacid generator. These studies suggested that the new copolymers synthesized by a simple and alternate method could have the same potential as a photoresist material when compared with the polymers synthesized by the polymerization of the corresponding functional monomer. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1902–1914, 2004

Key words: functionalization of polymers; polymer modification; synthesis; photoresists; lithography

INTRODUCTION

Polymers produced as functional materials serve in a multitude of applications such as additives, processing aids, adhesives, coatings, viscosity regulators, and lubricants, to cite but a few examples. Functional polymers are part of cosmetics, pharmaceutics, in all kinds of semiprepared foods, in printing inks and paints, superabsorbers in hygienic products, and in ceramics processing ("binders"), concrete, flocculants in wastewater treatment, and adhesive in the hardware production of electronic equipment, for example. The synthesis of new polymeric materials and especially functionalized polymers are important in the development of new applications such as photoresist materials, smart polymers, nanotubes, molecular imprinting, smart gels, and DNA microchips. Functional polymers in the "crosslinked" form are also useful in a number of applications such as column materials in chromatography, in combinatorial synthesis, and as simple chemical reagents.[1] Incorporating specific functional groups into polymers can influence their physical, mechanical, and rheological properties.[2]

A polymer with the desired pendant functional group can be synthesized in two ways: (1) by the incorporation of the functional group as a pendant unit of the monomer itself and polymerizing the same by any one of the chain-growth mechanisms; (2) by the chemical modification of the nonfunctionalized polymer.[3] With respect to vinyl polymers both routes are used on a regular basis. With polymeric resins the issue of whether to modify a polymer chemically or to carry out a polymerization using an appropriately functionalized comonomer is usually settled by the relative difficulty of the two methods of synthesis. The ready availability of the nonfunctionalized polymer of very high quality [in the case of polymers synthesized by living polymerization such as polystyrene (PS) narrow dispersed samples are easily available/synthesized] vis-à-vis the difficulty of synthesis of protected monomers and their subsequent polymerization makes the chemical modification of polymers an attractive route toward the synthesis of novel functionalized polymers. For example, following the chemical modification of polystyrene a series of new functional polymers based on variation of the type of functional group –X (such as –COOH, –OH, etc.) as well as its concentration relative to that of nonfunctionalized polystyrene repeat units can be achieved.

The chemical modification of polymers works by the principle that a linear polymer molecule consisting of repeat units should behave chemically in a manner similar to that of the small molecular analogue. The choice of the low molecular weight analogue made for
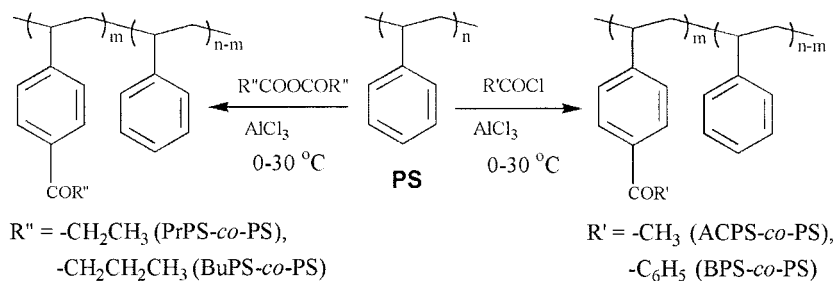
Scheme 1

the comparison is vital and it should reflect both the electronic and local steric properties of the polymer segment. For polymer modification to work efficiently the polymer should be completely dissolved in the reaction medium in a relatively expanded conformation, thereby providing reagent accessibility to each one of the repeat units and modification must occur without crosslinking. The introduction of functional groups on soluble polymers with the objective of synthesizing soluble, new, functional polymers has not been explored well in the literature, whereas the synthesis of functionalized polymers by performing a chemical reaction on insoluble polymers is a well-established area of research. Further, the literature cites fewer examples of chemical-modification reactions that result in essentially quantitative conversion as determined by the limits of structure-determining tools such as ^{1}H-NMR, which is attributed to the fact that polymer crosslinking reactions compete with polymer-modification reactions, in practice.

In this article, the synthesis of poly(4-(1-hydroxyalkyl)styrene-co-styrene) copolymers, which are somewhat analogous in structure to poly(4-hydroxy-1-phenylethyl)styrene) [PHPES], starting from PS is illustrated (PHPES has tertiary hydroxyl groups, whereas all the copolymers reported here have secondary hydroxyl groups). In this context, it is important to note that PHPES polymer has been reported to be the first and only example of a dual-tone imaging material based on polarity change from a polar to nonpolar state and possibly the most

sensitive resist currently known.[4,5] The reported synthesis of the monomer 4-(1-hydroxy-1-phenylethyl)styrene involved the reaction of a methyl Grignard reagent with 4-benzoylstyrene (which in turn was prepared by Stille's Pd-catalyzed tin coupling reaction on 4-bromobenzophenone).[6] PHPES polymer in turn was prepared by the polymerization of the monomer for a duration of 8 days. The new copolymers synthesized include poly(4-(1-hydroxyethyl)styrene-co-styrene) [PHES-co-PS], poly(4-(1-hydroxypropyl)styrene-co-styrene) [PHPS-co-PS], poly(4-(1-hydroxybutyl)styrene-co-styrene) [PHBS-co-PS], and poly(4-(1-hydroxyphenyl)styrene-co-styrene) [PHPMS-co-PS], as shown in Scheme 1 and Scheme 2.

EXPERIMENTAL

Methods

All the solvents and chemicals were reagent grade [Chimique Lab (I), Chennai, India] and unless specified were used as received. Commercial polystyrene [PS; Beekay Plastics, Chennai, M_n = 145,800; polydispersity index (PDI) = 1.3] was dissolved in tetrahydrofuran (THF) and was reprecipitated using excess methanol. This protocol was repeated twice to ensure removal of additives, if any. 1,2-Dicholoroethane (DCE), carbon disulfide (CS$_2$), chloroform (CHCl$_3$), and nitrobenzene (Ph-NO$_2$) were dried over anhydrous CaCl$_2$ and distilled before use. Acetyl chloride

R = -CH$_3$ (PHES-co-PS), -CH$_2$CH$_3$ (PHPS-co-PS),
-CH$_2$CH$_2$CH$_3$ (PHBS-co-PS), -C$_6$H$_5$ (PHPMS-co-PS)
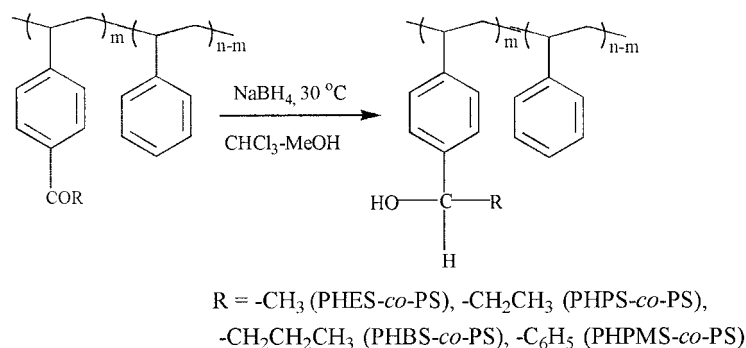
Scheme 2

(BDH, Chennai, India) and anhydrous aluminum chloride (E-Merck, Darmstadt, Germany) were used as received. Styrene (BTP India Pvt. Ltd., Chennai, India) was vacuum distilled over CaH_2 and stored under nitrogen at 4°C. Anionic polymerization of styrene was carried out as reported previously.[7] Atom-transfer radical polymerization of styrene was carried out as reported previously.[8] Cu(I)Br (Aldrich, Milwaukee, WI), $N,N,N'N',N''$-pentamethyldiethylenetriamine (Lancaster) and the initiator 1-phenylethyl bromide (Lancaster) were used as received. Sodium borohydride ($NaBH_4$) and propyleneglycol methyl ether acetate (PGMEA; Lancaster), benzoyl chloride (Vindhya Chemicals, Chennai, India), propionic anhydride (Fluka, Buchs, Switzerland), and butyric anhydride (Fluka) were used as received. The photoacid generator (PAG), triarylsulfonium hexafluoroantimonate salt (Aldrich; 50 w/w % in propylene carbonate), was used after appropriate dilution. THF and dioxane were freshly distilled over sodium-benzophenone just before use. Silicon wafers [Si (100)] were used after cleaning. Electronic-grade 5% HF, acetone, and methanol were used as received (SRL, Chennai, India).

A Shimadzu (Kyoto, Japan) GPC system (Phenomenox 500, 10^3, and 10^4 Å polystyrene-based columns with particle size of 5 μm) with LC-10 software was used for the determination of the number-average molecular weight (M_n) and PDI. A Jasco (Tokyo, Japan) FTIR 410 infrared spectrometer was used for recording IR spectra. A Shimadzu UV-240 and Jasco UV V-530 spectrophotometers were used for recording UV spectra. A JEOL (Tokyo, Japan) GSX 400 (400 MHz for ^{1}H) NMR spectrometer was used to record ^{1}H and ^{13}C (100 MHz) spectra. Lithographic evaluation was performed with an Optical Associated Inc. (San Jose, CA) IR mask aligner J500, UV (350 W) lamp, and KSM mask alignment and exposure system [MJB 3 Standard with UV 200 W lamp (Karl Suss KG, Germany)]. All the exposures were performed after the radiation dosage had reached a steady value of 27 mW/cm^2 in the analog meter of the exposure tool. Polymer films of about 3000 Å thickness were spun on an Si wafer using Model 709 photoresist spinner (Kulicke and Soffa Industries, Pennsylvania). Leitz Laborlux S microscope (Wetzlar, Germany) with Wild Leitz camera (Wild MSP46) and Leica DMRM (Wetzlar, Germany) with a Leica camera (Wild MPS 28) were used for taking photographs of the developed image. A CsCl disc was used to record the FTIR of the polymer film before and after exposure to UV radiation used in the lithographic studies.

Synthesis of copolymers of polystyrenes

Synthesis of poly(4-acetylstyrene) [ACPS] and its copolymers [ACPS-*co*-PS]

Polystyrene (PS, 5 g, 48 mmol) was dissolved in 150 mL of a solvent mixture consisting of DCE and nitro-

TABLE I
List of ACPS-*co*-PS and ACPS Copolymers Synthesized[a]

Entry	M_n and PDI of PS used	Mol % acetylated[b]	M_n and PDI of ACPS-*co*-PS
1	2800, 1.05	36	3938, 1.04
2	2700, 1.12	44	5474, 1.07
3	6700, 1.07	65	9028, 1.07
4	6900, 1.07	76	9115, 1.07
5	2500, 1.19	99	4194, 1.15

[a] ACPS-*co*-PS of extent of acetylation 5, 13, 17, 33, 58, and 94 were also synthesized starting from commercial PS of M_n 145,800 and PDI 1.3. The sample corresponding to entry 1 was used extensively in photoresist evaluation studies.
[b] As estimated by 400-MHz ^{1}H-NMR; for entry 2 PS was synthesized by anionic polymerization of styrene in benzene using *sec*-butyl lithium as the initiator; for entries 1, 3, 4, and 5 PS were synthesized by bulk atom transfer radical polymerization using CuBr/1-PEBr/PMDETA at 90°C.

benzene (5% v/v) in a two-neck round-bottom flask fitted with a condenser and $CaCl_2$ guard tube. The whole system was kept cold in an ice bath to avoid vigorous reaction, which would otherwise lead to crosslinking. It was stirred vigorously with a magnetic pellet. $AlCl_3$ (14 g, 105 mol) was added to the polymer solution, which imparts an orange-red color to the solution. Acetyl chloride (6 mL, 84.5 mmol) was added gradually to the reaction mixture through a dropping funnel. At the end of the addition, the reaction mixture was allowed to warm to room temperature and was stirred for an additional 2 h. After this, the reaction mixture was added to crushed ice followed by the addition of concentrated HCl. The polymer that separated from the organic layer was removed, diluted with dichloroethane, and precipitated into excess methanol. It was redissolved in a small quantity of THF and reprecipitated using excess methanol and dried under vacuum.

Yield: 6.8 g (97%). ^{1}H-NMR (400 MHz, CDCl$_3$, δ, ppm): 1.6 (br.s, CH$_2$), 1.9 (br.s, CH—Ar), 2.5 (s, CH$_3$—CO), 6.5–7.5 (m, Ar—H); extent of acetylation is 99%. ^{13}C-NMR (100 MHz, CDCl$_3$, δ, ppm): 26.5, 40.5, 43.7 (CH$_3$, CH$_2$, CH), 125, 128, 134, 145 (Ar—C), 197 (C=O). IR (film form) ν (cm^{-1}): 3024 (m, Ar—C—H), 2912 (s), 1680 (s, –C=O), 1600 (s, Ar—C=C), 1490, 1414, 1280. UV (THF) λ_{max}, nm: 212, 250. M_n and PDI: 145,800 and 1.3 (before); 123,400 and 1.4 (after). Copolymers of polystyrene with the desired degree of acetylation (ACPS-*co*-PS) were obtained by varying the concentration of the acetyl chloride used for acetylation as shown in Table I.

Synthesis of poly(4-propionylstyrene-*co*-styrene) (PrPS-*co*-PS)

PS (1 g, 9.6 mmol) was dissolved in 30 mL of CS$_2$ in a two-neck round-bottom flask fitted with a condenser and a CaCl$_2$ guard tube. The whole system was maintained around 4°C in an ice bath while stirring it

vigorously with a magnetic pellet. AlCl$_3$ (3 g, 22.48 mmol) was added to the polymer solution upon which it turned orange-red in color, in 1 h. Propionic anhydride (1 mL, 7.7 mmol) in 10 mL of CS$_2$ was gradually added through a dropping funnel. After completion of the addition, the ice bath was removed and the reaction mixture was allowed to warm to room temperature, gradually (~ 2 h). After this the reaction mixture was added to crushed ice, followed by the addition of concentrated HCl. The polymer that separated out from the organic layer was removed, diluted in DCE appropriately, and precipitated into excess methanol, to obtain a white precipitate. It was redissolved in a small quantity of THF and reprecipitated into excess methanol and dried under vacuum.

Yield: 1.25 g (82%). Extent of propionylation = 60 ± 2 mol %; ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): 1.20 (br.s, CH$_3$), 1.39 (br.s, CH$_2$, CH), 2.89 (s, CH$_2$—CO), 6.44 to 7.57 (m, Ar—H); ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): 8.2, 31.6, 40.5, 42.4, 45.0 (CH$_3$, CH$_2$, CH$_2$, CH), 125, 126, 127, 134, 143, 144, 149 (Ar—C), 200 (C≡O); IR film form ν, cm^{-1}: 3026 (m, Ar—C—H), 2976 (s), 2933 1682 (s, C≡O), 1605 (s, Ar—C≡C), 1493, 1453, 1415, 1350, 1224, 1281, 1182, 952, 800, 701; UV in THF λ_{max}: 251 nm; M_n and PDI: 145,800 and 1.3 (before); 141,900 and 2.0 (after). PrPS-co-PS of desired composition were obtained by varying the amount of propionic anhydride in the above reaction.

Synthesis of poly(4-butroylstyrene-co-styrene) (BuPS-co-PS)

The synthesis and isolation of BuPS-co-PS were performed according to the procedure reported for PrPS-co-PS using butyric anhydride (1 mL, 6.1 mmol).

Yield: 1.3 g (78%). Extent of butyroylation = 64 ± 2 mol %; ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): 1.0 (br.s, CH$_3$), 1.4, 1.7 (br.s, CH$_2$, CH), 2.80 (s, CH$_2$—CO), 6.4 to 7.5 (m, Ar—H); ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): 13.8, 17.6, 31.0, 40.2, 40.9 (CH$_3$, CH$_2$, CH$_2$, CH), 125, 127, 135, 149 (Ar—C), 197 (C≡O); IR film form ν, cm^{-1}: 3027 (m, Ar—C—H), 2961, 2930 (s), 2873, 1681 (s, C≡O), 1604 (s, Ar—C≡C), 1493, 1454, 1415, 1364, 1275, 1216, 1182, 1000, 826, 701; UV in THF λ_{max}: 252 nm; M_n and PDI: 145,800 and 1.3 (before); 163,700 and 1.4 (after). BuPS-co-PS of desired composition were obtained by varying the amount of butyric anhydride in the above reaction.

Synthesis of poly(4-benzoylstyrene) (BPS) and copolymers poly(4-benzoylstyrene-co-styrene) (BPS-co-PS)

BPS was synthesized according to the procedure reported previously.[9] BPS-co-PS of desired composition was obtained by varying the amount of benzoyl chloride in the above reaction.

Synthesis of poly(4-(1-hydroxyethyl)styrene) (PHES) and copolymers poly(4-(1-hydroxyethyl)styrene-co-styrene) (PHES-co-PS)

PHES was synthesized by the reaction of 250 mg (1.71 mmol) of ACPS (~ 99% acetylated PS) dissolved in 10 mL of distilled CHCl$_3$ and 3 mL of distilled methanol with 250 mg (6.6 mmol) of NaBH$_4$, for 9 h at room temperature. After the reaction, the mixture was rinsed with dilute HCl, precipitated in hexane, and finally dried under vacuum.

Yield: 240 mg (95%). Extent of reduction 100%; ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): 1.4 (br.s, CH$_2$, CH$_3$—C), 3.8, 4.7, 6.5 to 7.0 (m, Ar—H); ^{13}C-NMR (100 MHz, CDCl$_3$—CD$_3$OD, ppm): 25, 40 (CH$_2$, CH), 70 (C—OH), 125, 126, 127, 143, 144 (Ar—C); IR film form ν, cm^{-1}: 3375 (–OH), 2970 (m, Ar—C—H), 2924 (s), 1603 (s, Ar—C≡C), 1509, 1448, 1417, 1070, 700; UV in PGMEA λ_{max}: 263 nm. PHES-co-PS was synthesized by the NaBH$_4$ reduction of the corresponding acetylated copolymers (ACPS-co-PS).

Synthesis of poly(4-(1-hydroxypropyl)styrene-co-styrene) (PHPS-co-PS)

PHPS-co-PS with 60 ± 2 mol % of propionyl functionality was synthesized and isolated according to the procedure followed for PHES.

Yield: 180 mg (71%). Extent of reduction 100%; ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): 0.8 (br.s, CH$_3$—C), 1.4, 1.7 (br.s, CH$_2$), 3.7, 4.4, 6.4 to 6.9 (m, Ar—H); ^{13}C-NMR (100 MHz, CDCl$_3$—CD$_3$OD, ppm): 10.3, 31.9, 40.4 (CH$_3$, CH$_2$, CH), 75.6 (C—OH), 125, 127, 128, 142, 167.8 (Ar—C); IR film form ν, cm^{-1}: 3394 (–OH), 3022 (m, Ar—C—H), 2924 (s), 1603 (s, Ar—C≡C), 1493, 1452, 1042, 762, 701; UV in PGMEA λ_{max}: 264 nm.

Synthesis of poly(4-(1-hydroxybutyl)styrene-co-styrene) (PHBS-co-PS)

PHBS-co-PS with 64 ± 2 mol % of butyroyl functionality was synthesized and isolated according to the procedure followed for PHES.

Yield: 190 mg (75%). Extent of reduction 100%; ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): 0.9 (br.s, CH$_3$—C), 1.3, 1.7 (br.s, CH$_2$), 4.2, 4.5, 6.4 to 7.0 (m, Ar—H); ^{13}C-NMR (100 MHz, CDCl$_3$—CD$_3$OD, ppm): 13.6, 19.3, 40.4 (CH$_3$, CH$_2$, CH), 73.9 (C—OH), 121, 125, 127, 132, 142, 144 (Ar—C); IR film form ν, cm^{-1}: 3384 (–OH), 3020 (m, Ar—C—H), 2926 (s), 1607 (s, Ar—C≡C), 1509, 1452, 1022, 831, 701; UV in PGMEA λ_{max}: 263 nm.

Synthesis of poly(4-(1-hydroxy-1-phenylmethyl)styrene-co-styrene) (PHPMS-co-PS)

PHPMS-co-PS with 67 ± 2 mol % benzoyl functionality was synthesized by reacting BPS-co-PS (67 ± 2 mol % benzoylated) (500 mg, 2.4 mmol) with sodium borohydride (500 mg, 13.2 mmol) in 20 mL of distilled CHCl$_3$/DCE and 5 mL of distilled methanol for 24 h at room temperature. After the reaction, the mixture was rinsed with dilute HCl, precipitated in hexane, and finally dried under vacuum.

Yield: 480 mg (95%). Extent of reduction 100%; ^{1}H-NMR (400 MHz, CDCl$_3$—CD$_3$OD, ppm): 1.3, 1.7 (br.s, CH$_2$ CH), 6.4 to 7.4 (m, Ar—H); ^{13}C-NMR (100 MHz, CDCl$_3$—CD$_3$OD,

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based on PHPES and related polymers.
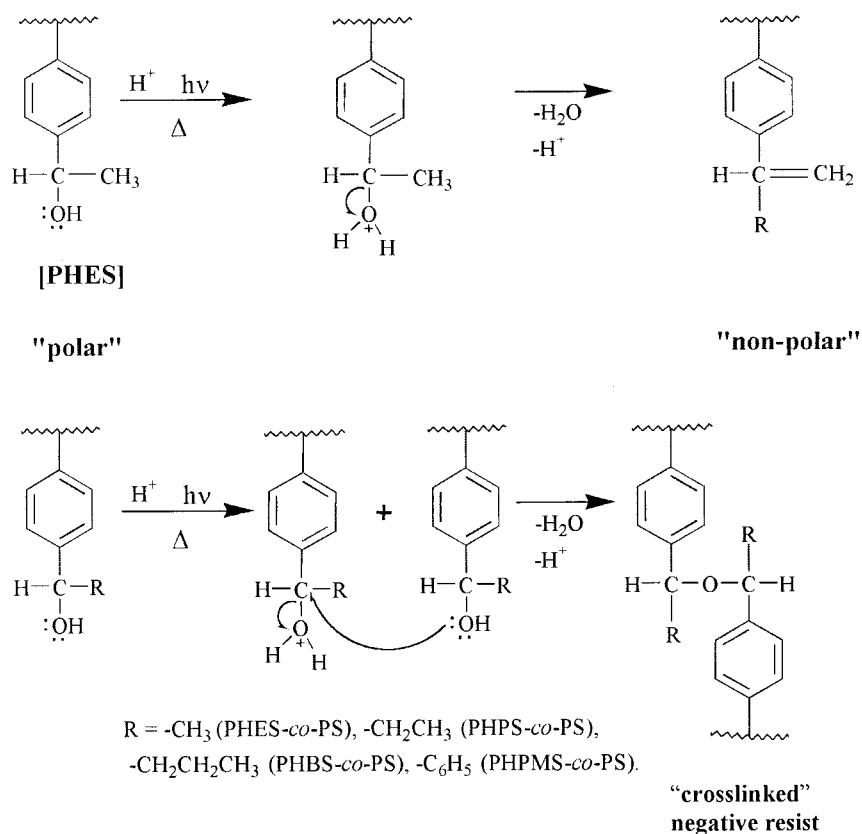
Scheme 3

ppm): 40.1 (CH$_2$, CH), 75.7 (C—OH), 126, 127, 128, 141, 144 (Ar—C); IR film form ν, cm^{-1}: 3397 (–OH), 3025 (m, Ar—C—H), 2922 (s), 1601 (s, Ar—C=C), 1491, 1449, 1175, 1016, 700; UV in PGMEA λ_{max}: 257 nm.

Photolithographic process

Silicon wafers were cleaned with electronic-grade acetone and methanol to remove any organic material present, followed by rinsing with electronic-grade 5% HF, and finally with double-distilled water and dried in oven at 120°C for 2 h. The designed formulation in the given solvent was applied to clean silicon wafer by spin coating at 4000 rpm for 30 s to obtain a very thin layer of photoresist formulation ($\sim$ few thousand Angstroms; color of the film varied from green to purple at normal incidence). Then the wafer was pre-baked at 80°C for the desired time after which it was exposed to UV radiation through a mask for the desired time. After the exposure, the wafer was post-baked (PEB) for the desired time at 120°C and was developed in the appropriate developing solution based on the type of photoresist. It was then thoroughly washed with double-distilled water after which it was once again heated at 80°C for 10 min to

remove traces of water as well as to harden the pattern formed. Finally it was viewed through an optical microscope for the developed features. The entire photolithographic process was performed in the laboratory of Prof. K. N. Bhat of the Electrical Engineering department at I.I.T. Madras. The masks used were from this laboratory as well. The image viewing was done at G.S. Gill Research Institute, Gurunanak College (courtesy of Shajahan Johny) and Center for Ceramic Technology, Anna University (courtesy of Dr. P. Manohar and R. V. Mangalaraja). Several photoresist formulations consisting of PHES and its copolymers with PS, PHPS-*co*-PS, PHBS-*co*-PS, and PHPMS-*co*-PS with a photoacid generator were developed.

RESULTS AND DISCUSSION

Recently, Ito et al.[4] reported on the synthesis of poly(4-(1-hydroxy-1-phenylethyl)styrene [PHPES] from the monomer 4-(1-hydroxy-1-phenylethyl)styrene. This polymer was reported to be the only example of a dual-tone imaging material based on polarity change from a polar to nonpolar state upon exposure to radiation (see Scheme 3) and is possibly the most sensitive
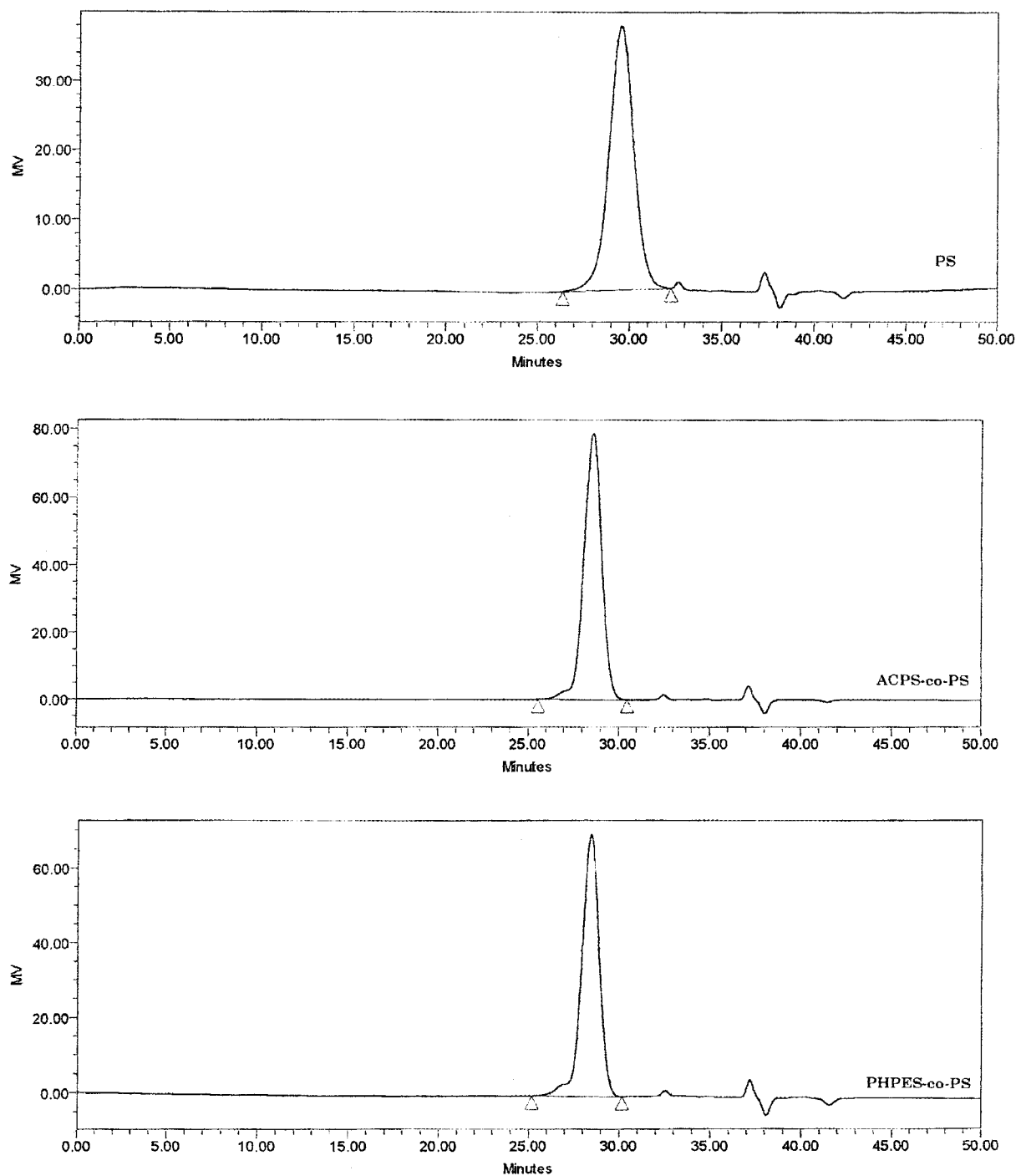
Figure 1   GPC chromatograms of PS, ACPS-*co*-PS (36 mol % the acetyl group), and PHES-*co*-PS (36 mol % of hydroxyl group) corresponding to Table I, entry 1.

resist known.[4,5] The reported synthetic methodology of this polymer involves the synthesis of the monomer 4-(1-hydroxy-1-ethyl)styrene by the reaction of a methyl Grignard reagent with 4-benzoylstyrene. It is important to note that the synthesis of the polymer [PHPES] from the monomer took 8 days.[5] Based on the mechanism of photoresist functioning, given in Scheme 3, it is clear that the desired functional groups can also be introduced by the chemical modification of polystyrene, which in turn can be achieved in a much shorter time than 8 days. Therefore, the synthesis of PHPES, its copolymers, and the related copolymers were undertaken starting from PS as detailed below. It must be emphasized here that we previously reported on the synthesis of polymers carrying glycerol[10] and hydroxy barbiturate pendant groups[11] by the chemical modification of PS.

TABLE II
List of PrPS-*co*-PS, PHPS-*co*-PS, BuPS-*co*-PS, PHBS-*co*-PS, BPS-*co*-PS, and PHPMS-*co*-PS Copolymers Synthesized[a]

Entry	Mol % acylated[b]	Copolymer	Mol % (–OH group)	Polymer identification
1	2	PrPS-*co*-PS	2	PHPS-*co*-PS
2	7	PrPS-*co*-PS	7	PHPS-*co*-PS
3[b]	39	PrPS-*co*-PS	39	PHPS-*co*-PS
4	60	PrPS-*co*-PS	60	PHPS-*co*-PS
5	2	BuPS-*co*-PS	2	PHBS-*co*-PS
6	18	BuPS-*co*-PS	18	PHBS-*co*-PS
7[b]	40	BuPS-*co*-PS	40	PHBS-*co*-PS
8	64	BuPS-*co*-PS	64	PHBS-*co*-PS
9	10	BPS-*co*-PS	10	PHPMS-*co*-PS
10	26	BPS-*co*-PS	26	PHPMS-*co*-PS
11[b]	46	BPS-*co*-PS	46	PHPMS-*co*-PS
12	67	BPS-*co*-PS	67	PHPMS-*co*-PS
13	77	BPS-*co*-PS	77	PHPMS-*co*-PS
14	83	BPS-*co*-PS	83	PHPMS-*co*-PS
15	~100	BPS-*co*-PS	100	PHPMS

[a] Commercial PS of $M_n = 145,800$; PDI = 1.3 was used for acylation reaction.
[b] PS synthesized by ATRP, $M_n = 2500$; PDI = 1.19.

The synthesis of PS with acetyl functional group was performed by the Friedel–Crafts acylation reaction using acetyl chloride, as reported before.[12] Several copolymers, as listed in Table I, with varying degrees of acetylation, briefly referred to as ACPS-*co*-PS, were synthesized by varying the concentration of acetyl chloride. The extent of acetylation was determined by

^{1}H-NMR from the integrated peak areas under the –CO—CH₃ protons and the aromatic protons. These data are reliable to within ±2 mol %. Initially, commercially available polystyrene (PS; $M_n = 145,800$; PDI = 1.3) was used for the acetylation reaction. However, some polymers required for the testing of lithographic performance (lower molecular weight polymers of narrow polydispersity are required for this purpose) were synthesized by living anionic polymerization of styrene initiated by *sec*-butyl lithium in benzene as well as by the bulk ATRP of styrene with the system 1-phenylethyl bromide/Cu(I)Br/PMDETA at 90°C.

^{1}H-NMR, ^{13}C-NMR, and other spectroscopic data characteristic of ACPS were previously reported.[13] From the ratio of the integrated areas under the aliphatic protons and the aromatic protons the extent of acetylation was evaluated. For the quantitatively acetylated PS [ACPS] it was 1.5 : 1. The GPC of one of the PS samples used for acetylation (Table I, entry 1) and that of ACPS-*co*-PS (36 mol %) obtained from this polymer are shown in Figure 1. Based on the extent of acetylation obtained from NMR the M_n of ACPS-*co*-PS should be 3300. However the M_n obtained from GPC (based on narrow molecular weight PS calibration) was 3900. This is not surprising because the hydrodynamic dimensions of ACPS-*co*-PS are bound to be different from those of PS of similar molecular weight and therefore a precise analysis of molecular weight changes cannot be assessed from GPC data. The other
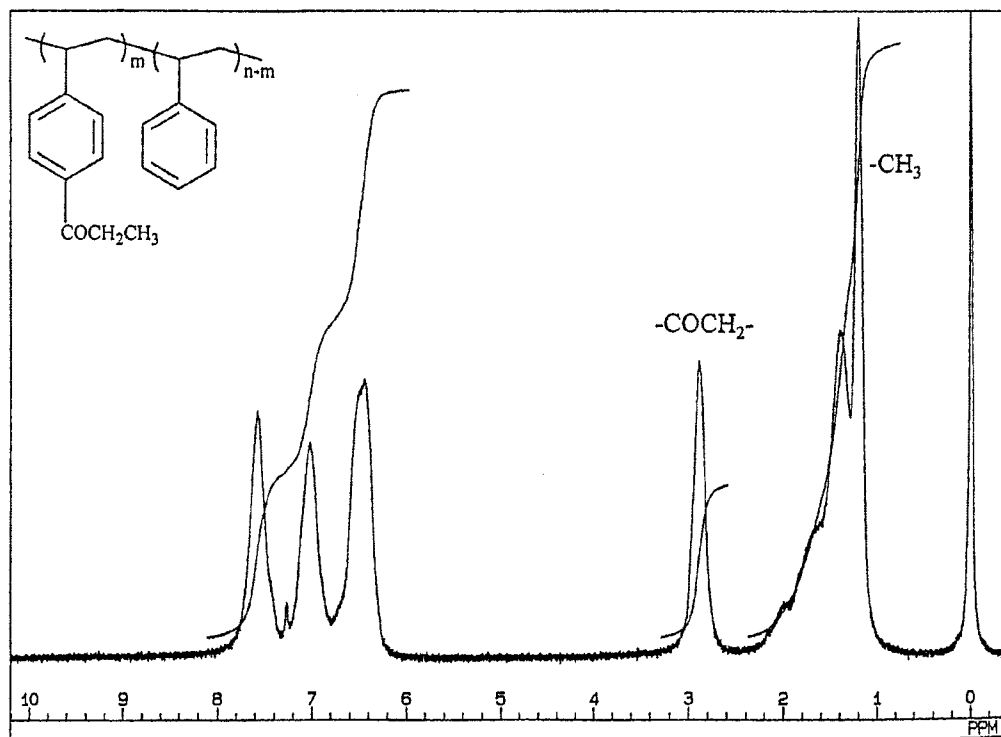

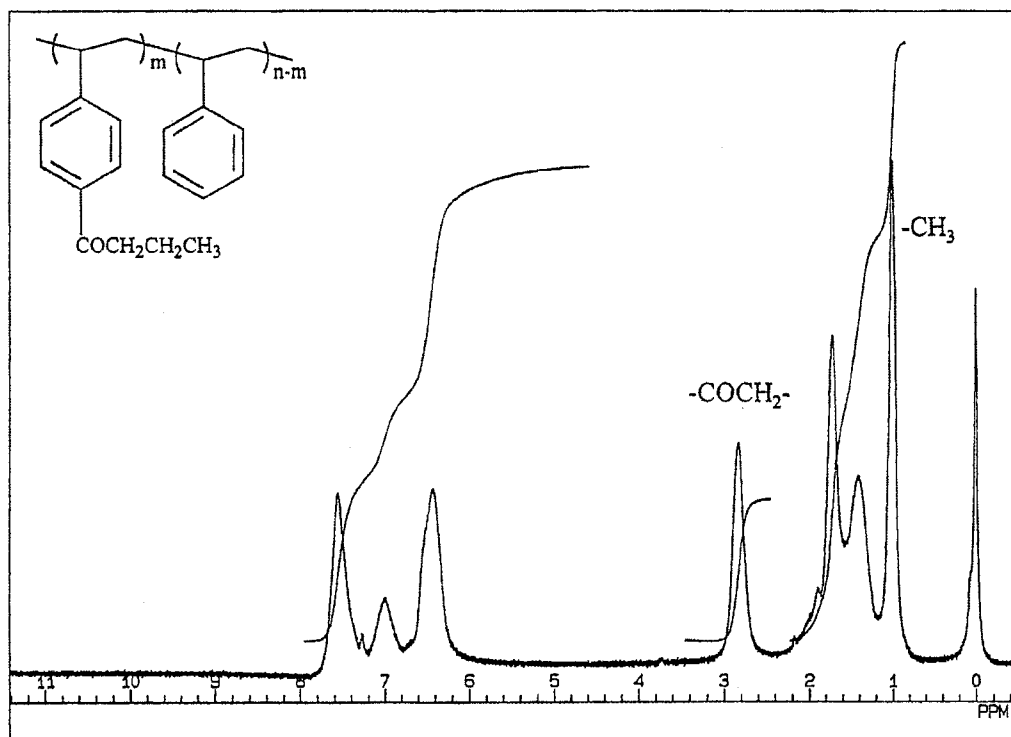**Figure 2** ^{1}H-NMR spectrum of PrPS-*co*-PS (60 mol % of the propionyl groups).

Figure 3 ¹H-NMR spectrum of Bu-*co*-PS (64 mol % of the butyroyl groups).

spectroscopic data of ACPS-*co*-PS were consistent with those reported earlier for ACPS.[12,13]

The synthesis of propionylated, butroylated, and benzoylated polystyrene was also performed accord-

ing to the methodology used for acetylation. The general synthetic procedure is presented in Scheme 1 and the list of polymers synthesized is given in Table II. The ¹H-NMR spectra of PrPS-*co*-PS (60 mol % propi-
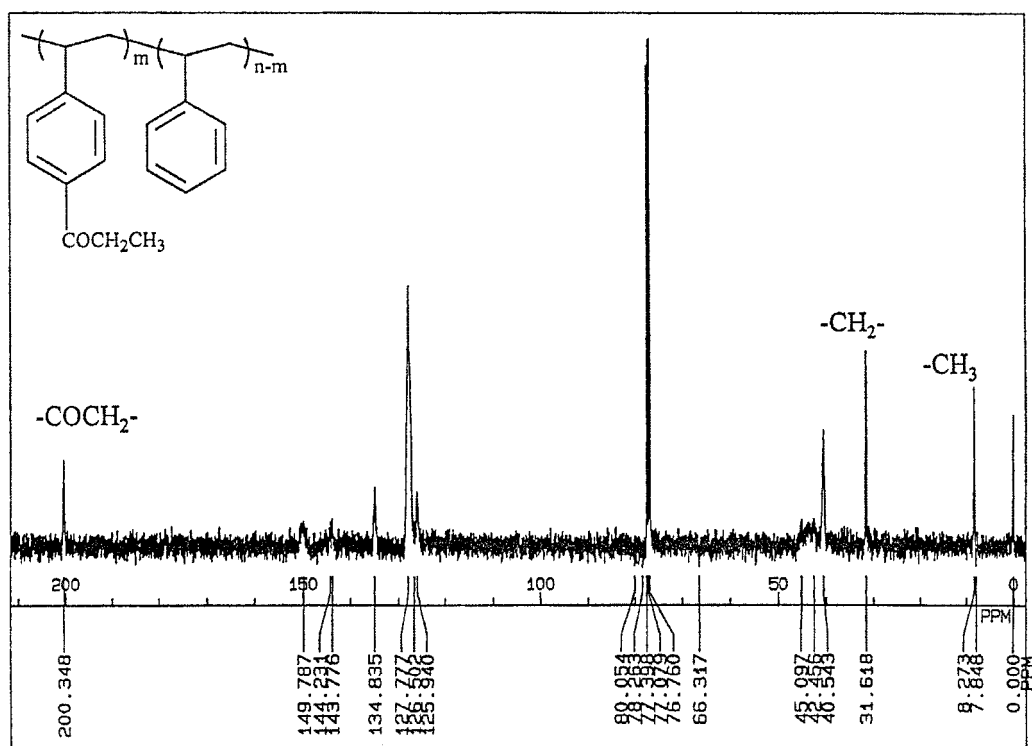

Figure 4 ¹³C-NMR spectrum of PrPS-*co*-PS (60 mol % of the butyroyl groups).
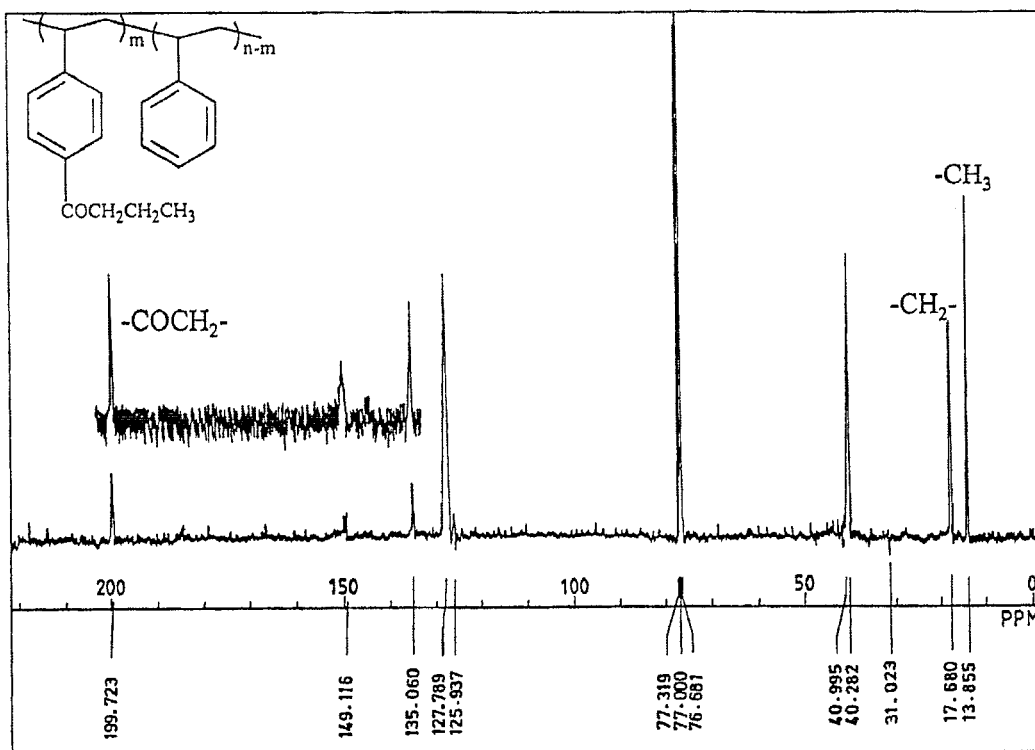
Figure 5 ^{13}C-NMR spectrum of Bu-*co*-PS (64 mol % of the propionyl groups).
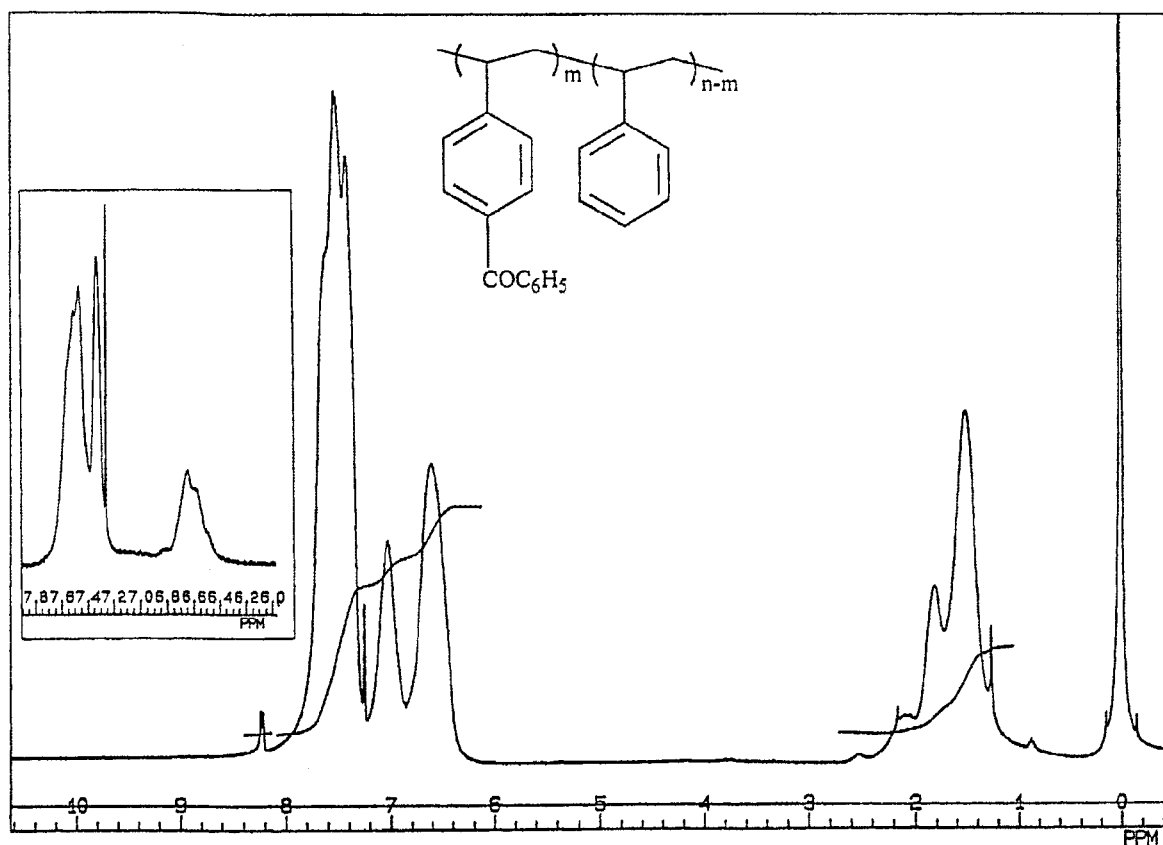

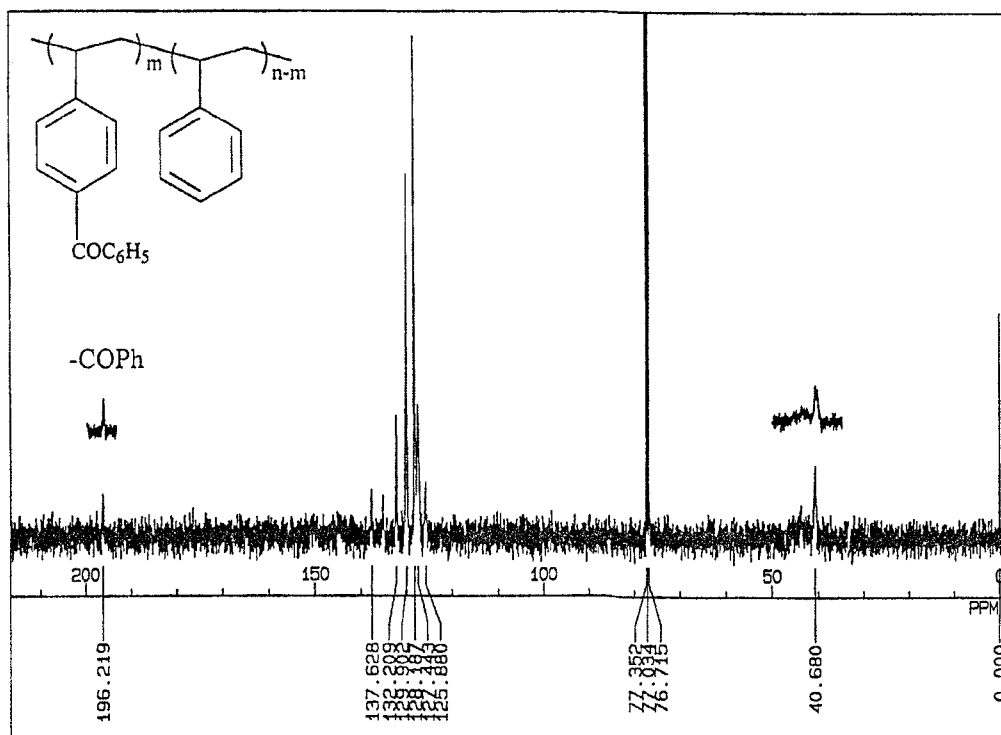**Figure 6** ^{1}H-NMR spectrum of BPS-*co*-PS (77 mol % of the benzoyl groups).

Figure 7 ^{13}C-NMR spectrum of BPS-*co*-PS (77 mol % of the benzoyl groups).

noyl groups) and BuPS-*co*-PS (64 mol % butyroyl groups) are shown in Figures 2 and 3. The extent of propionylation and butyroylation in all these copolymers was estimated from the integrated peak areas under the –CO—CH$_2$ protons and the aromatic protons. The ^{13}C-NMR spectra of PrPS-*co*-PS (60 mol %
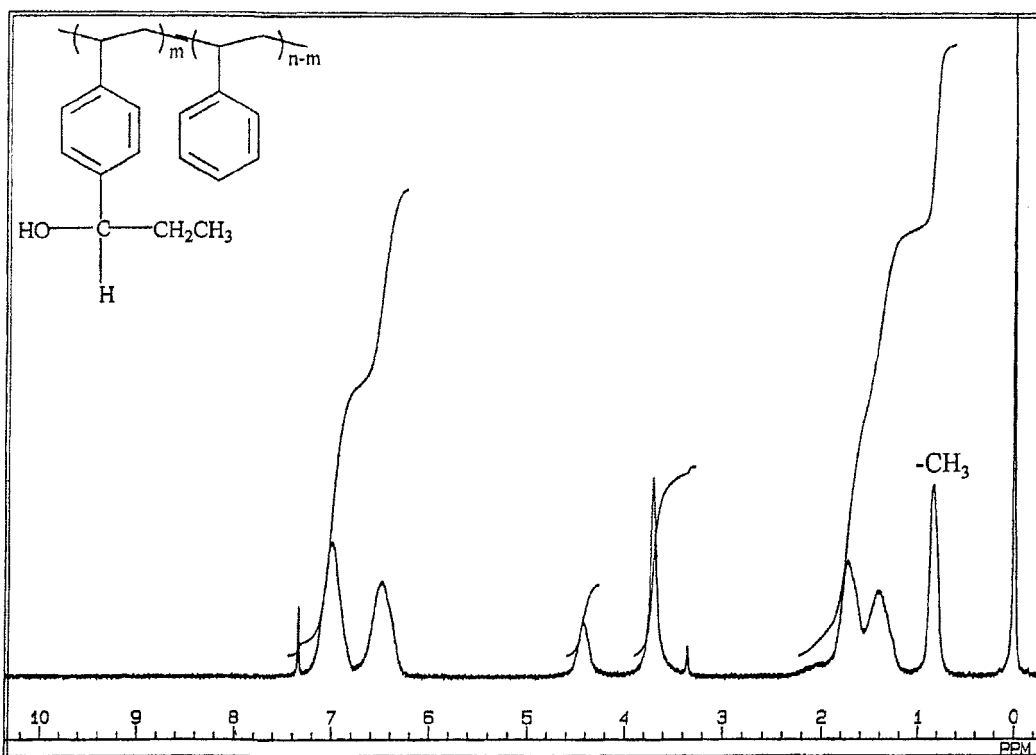

Figure 8 ^{1}H-NMR spectrum of PHPS-*co*-PS obtained by the complete reduction of PrPS-*co*-PS (60 mol % of the propionyl groups).

TABLE III
Deep-UV Photoresist Formulation Tested[a]

Entry	Mol % (–OH group)	M_n (of PS)	Polymer	Weight % polymer	PAG (w/w)
1	36	2800	PHES-*co*-PS	14	5%
2	36	2800	PHES-*co*-PS	13	5%
3	36	2800	PHES-*co*-PS	10	5%
4	99	2500	PHES	18	5%
5	99	2500	PHES	12	5%
6	58	CP[b]	PHES-*co*-PS	10	5%

[a] PGMEA was the casting solvent in all the formulations.
[b] CP, commercial PS of $M_n = 145,800$, PDI = 1.3 was used.

propinoyl groups) and BuPS-*co*-PS (64 mol % butyroyl groups) are shown in Figures 4 and 5, respectively, along with the peak assignments. The FTIR of these copolymers exhibit the characteristic aromatic ketone stretch between 1681 to 1682 cm^{-1} over and above the characteristic peaks of PS as detailed in the experimental section.

PS was benzoylated using a procedure that is a mild modification of that reported widely in the literature.[9] Thus BPS was prepared by Friedel–Crafts benzoylation of PS in dichloroethane and nitrobenzene using benzoyl chloride and aluminum chloride. Polymers with different extents of benzoylation were prepared by adding required quantities of benzoyl chloride and DCE was used as the solvent. The list of BPS-*co*-PS polymers synthesized and the extent of reaction (as estimated by 400 MHz ^{1}H-NMR) are summarized in Table II. The ^{1}H-NMR spectrum of BPS-*co*-PS (77 mol % benzoyl groups) is shown in Figure 6. The extent of benzoylation was estimated from the integrated peak areas under the aliphatic protons and the aromatic protons. The ^{13}C-NMR spectrum of BPS-*co*-PS (77 mol % benzoyl groups) is shown in Figure 7 along with assignments. The FTIR of these copolymers exhibit the characteristic benzophenone-type ketone stretch at 1658 cm^{-1} over and above the characteristic peaks of PS as detailed in the experimental section.

Pendant secondary hydroxyl functionality was introduced in each one of the copolymers synthesized by the NaBH$_4$ (mediated) reduction of ACPS-*co*-PS, PrPS-*co*-PS, BuPS-*co*-PS, and BPS-*co*-PS carried out in chloroform in the presence of a small quantity of methanol (so that the reduced polymer would remain in solution). The reduction is deemed to be complete (100%) if all the carbonyl groups are converted to the hydroxyl groups as confirmed by proton NMR spectroscopy (that is the signal corresponding to the –CO—CH$_3$ or –CO—CH$_2$ protons, as the case may be, vanishes). An example corresponding to the complete reduction of PrPS-*co*-PS to PHPS-*co*-PS is shown in Figure 8. Further, the disappearance of the peak corresponding to the –C=O stretch in the FTIR (experimental section) spectrum can also be taken as additional proof for the complete reduction of the polymer. The general synthetic procedure followed is presented in Scheme 2, whereas Tables I and II list the polymers of PHES-*co*-PS, PHPS-*co*-PS, PHBS-*co*-PS, and PHPMS-*co*-PS synthesized. The GPC of PHES-*co*-PS (36 mol % hydroxyl groups) is shown as a part of Figure 1.

Preliminary evaluation of photoresist formulation based on PHES and PHES-*co*-PS copolymers

PHES and PHES-*co*-PS were dissolved in PGMEA along with the PAG, triphenylsulfonium hexafluoroarsenate, with specific compositions as mentioned in Table III. After the exposure to the deep UV radiation and postexposure bake (PEB) for the desired period, development was performed using a 1 : 1 mixture of 2-propanol and ethanol. In general, for the PHES sam-
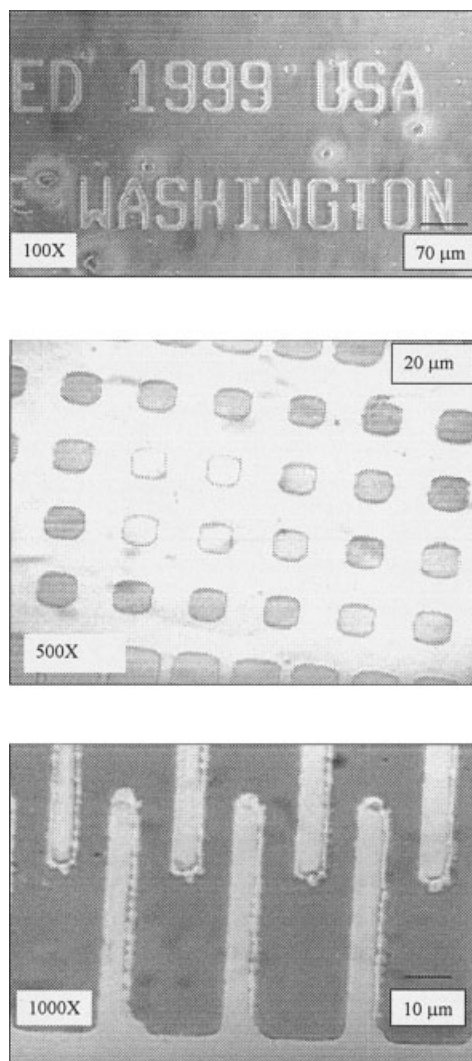

Figure 9 Optical micrographs of negative-tone images obtained from PHES-*co*-PS (Table III, entry 1) after 40 s of exposure and 10-min postexposure bake using different masks.
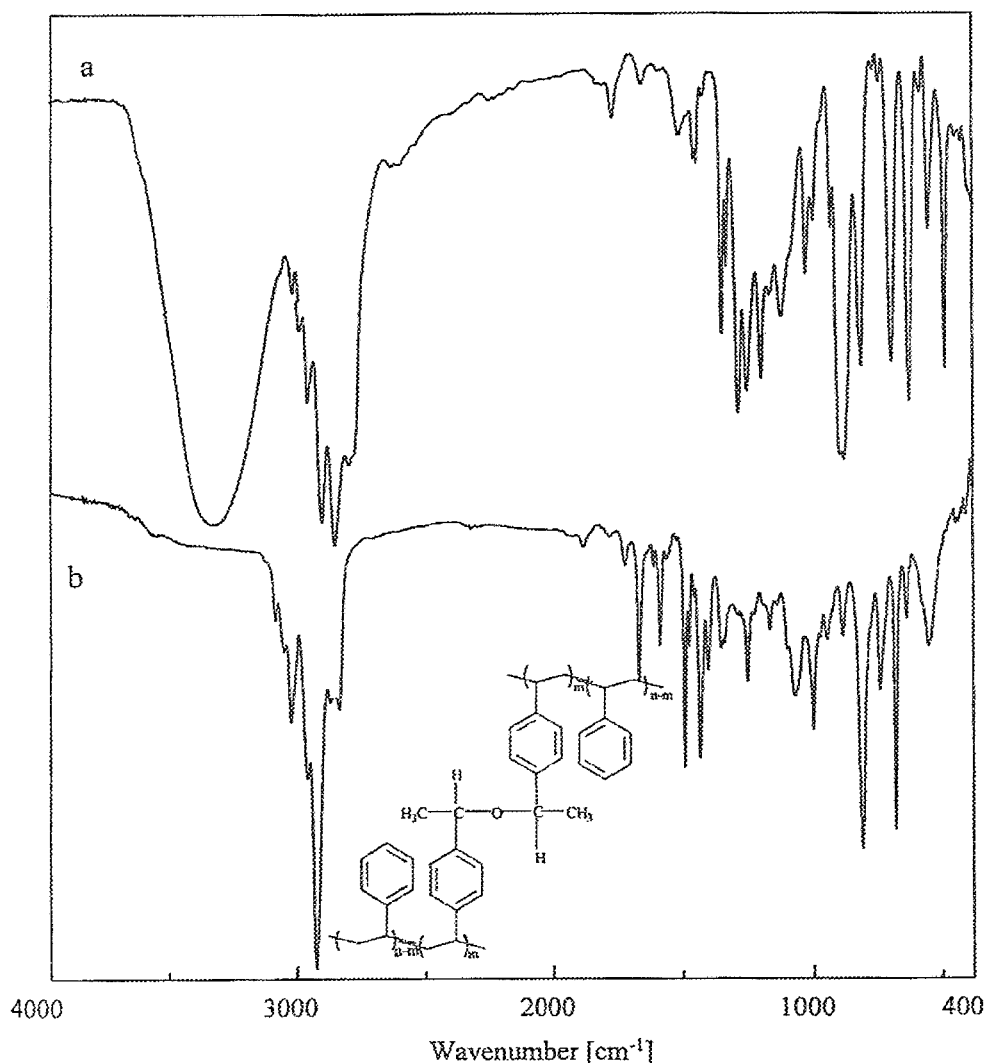
Figure 10   FTIR of PHES-*co*-PS before and after exposure to UV radiation.

ples, well-defined images with sharp boundaries were obtained after an exposure time of 40 s, and a 10-min PEB followed by development for 10 s. The minimum well-resolved feature size obtained was 3 μm. Because this material proved to be versatile in terms of ease of image development, a compositional variation study was conducted. It was observed that the PHES-*co*-PS copolymer with 36 mol % of PHES gives well-resolved patterns. A detailed investigation in terms of processing conditions such as wt % of the polymer, PAG, exposure time, and postexposure bake was conducted with this copolymer. A summary of the outcomes indicated that reasonably good results are obtained after a minimum exposure time of 15 s to the radiation followed by 5 min PEB. Some examples from the negative-tone images obtained (for various masks while fixing the exposure time and PEB to 40 s and 10 min, respectively) obtained are shown in Figure 9.

To understand the structural changes accompanying exposure to UV radiation and PEB in the presence

of the photogenerated acid, the FTIR characterization of all the copolymers under the same conditions as used in image development was performed. The FTIR spectra of PHES-*co*-PS before and after exposure are shown in Figure 10. It was observed that the –OH peak present in PHES-*co*-PS disappears completely after the exposure to UV radiation for 120 s and a PEB of 20 min at 120°C. In addition to this a less-intense peak attributed to the carbonyl group attached to aromatic moiety appears at 1680 cm^{-1}. This is similar to that observed in the precursor (i.e., ACPS-*co*-PS) and suggests that radiation in all probability transforms some of the alcohol functionality to the ketone functionality, although no simple mechanism can be proposed for this transformation. Based on the FTIR studies, a mechanistic scheme is proposed for the chemical transformations taking place in the latter part of Scheme 3. In all these cases, acid-catalyzed intermolecular dehydration, which induces crosslinking through self-condensation, appears to be the major

transformation. The protons for the transformation are introduced by the exposure of the PAG to the DUV part of the UV radiation used. Because of this the exposed regions are insoluble in the 2-propanol : ethanol (1 : 1) mixture and negative-tone images are obtained. It must be emphasized here that more detailed studies related to the sensitivity, contrast, etching rate, and normalized thickness will have to be carried out and the present work simply attempts to establish that the copolymers synthesized by the chemical modification route can be potentially useful as the PHPES polymer synthesized from the monomer.

CONCLUSIONS

The utility of the chemical modification of polystyrene toward the synthesis of a series of copolymers of styrene such as PHES, PHES-co-PS, PHPS-co-PS, PHBS-co-PS, and PHPMS-co-PS was demonstrated. The new polymers were thoroughly characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR, and UV spectroscopies and were shown to possess the desired structural features. Chemical modification of polystyrene can be considered as an alternative route for the synthesis of polymeric materials useful as dual-tone and negative-tone photoresist materials. Thus a preliminary lithographic performance evaluation of one of the newly synthesized copolymers with pendant secondary alcohol functionality was carried out. The optical micrographs thus obtained indicate that the new material promises to be a negative-tone material. Although resist sensitivity, contrast, resolution, and three-dimensional appearance of the images could not be examined in detail the results obtained clearly illustrate the importance of compositional control by polymer modification chemistry on the ability to synthesize new photoresist materials. In synthesizing copolymers by the polymer modification chemistry one can have wider control over the composition or the mol % functional groups. Based on this, it is possible to predesign the

solubility of the polymer after the exposure to the desired radiation (for ease of development).

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