

Facile Synthesis of Poly(4-hydroxy styrene) from Polystyrene

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ABSTRACT: A facile methodology to modify polystyrene, to incorporate alkali soluble hydroxy groups, is reported. Polystyrene of well-defined number-average molecular weights in the range of 3000 to 50,000 were prepared by suspension polymerization at 80°C by varying the relative mole ratio of carbon tetrachloride, used as chain transfer agent. Polystyrenes were acetylated; the acetyl groups were converted to acetoxy groups, by Baeyer–Villiger oxidation, and hydrolyzed in a nonaqueous alkaline medium to generate hydroxy groups. The extents of modifications were

monitored by infrared spectroscopy. The glass transition temperatures of poly(4-acetylstyrene-*co*-styrene), poly(4-acetylstyrene-*co*-4-acetoxystyrene-*co*-styrene), and poly(4-hydroxystyrene-*co*-4-acetylstyrene-*co*-styrene) were 107, 134, and 142°C, respectively. The polymers were evaluated in photoresist formulations. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3192–3201, 2004

Key words: lithography; photoresists; imaging

INTRODUCTION

Polymeric materials which undergo image-wise light-induced reactions are of technological importance. Photolithography is used in the printing industry, in photomachining of fine parts, and more recently, to delineate the tiny features that make up LSI, VLSI, ULSI, the modern integrated circuits.¹ The polymeric materials, used as radiation-sensitive resist films, must be designed to exhibit specific requirements of lithographic technology and device process. Although these requirements vary according to radiation source and device process, the properties that are required for high-resolution imaging systems are as follows: (1) sensitivity, (2) contrast, (3) resolution, (4) etching resistance, (5) shelf life, (6) and purity. All the commercial photolithographic devices used currently are in the 193- to 436-nm ultraviolet radiating region. Conventional G-line (436 nm) lithography employing 0.4- μm -high numerical aperture reduction lenses is used in devices that feature 0.8- μm regime. I-line (365 nm) lenses are available that feature a 0.5- μm regime. Deep UV (230–260 nm) systems have become effectively competent with I-line technology for features of 0.4- μm level.²

The recent technique is to develop photoresist materials for far ultraviolet region, having higher integration and higher operation speed. Particularly, device

generations will be produced with lithography systems employing shorter wavelengths by using KrF excimer laser light (248 nm), ArF excimer laser light (193 nm), and F₂ excimer laser light (157 nm) to produce patterns of size of 0.3 μm or less.³ Cresol-formaldehyde condensation polymers (ortho novalacs), with diazonaphthoquinone sulfonate esters as sensitizers, are used in photoresist formulations that use 436-, 405-, and 365-nm regions. The condensation polymerization of cresol with formaldehyde is difficult to control and results in a relatively low molecular weight polymer with number-average molecular weight (M_n) around 2500 and with a broad dispersity (20–40). Tight tolerances required for the modern photolithographic systems are met by exact fractionation of the polymer to obtain very narrow molecular weight distribution.⁴ The glass transition temperatures of these polymers are in the range (20–120°C) depending on molecular weight. Ortho novalacs can be replaced by poly(4-hydroxy styrene) (PHS) specifically to increase the binding efficiency. The molecular weight distribution of PHS, prepared by vinyl polymerization, can be exactly controlled as compared to ortho novalacs. The glass transition temperature of PHS is in the range (135–180°C) depending on the molecular weight, which allows higher pre- and post-bake temperatures for greater throughput and good image stability while the pattern is being transferred. Despite these advances, this system has been found to perform poorly as a photoresist because of low contrast due to excessive dissolution of the unexposed areas during the development step.⁵ This drawback

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can be circumvented by using a copolymer of styrene and hydroxy styrene.

Ito et al. introduced the concept of chemical amplification to develop high-resolution, dual-tone resist based on nonionic acid precursors (nitrobenzyl ester) photochemistry and poly[(4-*tert*-butoxycarbonyloxy]styrene.^{6,7} Poly(4-hydroxy styrene), of weight-average molecular weight in the range 8000 to 25,000 and a molecular weight distribution of 1.5 or less, with 10 to 60 mol % of the hydroxyl groups derivatized into *tert*-butoxycarbonyloxy groups, is used as a resist component along with a light sensitive compound such as nitrobenzyl tosylate ester in the deep ultraviolet region.⁸ Poly(4-hydroxy styrene) is particularly useful in the deep ultraviolet region of the spectrum because of its low light absorption as compared to commonly used ortho novolac resins. Poly(4-hydroxy styrene) functionalized with *t*-butoxycarbonyl has advantages over nonfunctionalized poly(4-hydroxy styrene) because the *tert*-butoxycarbonyl groups slow down the rate of dissolution in base, but are readily removed by traces of acid, which causes the decomposition of *t*-butoxycarbonyl groups to isobutylene and carbon dioxide.⁹ Ether derivatives of poly(4-hydroxy styrene) have been synthesized by Michael addition of an ethylenically unsaturated compound which contains an electron withdrawing group on the carbon atom alpha to unsaturation for use in photorealist application utilizing the retro-Michael reaction.¹⁰ Poly(4-hydroxy styrene) with number-average molecular weights in the range 5000–20,000, masked by thermally stable acid labile *tert*-butoxycarbonyl groups, are the primary constituents of deep ultraviolet chemically amplified liquid photoresist systems. Poly(4-hydroxy styrene) is conventionally prepared by polymerizing 4-acetoxy styrene, followed by hydrolysis. The starting monomer is prepared from 4-hydroxy benzaldehyde by Wittig reaction.

We report the synthesis of poly(4-hydroxy styrene-co-styrene) of controlled molecular weights as a replacement for *ortho*-novolacs in G and I line photoresists. This can be further modified for use in chemically amplified photoresist formulations.

EXPERIMENTAL

Styrene, carbon tetrachloride, acetyl chloride, anhydrous aluminum chloride, trichloroacetic acid, sodium perborate, sodium hydroxide, methanol, and acetone were procured from S.D. Fine Chemicals (India). PHS with 100% hydroxy groups, having weight-average molecular weight (M_w) of 8000, used as standard was obtained from Aldrich Chemicals. All the solvents were distilled and used as per standard procedure.¹¹ Shimadzu infrared spectrophotometer (model IR-470) was used for IR characterization. Samples were pelletized by using KBr. The samples were characterized by

NMR spectroscopy. A Brüker-DRX-500 spectrophotometer (a supercon magnet, 500 MHz) was used to record the ¹H spectra. Mettler TA 4000 series differential scanning calorimeter with DSC 30 cell was used to determine glass transition temperature. Molecular weights of polystyrene samples were determined by gel permeation chromatography technique having a pump of Spectra Series P 100, Auto Sample Spectra Series AS 300, UV detector Spectra Series UV 100 along with Spectra System RI-150, using chloroform as the solvent.

The reaction scheme is presented in Figure 1. The four distinct phases in the synthetic methodology are as follows: (1) synthesis of oligomeric polystyrene; (2) introduction of acetyl units; (3) oxidation of acetyl to acetoxy groups; and (4) hydrolysis of acetoxy to hydroxy groups.

Synthesis of low molecular weight polystyrene

A double-walled glass reactor connected to thermostated water bath, nitrogen gas inlet, condenser, and stirrer was heated to 80°C. Nitrogen gas was purged continuously into the reactor. The reactor was charged with 25 g (0.240 mol) styrene, 0.6 g benzoyl peroxide, 2 mL 1 wt % poly(vinyl alcohol) solution, diluted to 150 mL with distilled water, and 60 mL carbon tetrachloride (chain transfer agent). The contents were stirred at 260 rotations per minute. The suspension polymerization was allowed to proceed for 16 h. The polymer formed precipitate as the polymerization proceeded. The product was filtered, washed, and dried. Polymer samples of different molecular weights were synthesized by varying the molar concentration of carbon tetrachloride (chain transfer agent) (Yield: 85%).

Acetylation of polystyrene

Polystyrene (PS) 2.6 g (0.025 mol) was dissolved in 25 mL carbon disulfide. A three-necked round-bottom flask equipped with a condenser, dropping funnel, and magnetic needle for stirring was placed in an ice-water bath. Added were 6.7 g (0.05 mol) of anhydrous aluminum chloride (AlCl₃) and 25 mL carbon disulfide and the reactants were stirred vigorously. To this solution, 2.6 mL (0.0375 mol) acetyl chloride (CH₃COCl) was added dropwise. The reaction mixture turned red, with the evolution of hydrogen chloride (HCl) gas during the addition. The reaction was continued (6 h) until the evolution of hydrogen chloride ceased. The reaction was stopped, and carbon disulfide was distilled off by using rotavapor. The residue obtained was air dried and transferred into a beaker containing 100 g crushed ice and 5 mL hydrochloric acid. Aluminum chloride decomposed and polymer was obtained as a yellow precipitate. It was

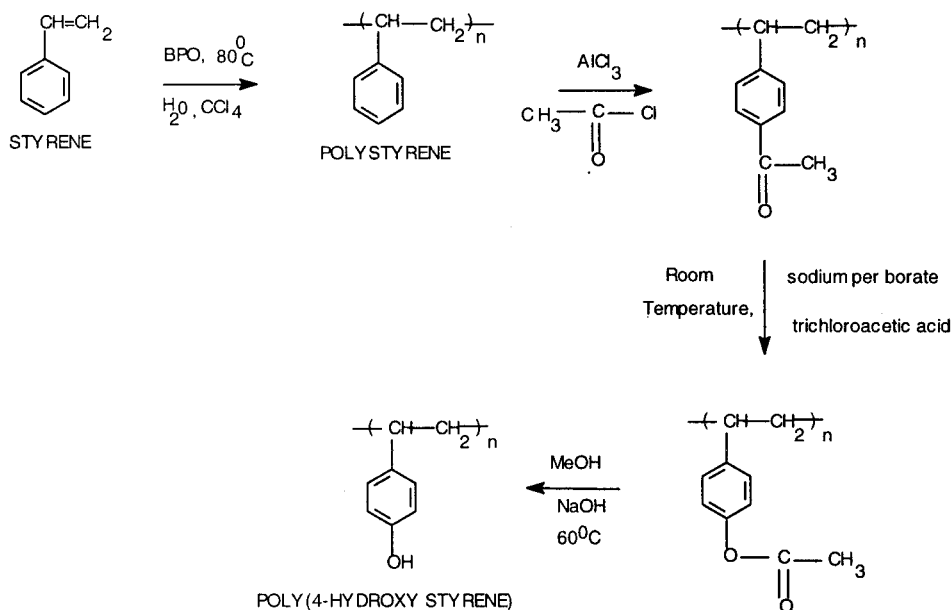


Figure 1 Reaction scheme.

filtered, dried, dissolved in acetone, and precipitated in water. The pure polymer was filtered and dried.¹² Acetylation was evaluated by using infrared (IR) spectroscopy. The parameters varied were as follows: (1) reaction time; (2) mole ratios of polystyrene : acetyl chloride : aluminum chloride (PS : RX : AlX₃); (3) molar concentration; and (4) solvent. In the optimized reaction, the yield was 55%. The changes in IR spectra peaks were as follows: 3024 cm⁻¹ (m, Ar—C—H), 2192 cm⁻¹, 1680 cm⁻¹ (C=O), and 1600 cm⁻¹ (Ar—C=C).

Oxidation of poly(4-acetyl styrene-co-styrene)

Hydrogen peroxide (H₂O₂) and peracetic acid have hitherto been used to oxidize acetyl-to-acetoxy groups.¹³ We evaluated sodium perborate and trichloroacetic acid as oxidizing agents. Poly(4-acetyl styrene) (1 g repeat unit) was dissolved in 10 mL glacial acetic acid. The polymeric solution was stirred in a round-bottom flask. To the stirring solution, 3 mol sodium perborate and 4 mol trichloroacetic acid were added in small lots at regular time intervals.¹⁴ The reaction mixture was stirred at room temperature for periods up to 120 h. The reaction mixture was filtered; the filtrate was precipitated with 250 mL distilled water, washed with water, filtered, and dried¹⁵ (Yield: 70%). The product is a terpolymer of styrene, 4-acetyl styrene, and 4-acetoxy styrene. 4-Acetoxy styrene has IR peaks at ν (cm⁻¹): 3024 (m, Ar—C—H), 2912 (s) 1753 (s, O—C=O), 1680 (C=O) 1600 (s, Ar—C=C), 1500, 1414, and 1200.

Hydrolysis of poly(4-acetylstyrene-co-4-acetoxystyrene-co-styrene)

Sodium hydroxide (0.2 g) was dissolved in 10 mL methanol, taken in a round-bottom flask equipped with a magnetic pellet for stirring and a reflux condenser. Poly(4-acetylstyrene-co-4-acetoxystyrene-co-styrene) (1 g; 0.0068 mol) was taken in round-bottom flask and heated in an oil bath at 60°C for 5 h, cooled, and filtered. The filtrate was added to 250 mL distilled water and acidified with 5 mL of concentrated hydrochloric acid. The product, obtained as a cream-colored precipitate, is poly(4-hydroxystyrene-co-4-acetylstyrene-co-styrene). The precipitate was filtered and washed with water and dried under vacuum. Yield was approximately 80%. IR spectra of 4-hydroxystyrene show peaks at 3500–3200 cm⁻¹ (Br-OH), 3024 cm⁻¹ (Ar—C—H) 2912 cm⁻¹, 1680 cm⁻¹ (C=O), 1600 cm⁻¹ (Ar—C=C), 1510, 1440, and 1219 cm⁻¹.

RESULTS AND DISCUSSION

Styrene was polymerized by suspension polymerization. The molecular weight of the polymer was controlled by addition of the chain transfer agent, carbon tetrachloride. The details of the variations in chain transfer agent added and the changes in molecular weight of the polymer obtained are tabulated in Table I. As expected, the molecular weight decreased with an increase in concentration of the chain transfer agent. GPC data (Table I) reveal a decrease in polydispersity index with increase in the relative mole ratio of the chain transfer agent to give polymers with narrow molecular weight distribution.

TABLE I
Synthesis of Polystyrene

Code No.	Chain transfer agent (CCl ₄) (ml)	M_n	M_w	Polydispersity
PS-1	—	31,520	63,300	2.01
PS-2	4.8	16,560	35,380	2.14
PS-3	10.4	10,320	20,870	2.02
PS-4	30	5,830	8,700	1.6
PS-5	40	5,590	8,700	1.55
PS-6	60	5,190	7,680	1.5

Styrene, 25 ml. Benzoyl peroxide, 0.6 g. Reaction temperature, 80°C. Reaction time, 16 h.

The acetylation of polystyrene was conducted either exclusively in carbon disulfide (CS₂) or by a partial substitution of carbon disulfide with cyclohexane. Polystyrene acetylated in CS₂ was coded as AM-11 to AM-16, whereas AM-17 to AM-22 were polymers modified in cyclohexane as solvent.

The dependence of the extent of acetylation of polystyrene with variance in solvent, reaction time, temperature, and mole ratio of acetylating agent were monitored by the reduction in IR peak at 700 cm⁻¹, which is characteristic of monosubstituted benzene¹⁶ (e.g., polystyrene). The details are presented in Table II. This strong peak is due to C—H out-of-plane deformation of five adjacent free hydrogen atoms. Similarly, the peak at 750 cm⁻¹ is due to C—H out-of-plane deformation of four adjacent free hydrogen atoms. These peaks are absent in para-disubstituted aromatic ring. The peak at 829 cm⁻¹ is due to para-disubstituted benzene ring. C—H out-of-plane deformations of two adjacent free hydrogen atoms in disubstituted aromatic compounds is observed in the 860- to 800-cm⁻¹ region.

For quantitative estimation, the IR spectrum obtained was converted to baseline corrected normalized

spectrum. In a normalized spectrum of polystyrene, the absorbance at 700 cm⁻¹ is taken as 1, because this is the major peak. In other words, the spectrum is normalized with the major absorbance peak. IR spectra of poly(4-acetyl styrene) and poly(4-acetoxy styrene) was normalized with respect to the peak at 1680 cm⁻¹, due to C=O stretching. The continued presence of the peak at 700 cm⁻¹ clearly indicates that acetylation is never quantitative. The absorbance at this peak directly depends on fraction of monosubstituted aromatic ring in the normalized IR spectra of polymers containing para-disubstituted aromatic nucleus. The progress of acetylation in lower mass analogs such as benzene, toluene, and so on depends on catalyst, acyl component, addition sequence, solvent, and ratio of catalyst to acyl component.¹⁷ The percentage yield of the product increases as the reaction time, mole ratio of acylating agent, and temperature of reaction mixture is increased. The extent of the acylation of long chain molecules, such as in the present investigation, presents difficulty in the accessibility of a particular reaction site due to conformational complexity.

The effect of reaction time, temperature, and mole ratio of catalyst to acyl component is discussed with respect to two different solvents. Polymers AM-11 to AM-16 were synthesized by using carbon disulfide as solvent. Optimally, 80% acylation can be achieved at ambient temperature in 20 h with the molar composition of the reactants PS, AlCl₃, CH₃COCl (repeat unit, ru) as 0.025, 0.05, and 0.05 mol, respectively. It was observed that acetylation reactions conducted in non-polar solvents, such as cyclohexane, *n*-hexane, CS₂, is faster than acetylation reactions conducted in halogenated solvents.¹⁸ Monosubstituted benzene (e.g., styrene) is acylated at the para position because of the large steric requirement of the attacking reagent.

TABLE II
Synthesis of Poly(4-Acetyl Styrene)

Code No.	CH ₃ COCl (mole)	Solvent	Reaction temp. (°C)	Reaction time (h)	% Acetylation
AM-11	0.05	CS ₂	RT	3	66
AM-12	0.05	CS ₂	RT	6	54
AM-13	0.05	CS ₂	RT	20	82
AM-14	0.0375	CS ₂	RT	6	72
AM-15	0.0375	CS ₂	RT	17	77
AM-16	0.0375	CS ₂	RT	20	79
AM-17	0.05	CH ^b	RT	20	62
AM-18	0.05	CH ^b	RT	42	72
AM-19	0.05	CH ^b	45	20	87
AM-20 ^a	0.0375	CH ^b	RT	42	64
AM-21	0.05	CH ^b	55	5	79
AM-22	0.05	CH ^b	55	7	88
AM-23	0.05	CH ^b : CS ₂ ^b 4 : 1 v/v	RT	20	92

Polystyrene, 2.6 g (0.025 mol). AlCl₃: 6.7 g (0.05 mol). CH, cyclohexane; RT, room temperature.
^a4.33 g.

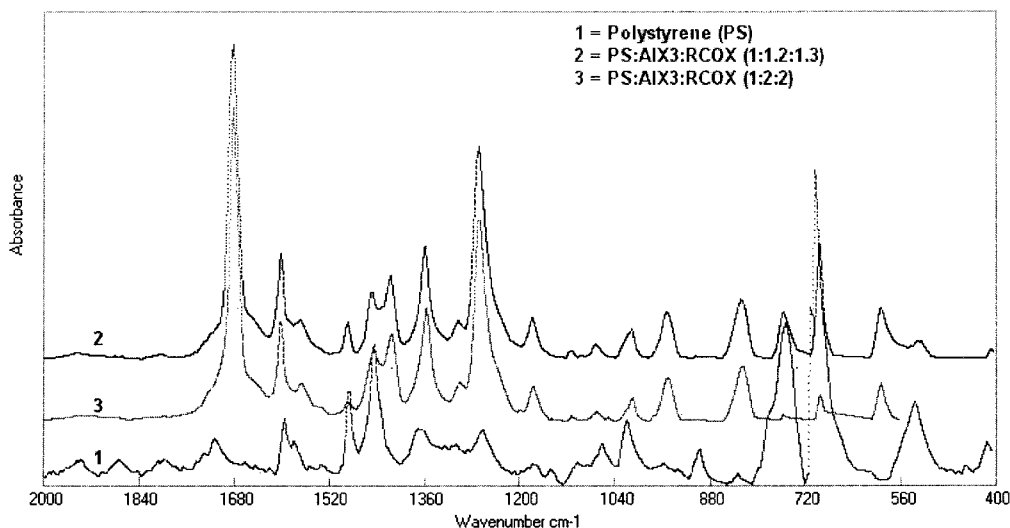


Figure 2 Comparison of infrared spectra of poly(4-acetyl styrene) with polystyrene: Effect of mole ratio of acetylating reagent.

Polymers AM-17 to AM-22 were products of acetylation in cyclohexane. IR spectra of two poly(4-acetyl styrene) samples (AM-18 and AM-20) prepared by using two different mole ratios of polystyrene to acetyl chloride are compared with polystyrene in Figure 2. The substitution reactions were conducted at the ambient (25°C) for 42 h. In Figures 2–7, the *y*-axis has arbitrary units because each spectrum is shifted upward to avoid crowding. It is evident from Figure 2 that the peak at 700 cm^{-1} is reduced drastically in the reaction where the mole ratio of reactants used is 1 : 2 (polystyrene : acetylating agent) [72%] as compared to the reaction where mole ratio of reactants used is 1 : 1.5 (polystyrene : acetylating agent) [64%]. Simultaneously, the C=O stretching peak of ketone appears at 1680 cm^{-1} . Higher extent of acetylation can be

achieved by increasing the reaction temperature from ambient to 45°C (AM-17 and AM-19). These two polymers were prepared by reacting for 20 h PS, AlCl_3 , CH_3COCl , having molar concentration of 0.025 (ru), 0.05, and 0.05 mol, respectively, at a reaction time of 20 h at 25 and 45°C, respectively. IR spectra of these two polymers are compared with that of polystyrene in Figure 3. The extent of acetylation in AM-17 and AM-19 are 62 and 87%, respectively. Reaction time can drastically be reduced to 5–7 h instead of 20 h to achieve around 85% acetylation (AM-21 and AM-22) by refluxing the reaction mixture at 55°C. IR spectra of these polymers are presented in Figure 4.

The above results indicate that acetylation reactions can be conducted in cyclohexane instead of toxic and

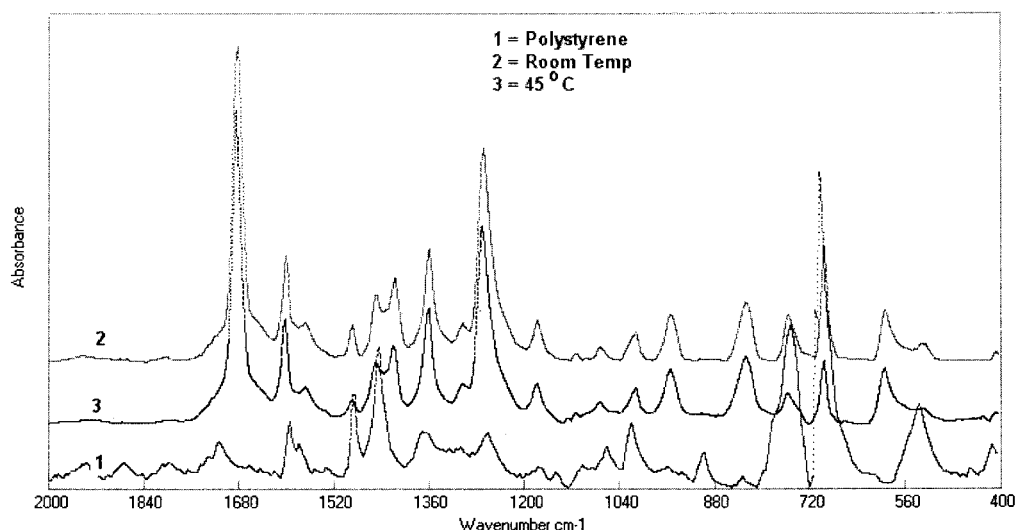


Figure 3 Comparison of infrared spectra of poly(4-acetyl styrene) with polystyrene: Effect of reaction temperature.

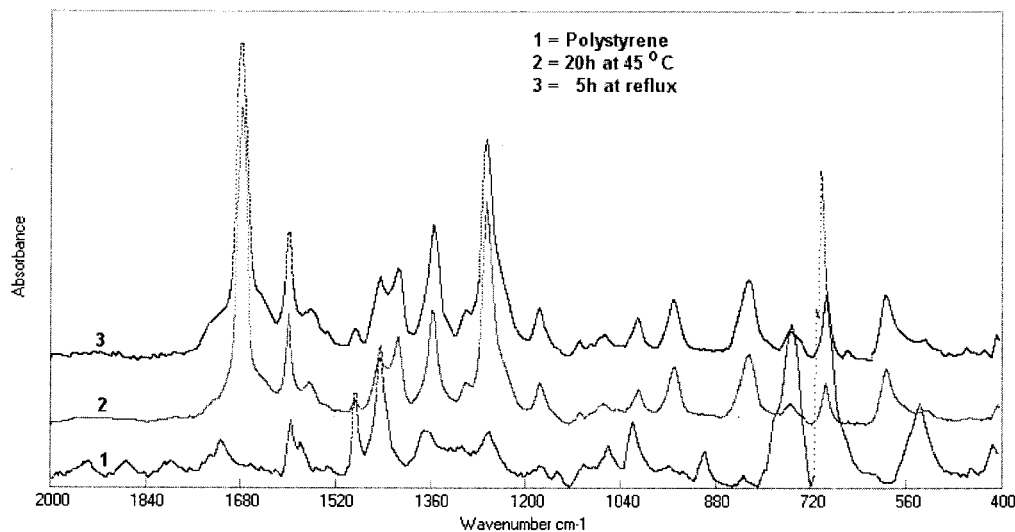


Figure 4 Comparison of infrared spectra of poly(4-acetyl styrene) with polystyrene: Reduction in reaction time under reflux condition.

flammable carbon disulfide by increasing reaction temperatures to achieve a similar extent of acetylation. Acetylation levels (AM-23) identical to that in carbon disulfide can be achieved at room temperature by a partial substitution of cyclohexane with carbon disulfide (CH : CS₂ 4 : 1 v/v) solvent mixture. The IR analysis for acetylated polymers (AM-13, AM-18, and AM-23) synthesized by using three different solvent systems is depicted in Figure 5. IR spectra in the aromatic substitution region of 900–600 cm⁻¹ of acetylated polystyrene prepared in carbon disulfide, cyclohexane, and mixed solvent system, along with polystyrene, are presented in Figure 6. This figure shows that the extent of acetylation obtained in the reaction where carbon disulfide is used is similar to the extent

of acetylation obtained in mixed solvent system (with 20% v/v of carbon disulfide in cyclohexane). This points to a possible catalytic effect of carbon disulfide in the reaction in addition to its role in solvation.

Acetoxy polystyrene is typically prepared by Baeyer–Villiger oxidation of poly(acetyl styrene). Several oxidizing agents have been reported to facilitate Baeyer–Villiger oxidation of low molar mass aromatic ketones to esters. These include permaleic acid,¹⁹ peracetic acid,²⁰ trifluoroacetic acid,²¹ and potassium peroxydisulfate.²² These oxidizing agents were evaluated for oxidation of acetyl polystyrene by Dhamodharan et al.²³ We have evaluated sodium perborate in acetic acid or acetic acid/trichloroacetic acid as oxidizing agents to effect the Baeyer–Villiger oxidation. Sodium

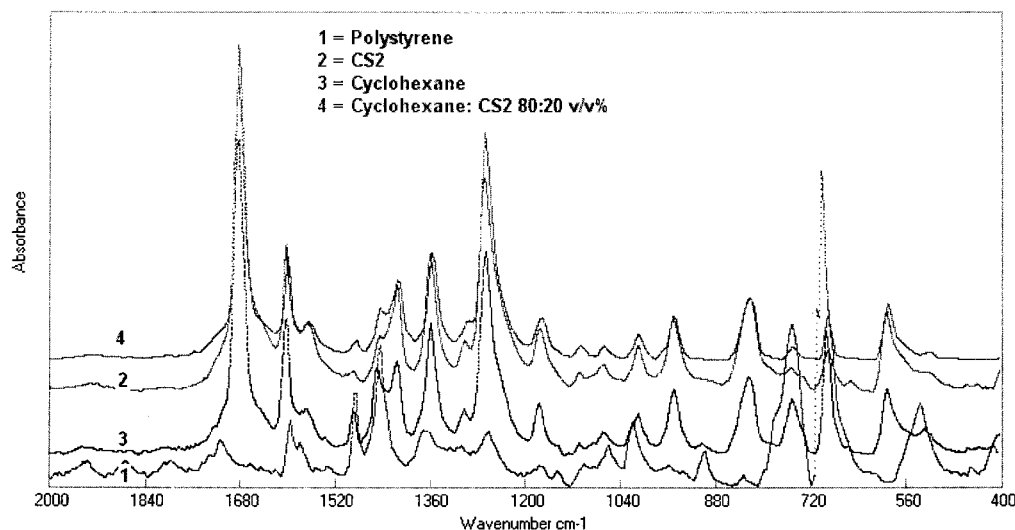


Figure 5 Comparison of infrared spectra of poly(4-acetyl styrene) with polystyrene: Effect of reaction medium.

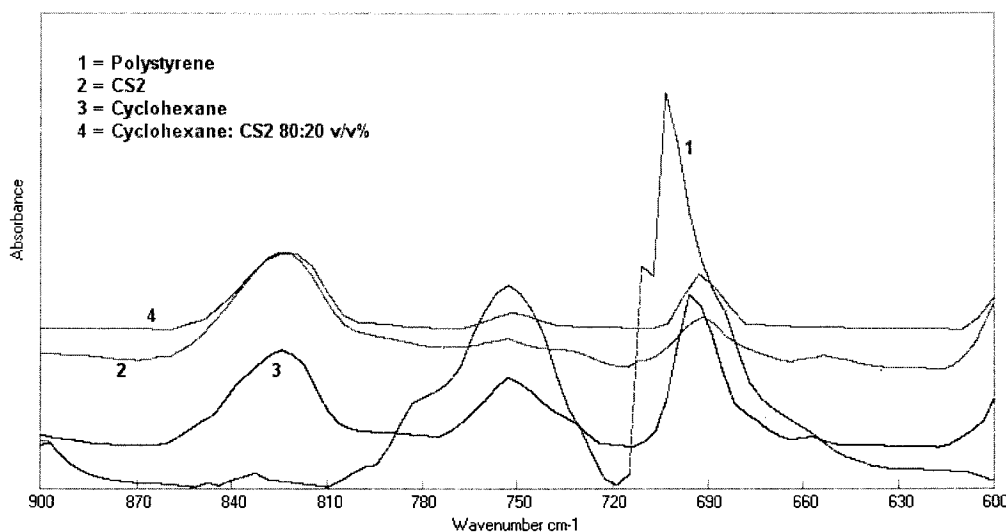


Figure 6 Comparison of infrared spectra of poly(4-acetyl styrene) with polystyrene in aromatic substitution region: Effect of reaction medium.

perborate is an industrially used source of active oxygen to cleave α -di-ketone and oxidation of aniline to azo compound. Oxidation of low molar mass sulfides to sulfoxides or sulfones and ketones to esters was studied by Mckillop et al.²⁴ We have evaluated the oxidizing agent for Baeyer–Villiger oxidation of the polymeric aromatic ketone containing at least one group of relatively high migratory aptitude, a fundamental requirement for oxidative procedure.

The results of the oxidation of acetyl polystyrene to acetoxy polystyrene under various reaction conditions are summarized in Table III. Oxidation was studied under three different sets of reactions. They are as follows: (1) variation in reaction time for sodium perborate in acetic acid (EM-1 to EM-3); (2) variation in trihaloacetic acid concentration at fixed reaction time (EM-4 to EM-6); and (3) variation in reaction time for sodium perborate in acetic acid/trihaloacetic acid mixture (samples EM-7 to EM-9).

All reactions were conducted at the ambient conditions (25°C). The oxidation yield increased from 28 to

50% with an increase in reaction time from 5 to 48 h, as observed in the first set of reactions. In Table III, % yield is given because it is difficult to quantitatively estimate spectroscopically the percentage of acetoxylation because C=O of ketone absorbs strongly in the region 1600–1840 cm^{-1} . The detailed estimation of these groups requires advanced IR peak convolution software to determine concentration of these peaks on the basis of area under the peak by using molar extinction coefficient.²⁵ IR spectra of three different acetoxy polystyrene samples with variance in oxidation time are compared in Figure 7 with poly(4-hydroxy styrene) (Aldrich standard) and parent poly(4-acetyl styrene). It is obvious from the figure that the peak at 1753 cm^{-1} due to O—C=O stretching emerges and increases with time. Partial hydrolysis is observed *in situ* when oxidation is conducted in the presence of strong trichloroacetic acid/acetic acid mixture. In the second set of experiments, yield levels off at 1 : 2 (sodium perborate : trichloroacetic acid) mole ratio. In other words, the effect of trichloroacetic acid concen-

TABLE III
Synthesis of Poly(4-Acetoxy Styrene)

Sample code	CCl_3COOH (mol)	Solvent	Reaction time (h)	%
EM-1	—	CH_3COOH	5	28
EM-2	—	CH_3COOH	24	29
EM-3	—	CH_3COOH	48	50
EM-4	0.0136	CH_3COOH	48	36
EM-5	0.0272	CH_3COOH	24	50
EM-6	0.0408	CH_3COOH	24	66
EM-7	0.0544	CH_3COOH	24	65
EM-8	0.0204	CH_3COOH	72	55
EM-9	0.0204	CH_3COOH	96	65
EM-10	0.0204	CH_3COOH	120	75

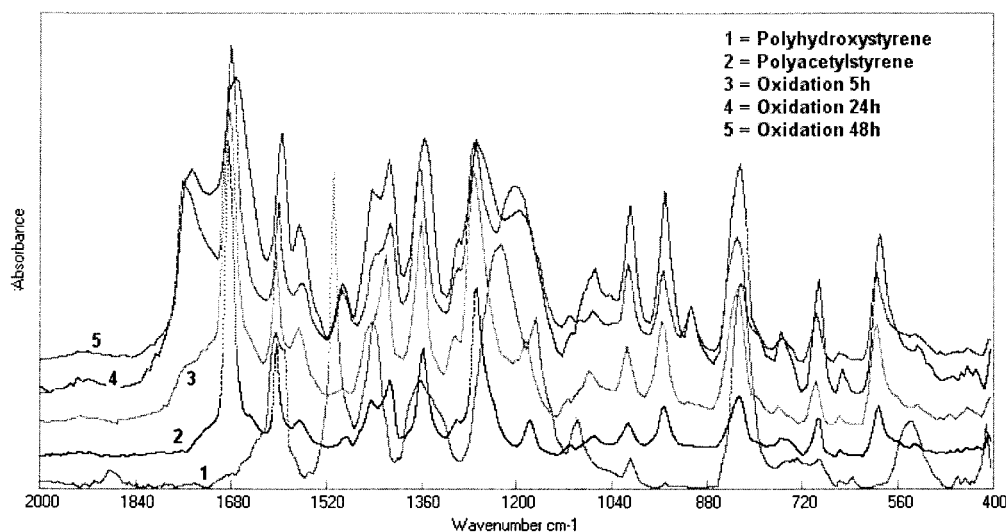


Figure 7 Comparison of infrared spectra of poly(4-acetyl styrene) with polystyrene and polyacetyl styrene: Effect of oxidation time.

tration levels off above 1 : mole ratio (sodium perborate : trichloroacetic acid). The final experimental set indicates an increase in yield from 55 to 75% as the reaction time was increased from 72 to 120 h, at room temperature. In this set, mole ratio of sodium perborate to trichloroacetic acid was kept constant (i.e., 1 : 1).

Acetoxy groups were hydrolyzed to hydroxy groups by alcoholic alkaline hydrolysis. In Figure 8, the IR spectra of synthesized poly(4-hydroxy styrene) is compared with poly(4-hydroxy styrene) obtained from Aldrich Chemicals. All peaks except that at 1680 cm^{-1} are found to match, which is due to unconverted acetyl groups. The conversions in each step was studied by NMR spectroscopy. Figure 9(a–e) shows the

NMR spectrum of polystyrene, poly(acetylstyrene-*co*-styrene), poly(acetoxystyrene-*co*-acetylstyrene-*co*-styrene) (CDCl_3 as solvent), poly(hydroxystyrene-*co*-acetoxystyrene-*co*-styrene), and standard poly(4-hydroxy styrene) from Aldrich (acetone- d_6 as solvent), respectively. Figure 9(a) shows the NMR spectrum of polystyrene in CDCl_3 . Figure 9(b) shows the NMR spectrum of poly(acetylstyrene-*co*-styrene) in CDCl_3 . In this spectrum, the broad peak at 7.14 ppm present in Fig. 9(a) is lowered, whereas a new peak at 7.58 appears that is due to protons ortho to acetyl groups. Appearance of broad peak at 2.54 ppm is due to $-\text{CH}_3$ of acetyl moiety. Figure 9(c) shows the NMR spectrum of poly(acetoxystyrene-*co*-acetylstyrene-*co*-styrene) in CDCl_3 . The broad peak at 2.54 is shifted to

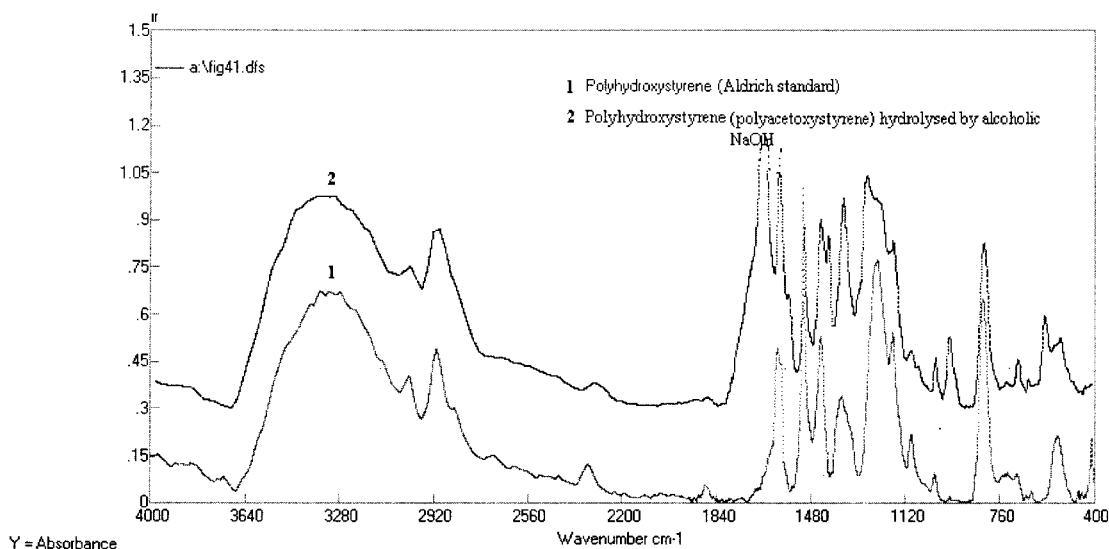


Figure 8 IR spectra of polyhydroxy styrene obtained by alcoholic alkaline hydrolysis.

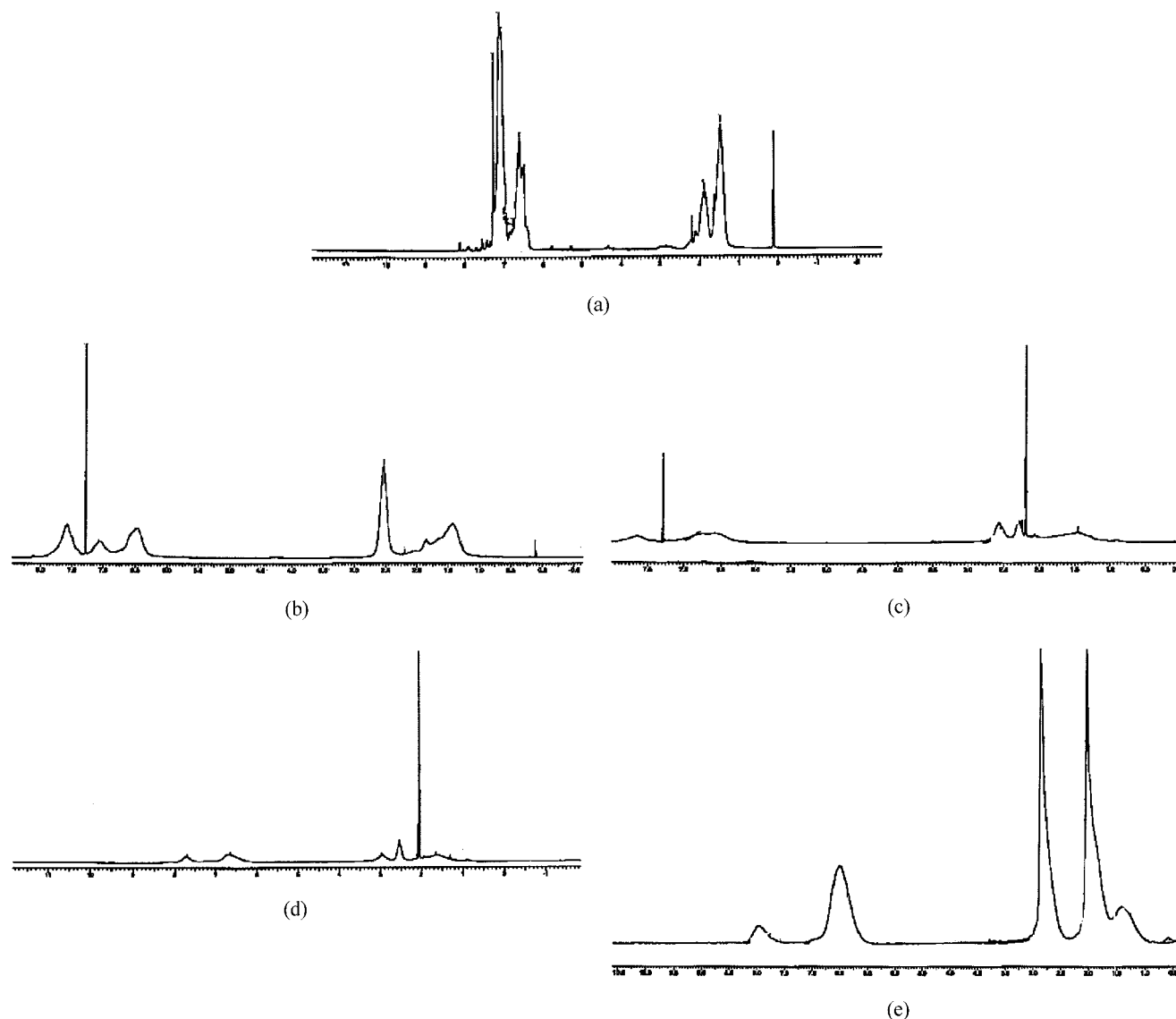


Figure 9 NMR spectra of (a) polystyrene, (b) poly(4-acetyl styrene-*co*-styrene), (c) poly(4-acetylstyrene-*co*-4-acetoxystyrene-*co*-styrene), (d) poly(4-hydroxystyrene-*co*-4-acetylstyrene-*co*-styrene), and (e) poly(4-hydroxy styrene) of standard Aldrich sample.

2.19, which is due to acetoxy ($\text{CH}_3\text{—COO}$) moiety. The small peak at 2.56 ppm is still present that is due to incomplete oxidation of acetyl groups. Figure 9(d, e) shows the NMR spectrum of poly(hydroxystyrene-*co*-acetoxystyrene-*co*-styrene) and standard poly(4-hydroxy styrene) from Aldrich in deuterated acetone as solvent. The signals at 7.68, 6.64, 2.07, and 2.9 ppm are observed. The peaks match except the signal at 2.55 ppm, which is due to incomplete oxidation of acetyl groups. The signals in the final product are not as sharp as seen in standard homopolymer of Aldrich because it is a terpolymer and hence resolution of NMR signals is difficult. The GPC analysis of polystyrene used in the study was $M_n = 5190$; $M_w = 7680$ and polydispersity is 1.5. The observed glass transition temperatures of poly(4-acetyl styrene), poly(4-acetoxy

styrene), and poly(4-hydroxy styrene) were 107, 134, and 142°C, respectively. The glass transition temperature of standard poly(4-hydroxy styrene), having weight-average molecular weight M_w of 20,000, is 151°C. The T_g of poly(4-hydroxy styrene) obtained by modification of this polystyrene was 142°C. The IR spectra of the final product showed that the polymer chain comprises styrene, acetyl styrene, acetoxy styrene, and hydroxy styrene, and, therefore, the T_g of the final product is low because it is a tetrapolymer. Preliminary studies indicate that the product obtained by this methodology can be used in photoresist formulations. The tetrapolymer obtained dissolves in 2.8 wt % of tetramethyl ammonium hydroxide (developer used in photoresists) in 120 s. Further evaluation is in progress. Figure 10(a, b) shows the use of copolymer

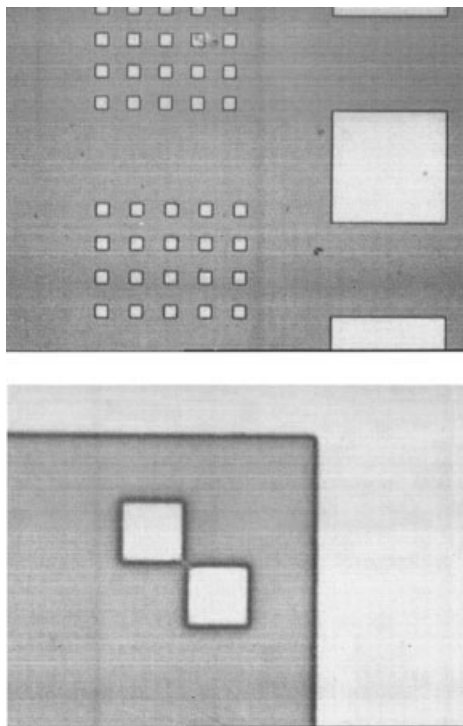


Figure 10 (a) Positive photoresist image on exposure to 365 nm (magnification, $\times 500$). (b) Positive photoresist image on exposure to 365 nm (magnification, $\times 2500$).

in positive photoresist formulation. The photoresist formulations were made by using the copolymer, naphthoquinonediazide sensitizer, and polymeric sensitizer in ethoxyethylacetate as solvent (unpublished data).

CONCLUSION

Hydroxy group is introduced at the para position of polystyrene by modification. Acetylation can be conducted by using cyclohexane as solvent, with 20% v/v carbon disulfide. Sodium perborate in acetic acid can be used effectively as an oxidizing agent instead of hydrogen peroxide, peracetic acid. Thus, a tetrapolymer suitable for photolithography can be obtained by a four-step synthesis starting from a cheap monomer, styrene.

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