

Well-Defined Diblock and Triblock Copolymers for KrF Lithography

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ABSTRACT: One of the major components of a photoresist formulation is polymer resin. Well-defined diblock and random copolymer of *tert*-butyl acrylate (tBA) and 4-acetoxystyrene (StyOAc), as well as triblock and random terpolymer of tBA, StyOAc, and Sty were prepared by reversible addition fragmentation chain transfer polymerization (RAFT) process. The polymers all possess M_w about ten thousand and PDI less than 1.23. After hydrolysis under basic condition, the hydroxystyrene (StyOH) analogs are obtained and

then are formulated as photoresist. Lithographic evaluation under KrF excimer laser shows that random copolymer based photoresist exhibits better S/L patterns according to SEM images. However, the lithographic performance of the terpolymer based resists is similar. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3245–3254, 2010

Key words: block copolymers; lithography; photoresist; controlled radical polymerization; RAFT

INTRODUCTION

Semiconductor industry has been the world's biggest sector of commerce and photolithography has been and will be the technological basis at the heart of this economically succeeding story. In this technology, one of the key materials keeping lines smaller and smaller is photoresist, of which the major components are resins.^{1,2} As the size is getting smaller, the properties of the resins in a particular photoresist formulation become more critical. Therefore, understanding the correlation between properties and microstructure of polymers in photoresist resins is very important for developing better photoresist. It was demonstrated that well-behaved resins, which possess precise ratios of the components (monomers), low polydispersities, as well as well-defined molecular weights could enhance the performance of the resists.^{3,4} The well-defined resins might be synthesized by reversible addition fragmentation chain transfer polymerization (RAFT), one of controlled radical polymerization techniques.^{5,6} Basically, RAFT technique uses dithio compounds as mediator to control the activation-deactivation cycles.^{5,6} In recent years, block copolymers have been intensively employed to pattern ordered structures at the nano-

scale in the form of thin film via self-assembly.^{7,8} RAFT process also enables the preparation of block copolymers.⁶ It is very interesting to figure out the behavior of block copolymers as photoresist resins in use of the lithography process. In this report, we describe the preparation of well-defined diblock and random copolymer of *tert*-butyl acrylate (tBA) and 4-acetoxystyrene (StyOAc), as well as triblock and random terpolymer of tBA, StyOAc, and styrene (Sty) by RAFT. It is also depicted the performance of these polymers after hydrolyzed and formulated as photoresist for 248 nm excimer laser lithography.

EXPERIMENTAL

Materials

All starting materials were purchased from Aldrich (St. Louis/MO), Alfa Aesar (Lancashire/UK), Riedel-de-Haën (Seelze/Germany) or TCI (Tokyo/Japan), and were used as received unless noted otherwise. All solvents were purchased from Mallinckrodt (Phillipsburg, NJ). $\text{CH}_3\text{SCSS}(\text{CH}_3)_2\text{CN}$ was prepared according to the published procedure.^{9,10}

General procedure

All air-sensitive compounds were manipulated under inert atmosphere using standard Schlenk and glove-box techniques. All the reactions were executed using standard Schlenk techniques in an atmosphere of high purity nitrogen or in glove box. Before radical polymerization reactions were

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performed, all reagents in the reactor were degassed by freeze-pump-thaw cycles.

Poly(*tert*-butyl acrylate)-*b*-poly(acetoxystyrene)

Charged were 0.112 g (0.59 mmol) of reagent $\text{CH}_3\text{SCSS}(\text{CH}_3)_2\text{CN}$, 0.04 g (0.24 mmol) of AIBN, 3 g (23.41 mol) of tBA in a Schlenk flask containing 3 g of toluene. After degassed by three times freeze-pump-thaw cycle process, the mixture was stirred and heated at 60°C under a close system for 24 h. After cooling to room temperature, the flask was transported into a glove box, and about 30 mg of the crude product was pipetted out for analysis. Three grams (18.50 mmol) of degassed acetoxystyrene was added into the flask, and the mixture was heated at 60°C again under a close system for another 24 h outside a glove box. After reaction, the solvent was removed by vacuum, and then 30 mL of acetone was added. Precipitation by pentane, followed by filtration and dryness gave the light yellow solid (5.67 g; conversion = 94.5%).

Random poly(*tert*-butyl acrylate)-poly(acetoxystyrene)

Into a Schlenk flask, 2.0048 g (12.36 mmol) of acetoxystyrene, 2.0053 g (15.65 mmol) of tBA, 0.0260 g (0.16 mmol) of AIBN, 0.0749 g (0.39 mmol) of $\text{CH}_3\text{SCSS}(\text{CH}_3)_2\text{CN}$, and 1.0 g of toluene were added. After degassed by three times freeze-pump-thaw cycle process, the mixture was stirred and heated at 60°C under a close system for 24 h. After cooling, the solvent was removed by vacuum, and then 25 mL of acetone was added. Precipitation by hexane, followed by filtration and dryness gave the light yellow solid (3.93 g; conversion = 98.1%).

Poly(*tert*-butyl acrylate)-*b*-poly(acetoxystyrene)-*b*-poly(styrene)

Charged were 0.0979 g (0.51 mmol) of reagent $\text{CH}_3\text{SCSS}(\text{CH}_3)_2\text{CN}$, 0.0354 g (0.22 mmol) of AIBN, 1.0053 g (7.84 mol) of tBA in a Schlenk flask containing 1.5359 g of toluene. After degassed by three times freeze-pump-thaw cycle process, the mixture was stirred and heated at 60°C under a close system for 24 h. After cooling to room temperature, the flask was transported into a glove box, and about 30 mg of the crude product was pipetted out for analysis. Degassed acetoxystyrene [5.0659 g (31.23 mmol)] was added into the flask, and the mixture was heated at 60°C again under a close system for another 21 h outside a glove box. After cooling to room temperature, the flask was transported into a glove box, and about 30 mg of the crude product was pipetted out for analysis. Degassed styrene

[1.3299 g (12.77 mmol)] was added into the flask, and the mixture was heated at 60°C again under a close system for another 16 h outside a glove box. After reaction, the solvent was removed by vacuum, and then 30 mL of acetone was added. Precipitation by hexane, followed by filtration and dryness gave the light yellow solid (5.51 g; conversion = 74.5%).

Random-poly(*tert*-butyl acrylate)-poly(acetoxystyrene)-poly(styrene)

Into a Schlenk flask, 5.06 g (31.20 mmol) of acetoxystyrene, 1.00 g (7.80 mmol) of tBA, 0.035 g (0.21 mmol) of AIBN, 1.33 g (12.77 mmol) of styrene, 0.098 g (0.51 mmol) of $\text{CH}_3\text{SCSS}(\text{CH}_3)_2\text{CN}$, and 1.5 g of toluene were added. After degassed by three times freeze-pump-thaw cycle process, the mixture was stirred and heated at 60°C under a close system for 24 h. After cooling, the solvent was removed by vacuum, and then 30 mL of acetone was added. Precipitation by pentane, followed by filtration and dryness gave the light yellow solid (6.72 g; conversion = 90.9%).

General procedure of hydrolysis of poly(acetoxystyrene) in the copolymers and terpolymers

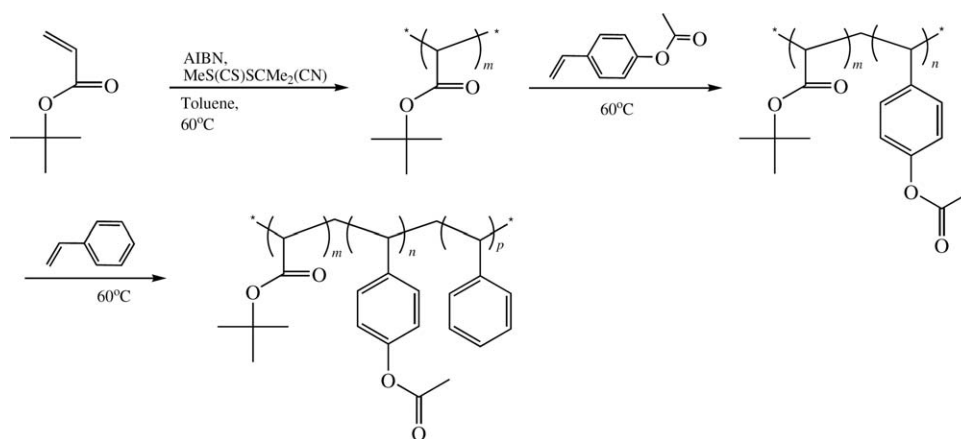
Into a Schlenk flask, the co/*tert*polymer, 15% of ammonia solution, and THF were added. The mixture was stirred at ambient temperature for 48 h. After reaction, Precipitation by 50% of MeOH/H₂O, followed by filtration, washing with toluene, and dried under vacuum gave the off-white solid, poly(hydroxystyrene) analogs. Yield >90%.

Characterization methods

Molecular weight of the polymers was determined on gel permeation chromatography instrument (Waters, UV996, RI410, pump600, autosampler717+). ¹H-NMR spectra were obtained on Bruker AC-200 instrument, Varian Mercury 300 Plus instrument or Bruker Avance DRX-400 NMR instrument.

Lithographic evaluations

The polymers (13.3 wt %) were dissolved in propylene glycol monomethyl ether acetate (PGMEA) along with a standardized amount of a photoacid generator (PAG) and quencher to yield photoresist solutions. In the spin-coating process, the photoresist solution was dropped onto the center of a silicon wafer, then spun at 4000 rounds per minute to distribute the resist over the surface of the wafer. The photoresist-spin-coated silicon wafer was soft baked (SB) at 130° for 90 s, exposed to 248-nm excimer laser radiation (Lambda Physik, COMPex110), post



Scheme 1 Synthetic route to poly(tBA)-*b*-poly(StyOAc) and poly(tBA)-*b*-poly(StyOAc)-*b*-poly(Sty).

exposure baked (PEB) at 130°C for 90 s, and developed using 2.38% aqueous tetramethyl ammonium hydroxide (TMAH) for 60 s. The patterning performance of the photoresists was investigated using scanning electron microscopy (SEM, FE-SEM, S-4200, Hitachi).

RESULTS AND DISCUSSION

Diblock copolymer, poly(tBA)-*b*-poly(StyOAc), and triblock copolymer, poly(tBA)-*b*-poly(StyOAc)-*b*-poly(Sty), with molecular weight about ten thousand were designed and synthesized by RAFT process (Scheme 1). In addition, their well-defined analogs with random composition were also prepared by RAFT. Deacetylation of the polymers gave their poly(hydroxystyrene) (poly(StyOH)) analogs. The segments, tBA and Sty type were chosen because they are commonly employed as the backbone of photoresist resins,¹¹ as well as the different hydrophilicity/hydrophobicity of styrenes and acrylates.¹² Although polyacrylates or polymethacrylates were the most popular resins in the use of 193 nm photoresist formulations,^{13,14} poly(tBA) was used here as the moiety for polarity change by acid activated chemical transformations under 248 nm lithographic process.

Preparation and characterization of poly(tBA)-*b*-poly(styOH)

Block copolymerization was carried out by RAFT process by using *S*-cyanoprop-2-yl-*S*-methyl trithiocarbonate as transfer reagent and AIBN as an initiator. Poly(tBA), as the first block of the copolymer was prepared by CRP process at 60°C under a close condition. After reaction, the flask was transported into a glove box. Few amount of the crude product was sampled for analysis of ¹H-NMR spectroscopy and GPC. The protons of the *tert*-butyl group appear

at about δ 1.4 ppm (Fig. 1). There was almost no proton resonance between 4 and 6 ppm in ¹H-NMR spectrum, which indicated the excellent conversion of the reaction. GPC chromatogram showed the resulting polymer with $M_w = 6260$, PDI = 1.18, and which confirmed that well-controlled poly(tBA) was obtained. The second monomer, acetoxystyrene was added into the rest of poly(tBA), and then the mixture was heated under the same condition as the above. Precipitation by pentane and purification gave the desired block copolymer, poly(tBA)-*b*-poly(StyOAc) in excellent conversion, and the polymer was also analyzed by ¹H-NMR spectroscopy and GPC. The multiplet resonance at δ about 7.0 in ¹H-NMR spectrum indicated the presence of aromatic protons, and the resonance signal at δ about 2.3 ppm represented the acetyl group (Fig. 2). Well-controlled polymerization was verified by the narrow molecular weight distribution (PDI = 1.21) and molecular weight = 11,120 in the GPC chromatogram of the copolymer.

It was reported that acetoxy groups on the benzene rings could be cleaved to generate the hydroxyl group under basic conditions.^{15,16} Hydrolysis of the copolymer by ammonium hydroxide gave poly(tBA)-*b*-poly(StyOH) with $M_w = 11,860$ and PDI = 1.30, which were determined by GPC. It has been noted that polydispersity would be increased slightly upon deprotection of the acetoxy moiety.^{15,16} Our result also showed the similar phenomenon. ¹H-NMR (Fig. 3) spectroscopy also revealed the hydrolysis occurrence by the minor difference in the region of aromatic proton resonances and the fading of the signal at δ about 2.3 ppm. During the hydrolysis of the acetoxy moiety, the *t*-butyl groups in the tBA fragment are possible to be hydrolyzed. The ¹H-NMR spectra (Figs. 1 and 3) show that about 15 mol % of the *t*-butyl groups is hydrolyzed based on the integration ratio of iso-H (δ about 2.2 ppm) and *t*-butyl-H (δ about 1.5 ppm) proton resonances.

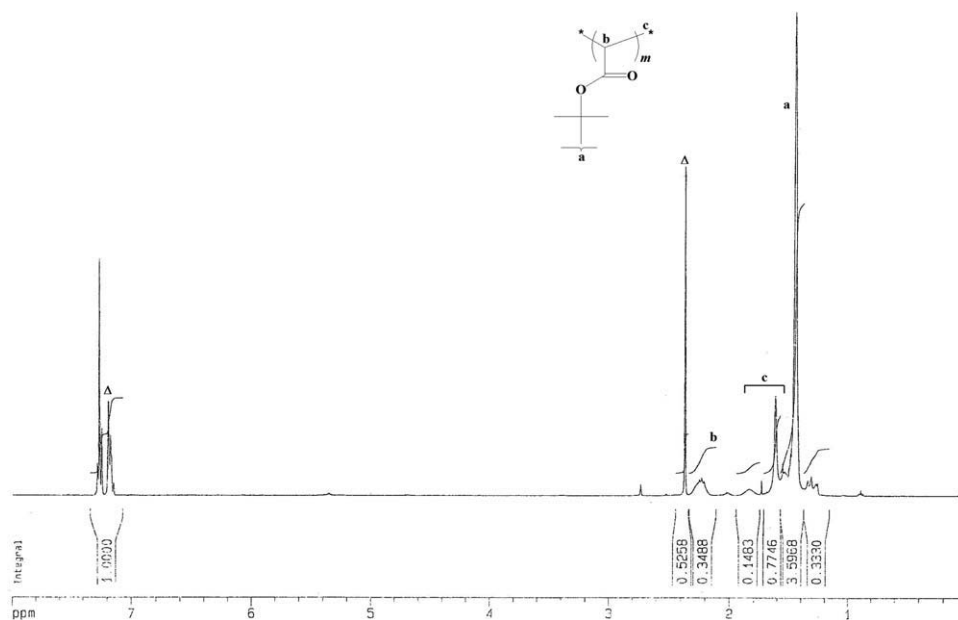


Figure 1 $^1\text{H-NMR}$ spectrum of poly(tBA), d-chloroform. Δ : the proton resonance of toluene.

Moreover, the carbonyl stretching frequency of poly(tBA) appeared at around 1730 cm^{-1} in the infrared spectra (Fig. 4) and the poly(tBA)-*b*-poly(StyOAc) copolymer showed two type of carbonyl stretching frequency at around 1730 and 1770 cm^{-1} . After hydrolysis, the resulting polymer, poly(tBA)-*b*-poly(StyOH) possessed the stretching frequencies at around 1730 cm^{-1} for carbonyl group and 3500 cm^{-1} for hydroxyl group. The disappearance of the

signal at 1770 cm^{-1} also confirmed the success of deprotection of the acetoxy moiety.

Preparation and characterization of random poly(tBA)-poly(styOH)

Since the reactivity ratios for the tBuA and Sty copolymerization possessed $r_{\text{tBA}} = 0.29$ and $r_{\text{Sty}} = 0.89$ in conventional radical polymerization as well

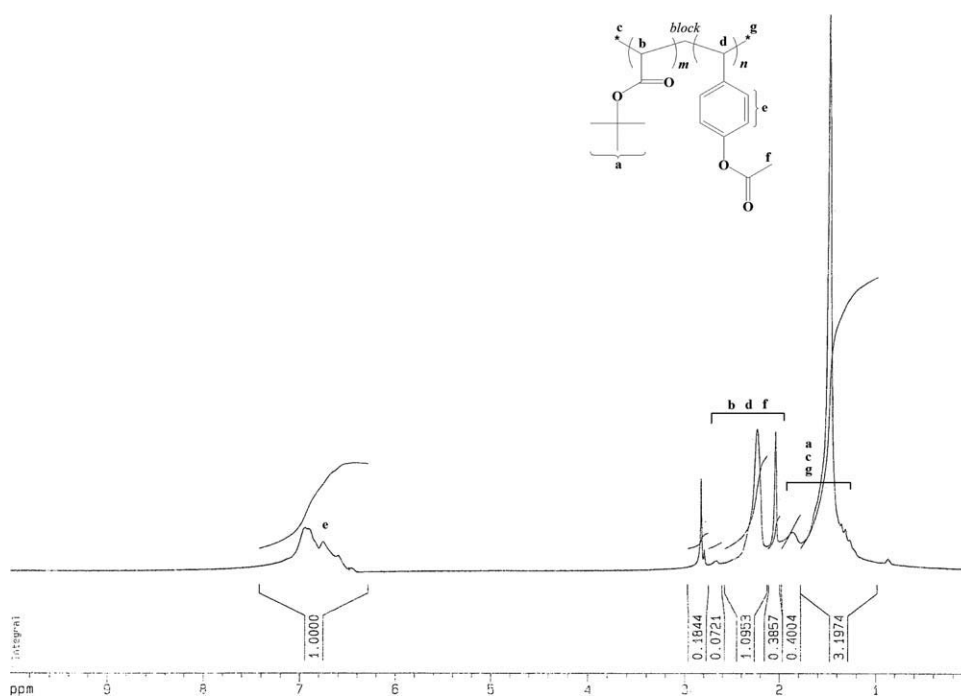


Figure 2 $^1\text{H-NMR}$ spectrum of poly(tBA)-*b*-poly(StyOAc), solvent in d-chloroform.

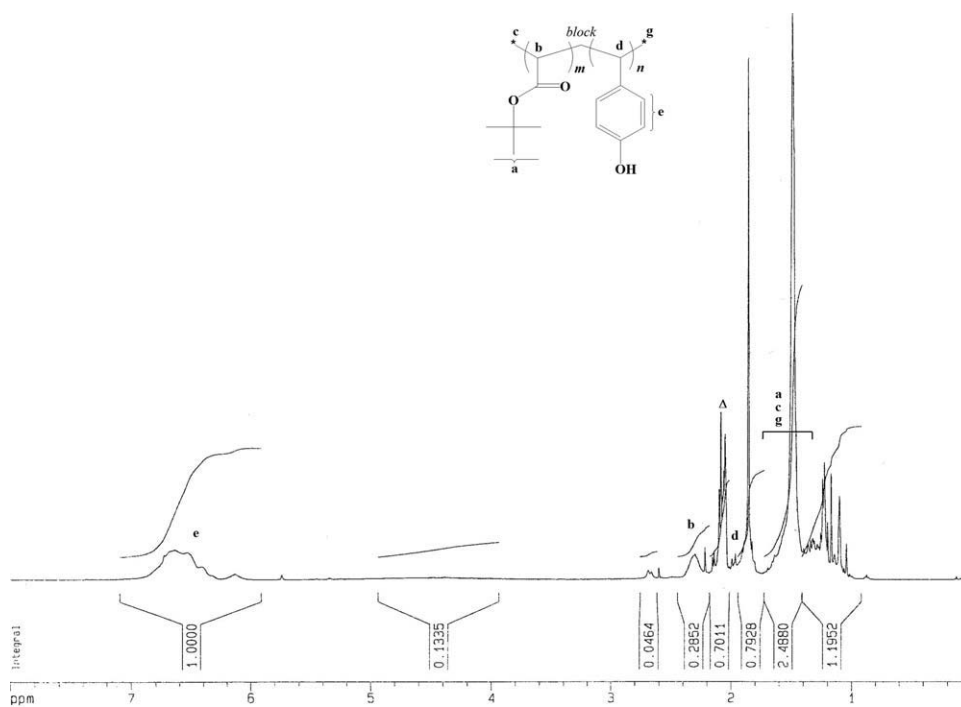


Figure 3 $^1\text{H-NMR}$ spectrum of poly(tBA)-*b*-poly(StyOH), solvent in d_6 -acetone.

as ranged from $r_{\text{tBA}} = 0.09$ to 0.12 and $r_{\text{Sty}} = 0.40$ to 0.49 in nitroxide-mediated polymerization,¹⁷ random tBuA/Sty copolymer may be prepared. Random copolymerization of tBA and StyOAc was carried out under the similar condition as the preparation of the block copolymers. After the reaction was complete, poly(tBA)-poly(StyOAc) was obtained by precipitation in hexane in excellent conversion ($\sim 98\%$). Well-controlled product was confirmed by GPC as the $M_w = 12,900$ and $\text{PDI} = 1.22$ for the copolymer.

$^1\text{H-NMR}$ showed that the shapes of the resonance signals of benzene rings in random poly(tBA)-poly(StyOAc) (Fig. 5) and block poly(tBA)-*b*-poly(StyOAc) (Fig. 2) were different. The stair-like resonance signals of the aromatic protons in poly(tBA)-*b*-poly(StyOAc) suggest that styrene fragment would be connected like a chain, and therefore the environments of the benzene rings close to the chain end would be different from those in the central moiety of the chain. On the other hand, the area of the

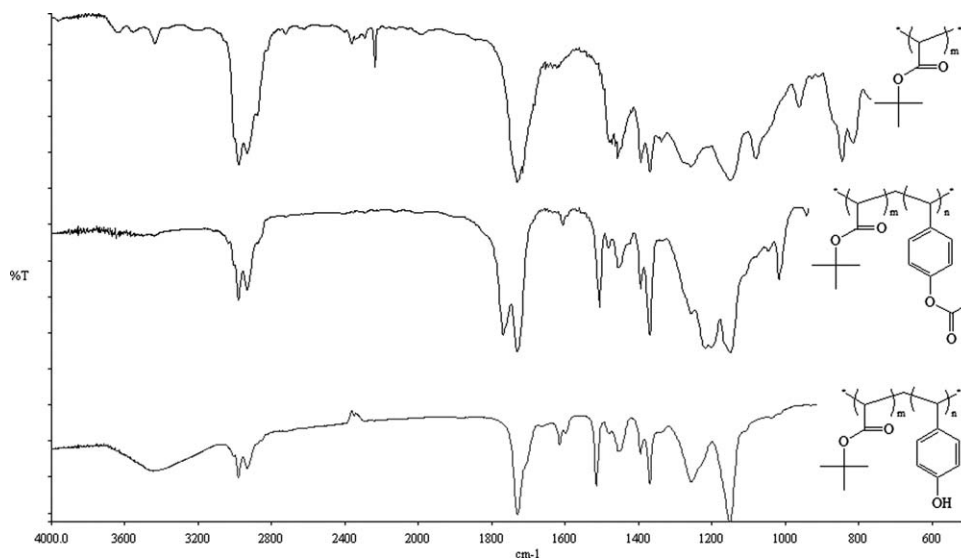


Figure 4 IR spectra of poly(tBA) (top), poly(tBA)-*b*-poly(StyOAc) (middle), and poly(tBA)-*b*-poly(StyOH) (bottom).

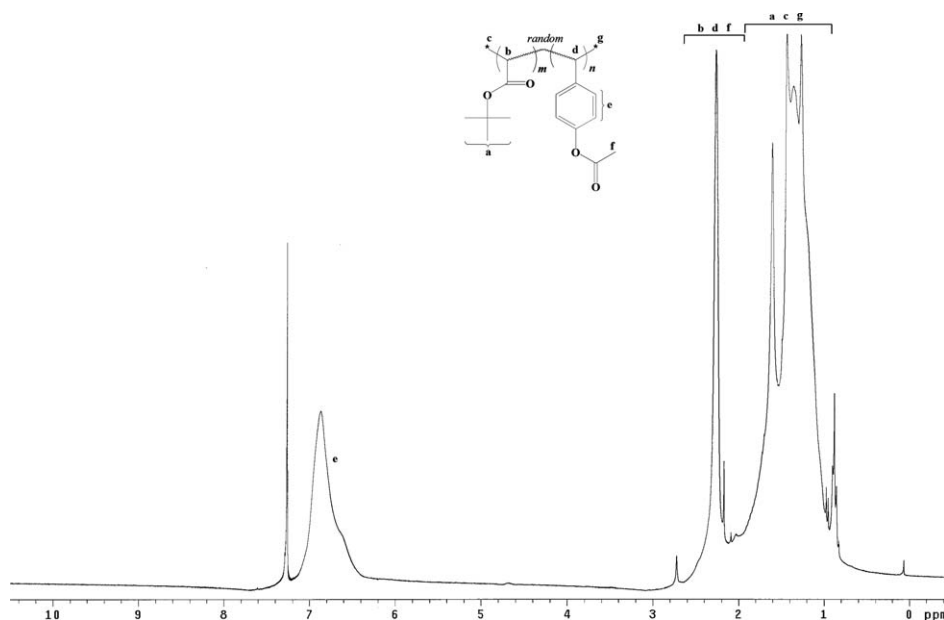


Figure 5 $^1\text{H-NMR}$ spectrum of random poly(tBA)-poly(StyOAc), solvent in d-chloroform.

aromatic proton in the ^1NMR spectrum (Fig. 5) of the random copolymer only showed a broad resonance, which implied that the environments of the benzene rings would be similar, i.e., random relative to tBA fragments. Therefore, the ^1NMR spectrum indicated it is a random copolymer. Deacetylation of the copolymer by ammonia solution gave random poly(tBA)-poly(StyOAc) with $M_w = 14,700$ and $M_w/M_n = 1.39$. The change of the resonance between 6 and 9 ppm in the ^1NMR spectrum (Fig. 6) indicated deacetylation reaction happening.

Preparation and characterization of poly(tBA)-*b*-poly(styOH)-*b*-poly(sty) and random poly(tBA)-(styOH)-(sty)

Similar strategy of CRP was applied to prepare block terpolymer, poly(tBA)-*b*-poly(StyOH)-*b*-poly(Sty). After block terpolymerization of tBA, StyOAc, and Sty sequentially, the polymer with $M_w = 13,700$ and $\text{PDI} = 1.14$ was obtained. While mixing the certain ratio of tBA, StyOAc, and Sty, followed by CRP process, random poly(tBA)-poly(StyOH)-poly(Sty) was obtained, and GPC chromatogram showed its

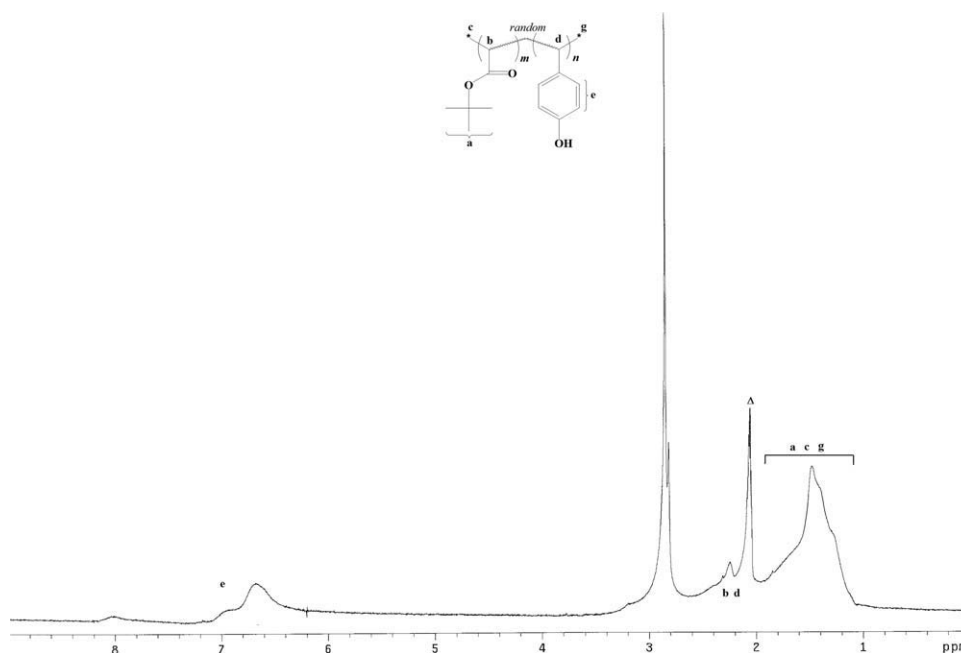


Figure 6 $^1\text{H-NMR}$ spectrum of random poly(tBA)-poly(StyOH), solvent in d_6 -acetone.

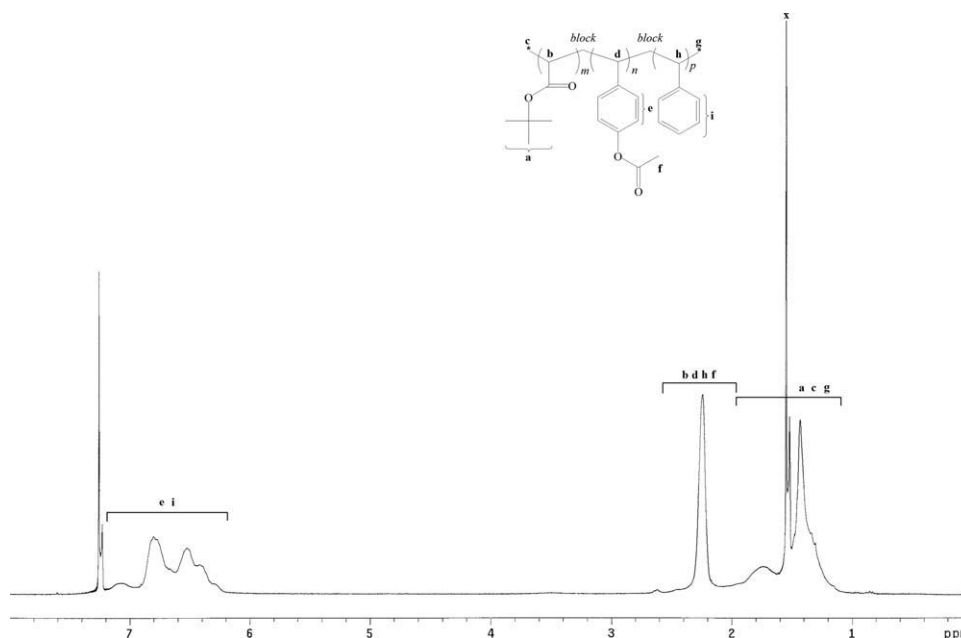


Figure 7 $^1\text{H-NMR}$ spectrum of poly(tBA)-*b*-poly(StyOAc)-*b*-poly(Sty), solvent in d-chloroform.

$M_w = 11,500$ and $\text{PDI} = 1.17$. The $^1\text{H-NMR}$ resonance signals (Fig. 7) of the aromatic protons in the block terpolymer appeared as several humps indicating the arrangement of acetoxystyrene and styrene in succession. However, the area of the aromatic proton in the ^1NMR spectrum (Fig. 8) of the random polymer showed less amounts of the hump resonances resulting from the average of random composition of the aromatic moieties.

Hydrolysis of the block and random terpolymer gave their hydroxystyrene analogs with $M_w =$

$10,500/\text{PDI} = 1.33$ and $M_w = 9100/\text{PDI} = 1.21$, respectively. The ^1NMR spectra (Fig. 9) also confirmed the success of deacetylation.

Lithographic evaluations

After irradiation using KrF excimer laser and PEB process, the acid-catalyzed deprotection reaction converted the *tert*-butyl ester group of the polymers to carboxylic acid group, which provided an extremely fast dissolution rate in the exposed

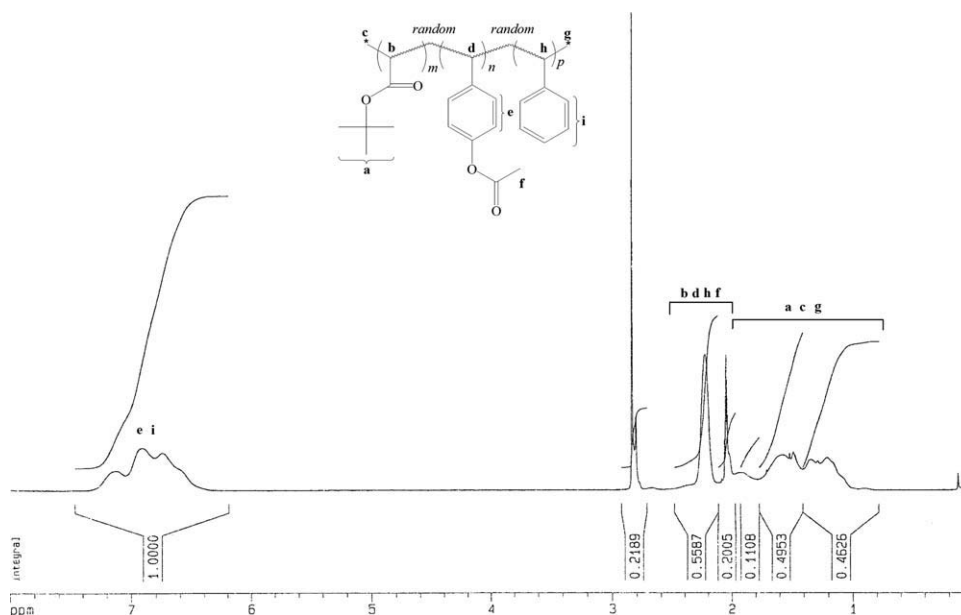


Figure 8 $^1\text{H-NMR}$ spectrum of random poly(tBA)-poly(StyOAc)-poly(Sty), solvent in d-chloroform.

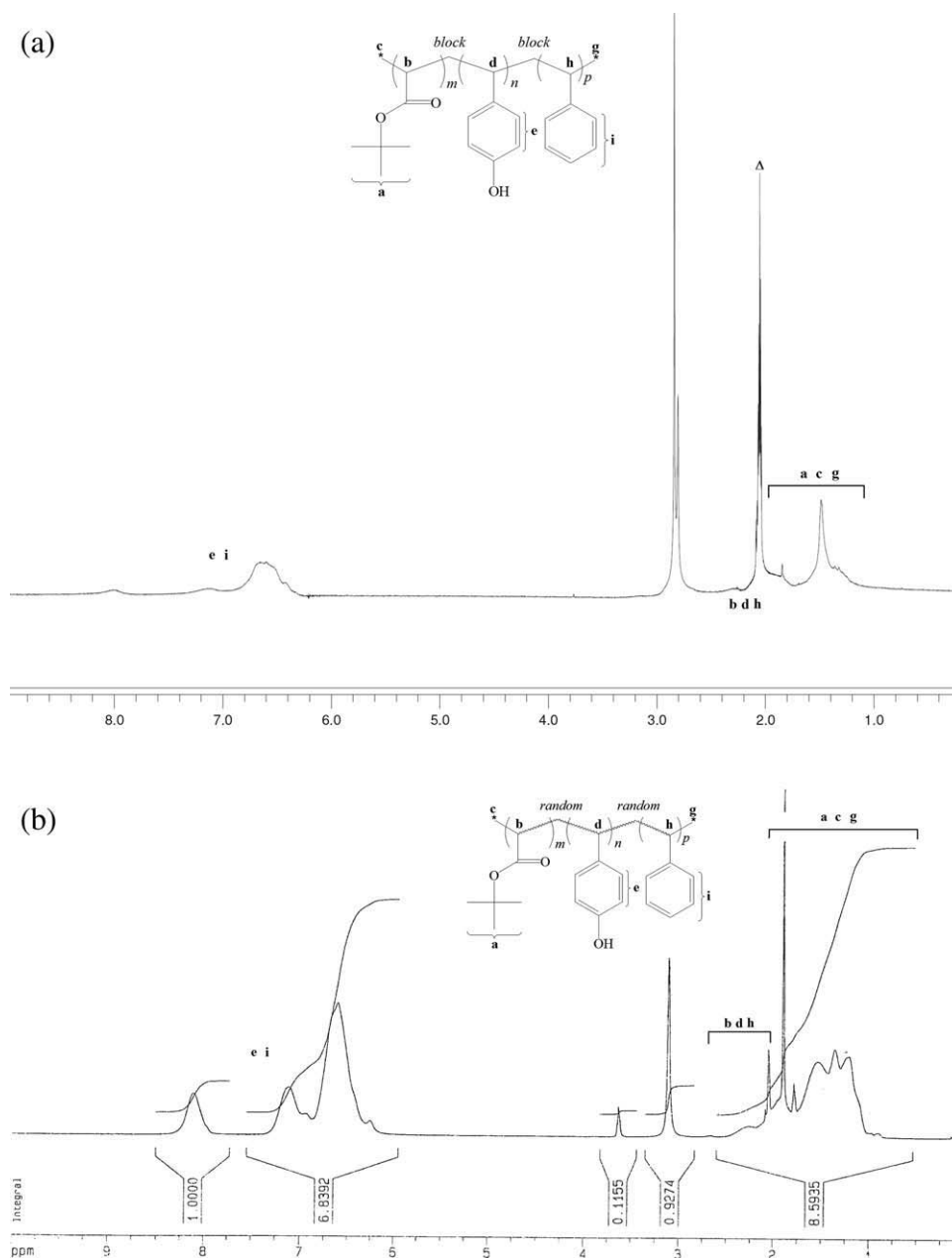


Figure 9 ¹H-NMR spectrum of (a) poly(tBA)-*b*-poly(StyOH)-*b*-poly(Sty) and (b) random poly(tBA)-poly(StyOH)-poly(Sty), solvent in d₆-acetone.

regions and large developer selectivity to form the line/space patterns. The SEM images in Figure 10 showed that the resist containing random poly(tBA)-poly(styOH) as resins presented better line/space patterns than the resist containing poly(tBA)-*b*-poly(styOH) as resins for CD = 0.75 μm, though the block based resist was endured by higher dose (24.8 mJ/cm²). After PEB step, the poly(tBA)-*b*-poly(styOH) copolymer in the irradiated area should turn into poly(acrylic acid)-*b*-poly(styOH), which is very soluble in the basic developer. In contrast, the copolymer should be retained in the unirradiated area. Little

and collapsed line/space patterns were observed in the SEM images in Figure 10(a), which indicated that most of the resist was deprotected even in the unirradiated region. On the other hand, clear line/space patterns were observed in the case of the random based resist [Fig. 10(b)]. The result might arise from the different nature of block and random polymers associated with the mismatched composition. For examples, the dissimilar blocks of poly(tBA)-*b*-poly(styOH) in the resist film could exist in distinct microdomains, which lead to uncontrolled acid diffusion rate and uncontrolled acid-catalyzed chain reaction.

However, the tBA groups were dispersed indiscriminately in the random based resist, and therefore the styOH motifs might obstruct the acid diffusion rate to regulate the deprotection step. The composition of the photoresist resin was modified as terpolymer by incorporation of hydrophobic and acidophobic monomer, styrene as well as regulation of the ratio of tBA, styOH, and Sty to 1 : 5 : 1.3. Evaluation of patterning performance of the random poly(tBA)-poly(StyOH)-poly(Sty) and block poly(tBA)-*b*-poly(StyOH)-*b*-poly(Sty) as photoresist resins was also determined by the SEM images after they were irradiated under an excimer laser at $\lambda = 248$ nm. Profiles of the line/space patterns (Fig. 11) showed that both resins exhibited good resolution for CD = 0.75 μm . The results divulged that incorporation of more styOH and Sty components into the resist resins would improve the

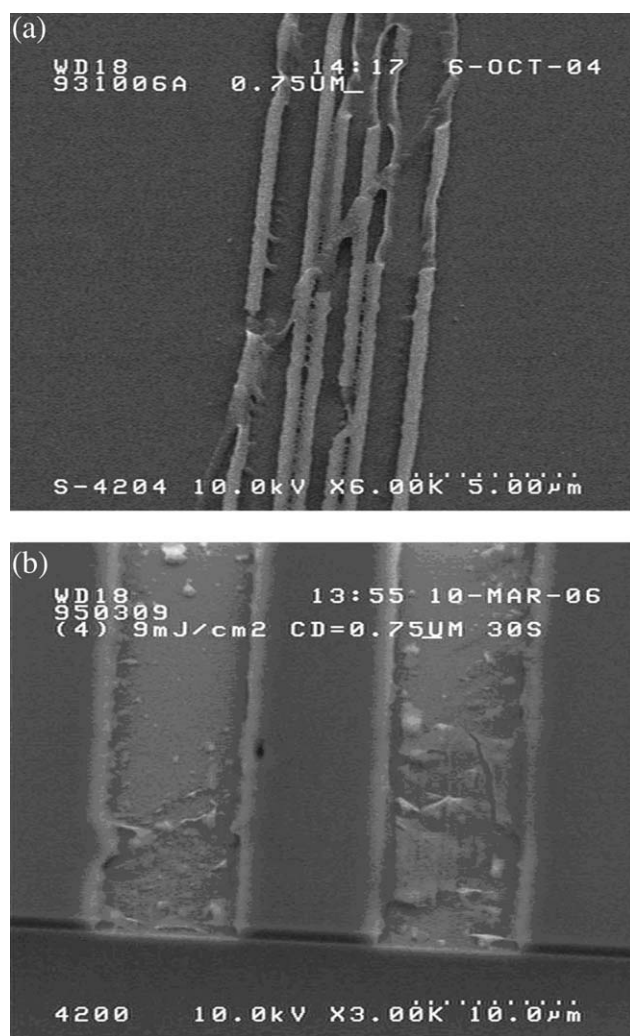


Figure 10 SEM micrograph of L/S patterns of (a) poly(tBA)-*b*-poly(StyOH) based photoresist under 248 nm exposure with 24.8 mJ/cm² and CD = 0.75 μm ; (b) random poly(tBA)-poly(StyOH) based photoresist under 248 nm exposure with 9.0 mJ/cm² and CD = 0.75 μm .

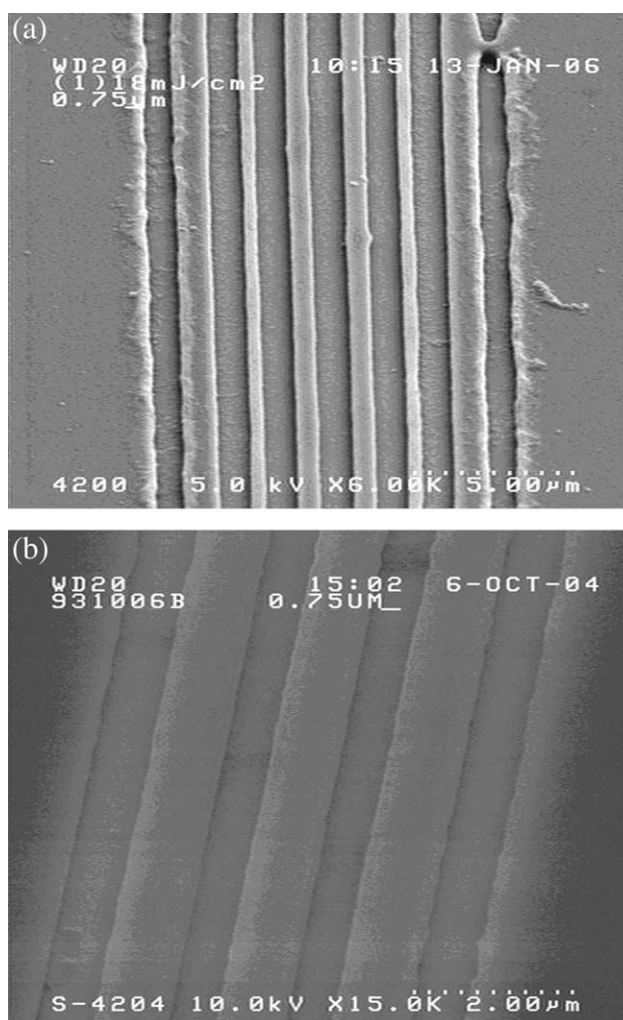


Figure 11 SEM micrograph of L/S patterns of (a) poly(tBA)-*b*-poly(StyOH)-*b*-poly(Sty) based photoresist under 248 nm exposure with 18.0 mJ/cm² and CD = 0.75 μm ; (b) random poly(tBA)-poly(StyOH)-poly(Sty) based photoresist under 248 nm exposure with 26.4 mJ/cm² and CD = 0.75 μm .

controllability of the acid-catalyzed reaction during the deprotection process. According to the patterning performance of the copolymers and terpolymers, it suggested that resins with random arrangement might be better than those with block arrangement for photoresist; however, modification of monomer ratio and composition might overcome the effect.

CONCLUSIONS

Well controlled random/block copolymer poly((tBA)-(StyOAc)) and terpolymer poly((tBA)-(StyOAc)-(StyOAc)) could be prepared by RAFT process. After hydrolysis by ammonium hydroxide in THF, the resulting polymers showed potential as photoresist resins. Primitive study revealed that random resin might be a better candidate for

photoresist application; however, composition of monomer also had great influence in lithographic performance.

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