Synthesis of Succinylated Poly(4-hydroxystyrene) and Its Application for Negative-Tone Photoresist

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Received 22 November 2005; accepted 9 June 2006
DOI 10.1002/app.24979
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Atom transfer radical polymerization (ATRP) was used to prepare poly(acetoxystyrene) (PAS) with a controlled molecular weight and narrow polydispersity. Using 1-phenylethylbromide (PEBr)/CuBr/Cu(0)/2,2′-bipyridine as an initiating system, the heterogeneous ATRP of 4-acetoxystyrene was carried out to form PAS as a precursor polymer. The reaction follows the first-order kinetics with respect to the conversion of monomer. A linear molecular weight (polydispersities Mw/Mn = 1.07–1.27) indicates the ''living''/controlled nature of polymerization. The obtained PAS was chemically modified to obtain succinylated poly(hydroxystyrene) (Succ-PHS). The formulation of Succ-PHS, crosslinker (benzoguanamine-formaldehyde), and triphenylsulfonium triflate (TPST) as a photo acid generator (PAG) was carried out by UV irradiation using an i-line tool. The performance of the resultant polymer as the negative resist pattern photoresist for photolithography was studied with instrumental techniques. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3560–3566, 2007

Key words: atom transfer radical polymerization (ATRP); succinylated poly(4-hydroxystyrene); lithography; photoresist; negative-tone image

INTRODUCTION

The chemically amplified photoresists (CAPs) for semiconductor manufacturing consists of either a two-component system composed of an acid reactive polymer and a photoacid generator (PAG) or a three-component system composed of acid reactive compounds, PAG, and matrix resin. In CAPs, the photolysis of a PAG liberates acid, which initiates deprotection on the polymer backbone. This acid-catalyzed deprotection increases polymer solubility in aqueous base. Poly(4-hydroxystyrene) (PHS) and its structural derivatives have been developed and commercially applied as matrix resins in the fabrication of many devices.[1,2] This is due to its very good etch depth versus time characteristics and good thermal properties at around 120°C, which ensures good image stability while the pattern is being transferred.[3,4] PHS and PHS-based polymers are extremely versatile specialty polymers useful for the design of light-emitting materials,[5,6] as curing agents for epoxy resins,[7] as polymeric adsorbents for the removal of organic matter from aqueous wastes,[8] in the preparation of membranes with selective permeability,[9] as radical scavengers and polymeric antioxidants, and as supports for solid-phase[10,11] and combinatorial synthesis.[12] They are expensive compared to the novolac-based polymers used in photoresist applications, but they are the best currently available materials.

From the application viewpoint, the development of steppers, lithographic equipment, and optimization of the exposure tools demands polymers of narrower molecular weight distribution, higher stability, and so on. Therefore, there is a need to develop more sensitive PHS-based materials with a proper protecting group because the deprotecting rate controls the resist's quality. Polymers with very narrow polydispersity are useful for more stable negative-tone images[13] and such polymers can be synthesized by atom transfer radical polymerization (ATRP).[14,15] ATRP[16] has emerged as a powerful method for the synthesis of well-defined polymers of controlled molecular weight and narrow molecular weight distribution. Its success is due to the effective minimization of termination and chain transfer reactions. An important advantage of ATRP is its tolerance to many functionalities, and thus a variety of functional polymers have been synthesized from a wide range of monomers, such as substituted styrenes, (meth)acrylates, and acrylamides.[17,18]

As photoresists, polymeric materials are used to define the features of individual elements in printed circuit boards (PCBs) and integrated circuit (Ic) devi-

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ces. 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 chemical modification of the nonfunctionalized polymer. It is well known that the introduction of carboxyl groups in a polymer chain improves solubility and resolution of the photoresist,[19] and that would afford the aqueous-based development of the uncrossed linked/nonexposed polymeric regions through a neutralization reaction. The introduction of a pendant aliphatic group on the polymer backbone would provide the necessary photoactivated imaging functionality via an acid-catalyzed crosslinking reaction. In addition, rich carbon-containing monomers are expected to enhance the etch resistance of the resist formulation.[20–24] In general, the existence of aliphatic groups could increase the thermostability of the polymers, whereas the existence of an aromatic ring in a polymer chain may increase the etch-resisting properties.

In this work, we synthesized PHS containing a succinyl group as a dissolution promoter in order to get the negative-tone pattern. Here we also report the thermogravimetric characteristics of the polymer, sensitivity, and resolution of the negative tone photoresist.

EXPERIMENTAL

Materials

Acetoxystyrene (97%), 1-phenyl ethyl bromide (PEBr), 2,2′-bipyridine (bpy), copper bromide (CuBr), copper powder, pyridine, succinic anhydride (98%), and dimethyl sulfoxide (DMSO) were purchased from Aldrich (Milwaukee, WI) and used as received except acetoxystyrene, which was purified by vacuum distillation. The crosslinker, benzoguanamine-formaldehyde monomer, was purchased from Cytec Industries (West Paterson, NJ). The photo acid generator (PAG), triphenylsulfonium triflate, was purchased from SMC (South Korea). The solvents methanol, 1,4-dioxane, *n*-hexane, ethyl acetate, and tetrahydrofuran (THF) were purified by vacuum distillation with drying agents. Other materials were used extra pure grade without further purification.

Measurements

FT-IR spectra were recorded on a Unicam 5000 spectrometer using the potassium bromide pellet technique. ^{1}H NMR spectra were recorded on a Varian Unity Inova 500 spectrometer at room temperature in $CDCl_3$ and DMSO-d_6. All chemical shifts are reported relative to tetramethylsilane as an internal standard.

Number-average molecular weight (Mn), weight-average molecular weight (Mw), and molecular weight distribution (MWD) were measured by gel permeation chromatography (GPC) with styrene gel columns (Waters, Milford, MA, Model 515) using THF as eluent at a flow rate of 1.0 mL/min employing refractive index and an ultraviolet detector.

The theoretical molecular weight (M_{th}) was calculated by:

$$M_{th} = \alpha[M]_0 M_M/[I]_0$$

where α is the conversion of monomer, $[M]_0$ and $[I]_0$ are the initial concentration of monomer and initiator, respectively, and M_M is the molecular weight of monomer.

Spin coating of the photoresist (PR) on a silicon wafer was done with a coater from Headway Research (Garland, TX). The thickness of the applied PR was measured with a KLA P-10 surface profiler. The i-line exposure tool (Thermo-oriel Model 66902) was used for irradiation. To measure the pattern image, we used a Nikon Optiphot optical microscopy (OM) and for the resolution measurement a Philips XL30 ESEM-FEG scanning electron microscope (SEM). A thermal analysis was done with a thermogravimetric analyzer (TGA 2050) and a differential scanning calorimeter (DSC 2910) at a heating rate of 10°C/min under an N_2 atmosphere.

Synthesis

Synthesis of poly(acetoxystyrene) (PAS) by ATRP

A 150-mL three-necked-round bottom flask equipped with a magnetic stirring bar was charged with 0.3 mol of acetoxystyrene monomer and 4.5 mmol of 2,2′-bipyridine. The solution was stirred for a few minutes and then 1.5 mmol of CuBr and the same amount of Cu powder were added to the reaction mixture. After sealing it with a rubber septum, the flask was degassed by three freeze–pump–thaw cycles and backfilled with nitrogen and then left under nitrogen. The reaction mixture was placed in a thermostated oil bath at 90°C. After sufficient agitation, 1-phenyl ethyl bromide (1.5 mmol) was slowly introduced into the reactor with a syringe and the reaction mixture was stirred for 2 h at 90°C. After polymerization, the reaction mixture was diluted with THF and then passed through a celite pad to remove metal salt. The excess THF was evaporated under reduced pressure. The polymer was precipitated into methanol, filtered, and dried in a vacuum oven at room temperature for 72 h. Yield: (45%). ^{1}H-NMR (500 MHz, $CDCl_3$), δ: 6.2–7.00 (m, Ar-H), 2.36 (s, $COCH_3$), 1.7–1.9 (br, —CH), 1.3–1.6 (br, —CH_2).[25–29]

Synthesis of PHS

In a 500-mL round-bottom flask equipped with a magnetic stirring bar were placed 315 mL of 1,4-dioxane,

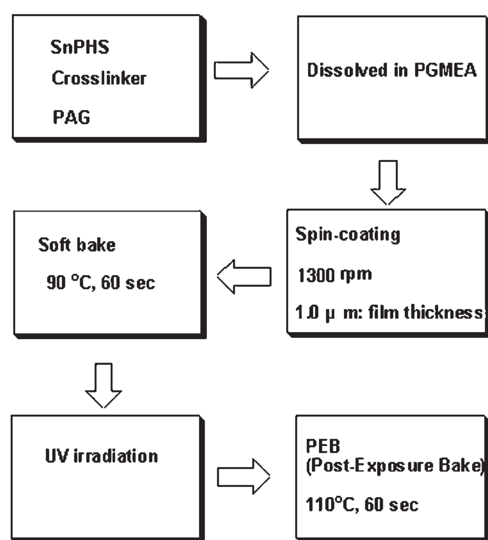


Figure 1 Sequence of the lithographic procedure.

35 mL of hydrazine hydrate and PAS (17.5 gm). The reaction mixture was stirred for 6 h and then poured into ice water. The crude product was filtered and washed well with 5% HCl, $NaHCO_3$ followed by distilled water. The polymer was obtained as a yellow solid, which was dissolved into ethyl acetate and reprecipitated by pouring it into *n*-hexane. The polymer was collected by filtration and dried under vacuum for 72 h. Yield: (99%). The hydrolysis of PAS to PHS was confirmed by NMR spectroscopy. ^{1}H-NMR (500 MHz, DMSO-d_6), δ: 8.8–9.1 (br, —O<u>H</u>), 6.1–6.7 (m, Ar-<u>H</u>), 1.6–1.8 (br, —CH), 1.2-1.5 (br, —CH_2).[30–33]

Synthesis of Succ-PHS

A 250-mL round-bottom flask equipped with a stirring bar was charged with 120 mL of DMSO and 15 g of PHS. After dissolution of polymer in the solvent, pyridine, 7.6 g, and succinic anhydride, 7.5 g (1.2 : 1 mole ratio), were added and the whole assembly was kept at 65°C under constant stirring conditions for 24 h. Then the reaction mixture has poured into the aqueous HCl. The desired polymer **(3)** was collected after filtration and dried under vacuum for 3 days. The composition ratio (as 13%) of the succinyl group in the formed copolymer was confirmed by ^{1}H-NMR and FTIR spectroscopy. ^{1}H-NMR (500 MHz, DMSO-d_6), δ: 6.2–6.7 (m, Ar-<u>H</u>), 2.6–2.8 (m, —CH_2—CH_2), 1.6–1.8 (br, —CH), 1.2–1.5 (br, —CH_2) 1.00–2.00 (m and broad, Hs, —[C<u>H</u>$_2$—C<u>H</u>]—). FTIR (cm^{-1}): 3500 (OH stretching), 1713 (C=O stretching), 1599 (C=C of aromatic stretching), 1085 (C—O—C linkage).

Formulation for photoresist and photoimaging

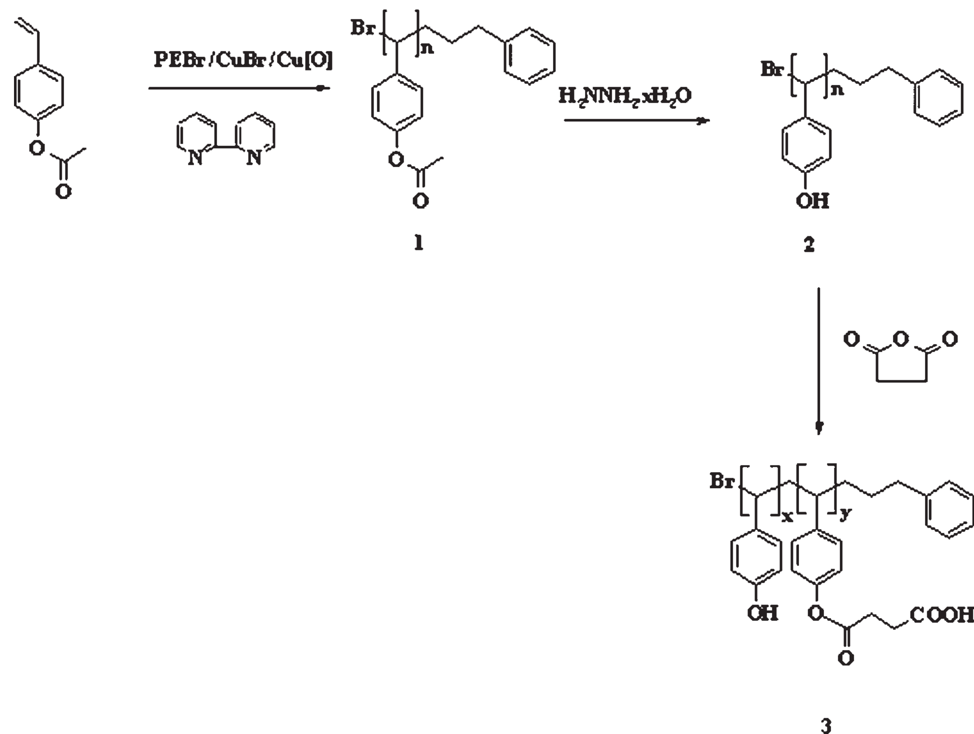
Photosensitive solution was obtained by dissolving copolymers **(3)** (16.75 wt %), triphenylsulfonium triflate (TPST) (1 wt % to the polymer), and crosslinker, benzoguanamine-formaldehyde (5 wt % to the polymer) in propylene glycol. The photosensitive solution was filtered with a 1 μm filter, then spin coated on a 4-inch diameter silicon wafer plate at 1300 rpm for 60 s. The polymer film was prebaked at 90°C for 60 s. The photoresist was exposed with a mercury lamp at intensity 6.5 mW/s at 365 nm wavelength with the i-line exposure tool. After exposure the resist was postbaked at 110°C for 60 s, then developed in 2.38% tetra methyl ammonium hydroxide (TMAH) solution. It was then thoroughly washed with double-distilled water and dried 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 sequence of the lithographic procedure is shown in Figure 1. The pattern was examined with OM and SEM.

RESULTS AND DISCUSSION

PHS, a polymeric phenol, is one of the most interesting of the substituted polystyrenes. This polymer cannot be directly polymerized in a controlled manner by any known polymerization method. Therefore, a protected monomer, 4-acetoxystyrene, was polymerized by ATRP for the preparation of a precursor polymer. We carried out ATRP using a Cu(0)/CuBr system in order to obtain controlled molecular weight and narrow polydispersity for a negative tone lithographic process. The reactions details are depicted in Table I.

TABLE I
Reaction Conditions and Molecular Weight Data of PAS by ATRP

Monomer	Initiator PEBr/CuBr/bpy	Cu [0]	Reaction Temperature °C	Reaction time (h)	Mn	Mw	Polydispersity
1	1 / 1 / 3	0	90	4	3728	4047	1.08
1	1 / 1 / 3	0	90	5	5503	6172	1.12
1	1 / 1 / 3	0	110	4	6857	8703	1.27
1	1 / 2 / 6	0	90	4	5667	6609	1.16
1	1 / 2 / 6	0	90	5	7909	8493	1.07
1	1 / 1 / 3	1	90	2	15452	16993	1.09
1	1 / 1 / 3	1	90	3	22091	23811	1.07



Scheme 1 Synthesis of succinylated poly(hydroxystyrene).

The resulting PAS was hydrolyzed by hydrazine hydrate to PHS, which was further treated with succinic anhydride to get Succ-PHS. The synthetic route is shown in Scheme 1.

It was difficult to raise the molecular weight usually needed for negative resist because of the electron-donating acetoxy group. Therefore, the transition metal activity was enhanced by combining Cu(0) with CuBr in order to obtain the required molecular weight polymer for a negative resist lithographic process.

Experiments indicated that 90°C is sufficient to reach high conversions of **(1)** in the presence of PEBr/CuBr/Cu(0)/bpy with a 1 : 1 : 1 : 3 molar ratio in 2–3 h. Number-average molecular weight (Mn), weight-average molecular weight (Mw), and molecular weight distribution were measured by gel permeation chromatography (Fig. 2). The polydispersity values show the formation of **(1)** with narrow molecular weight distribution (Mw/Mn = 1.07–1.27). The linear Mn/monomer conversion graph and narrow MWD of the resulting polymer indicate living ATRP of PAS. PAS having

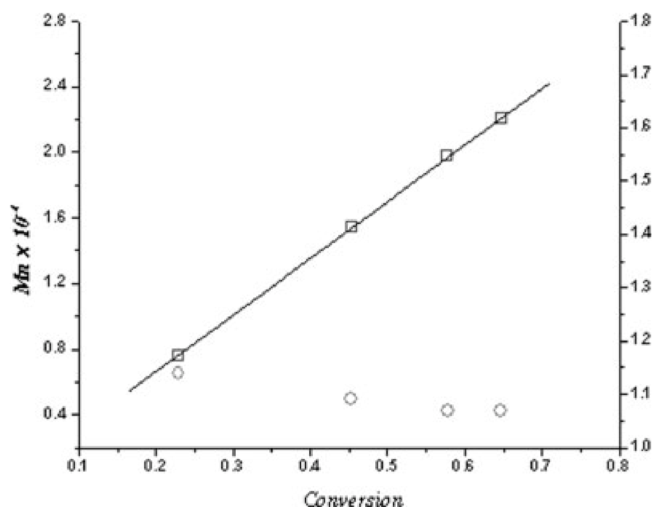


Figure 2 Mn and PDI as a function of monomer conversion in the 4-acetoxystyrene/PEBr/CuBr/2,2′-bipyridine/Cu[0]/90°C initiating system.

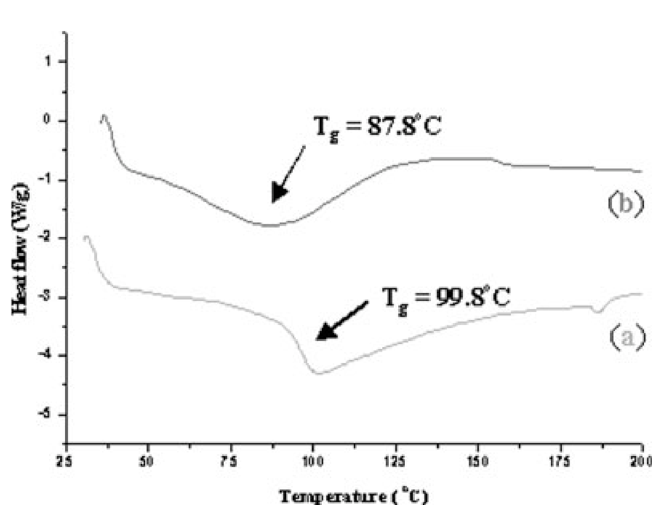


Figure 3 DSC thermograms of (a) poly(4-hydroxystyrene), (b) succinylated-poly (4-hydroxystyrene) 13 mol % hydroxyl group blocking.

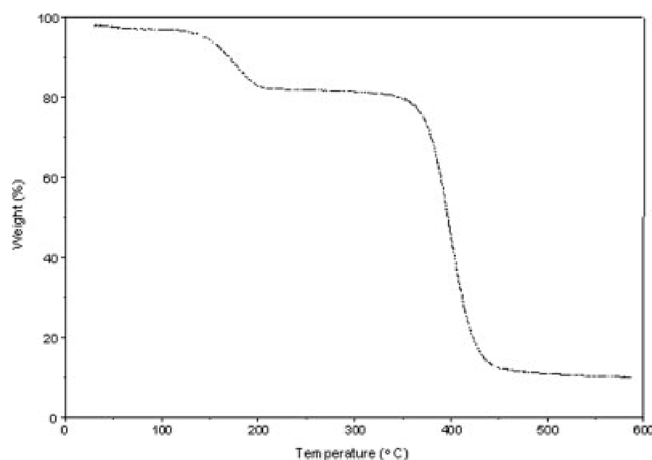


Figure 4 TG curve of succinylated PHS.

a weight-average molecular weight (Mw) $= 1.70 \times 10^4$ and polydispersity index (PDI) (Mw/Mn) $= 1.1$ was selected for chemical modification in order to obtain Succ-PHS.

The FT-IR spectrum of **(2)** exhibits the characteristic absorption bands at 3500 cm^{-1} corresponding to the hydroxyl group, whereas the IR spectrum of **(3)** exhibits its bands at 3500 cm^{-1} and 1713 cm^{-1} for the corresponding hydroxyl and carbonyl groups, respectively.

The thermal properties of the polymer were assessed by DSC and TGA. The thermogram of DSC and TGA is shown in Figures 3 and 4, respectively. It can be seen from Figure 3 that the glass transition temperature (Tg) value of polymer **(2)** is 99.8°C, whereas for polymer **(3)** it is 87.8°C. This indicates a decrease in the Tg value of polymer **(3)**, which may be because of the presence of a flexible succinyl group in the main chain. In addition, the thermogravimetric curve of polymer **(3)** shown in Figure 4 exhibits a first weight loss at 150°C and second weight loss at a temperature higher than 350°C.

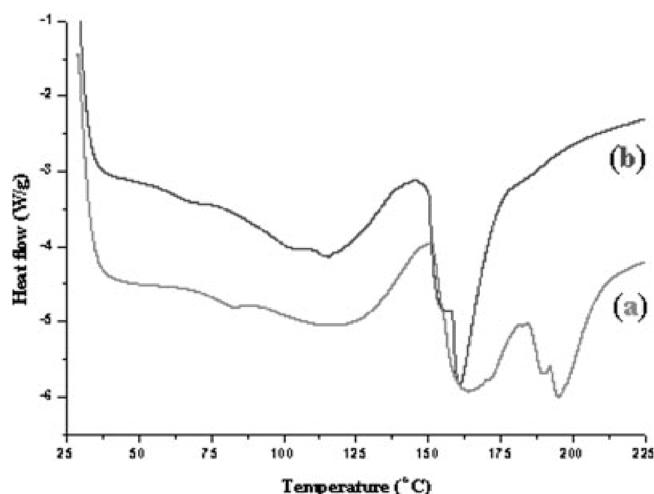


Figure 5 DSC curves of casting succinylated PHS formulated with benzoguanamine-formaldehyde/PAG. (a) Without exposure, (b) exposed to 365 nm UV with 250 mJ/cm^2.

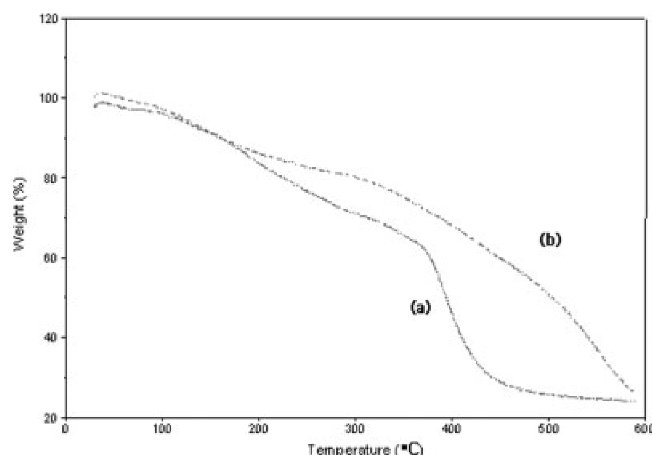


Figure 6 Thermograms of resin, crosslinker, and PAG (a) before exposure, (b) after exposure to 365 nm i-line beam.

The results suggest that the existence of the pendant succinyl groups may increase the steric hindrance and decrease the mobility of the copolymers. In general, the existence of aromatic rings in the polymer chain may increase the thermo properties and the etching resistance. The introduction of succinyl groups onto the copolymers, however, may decrease the benzene ring density and intermolecular π–π interaction, causing a drop in thermal resistance.

The formulation of Succ-PHS, TPST as a PAG, and benzoquanamine-formaldehyde crosslinker was carried out using a broadband UV-A (365 nm, with energy 250 mJ/cm^2) illuminator, which showed a normalized thickness change in the range of 150–185 mJ/cm^2) (Fig. 7).

The recorded FTIR spectrum of the formulated resist showed a characteristic peak at ~ 1085 cm^{-1}.

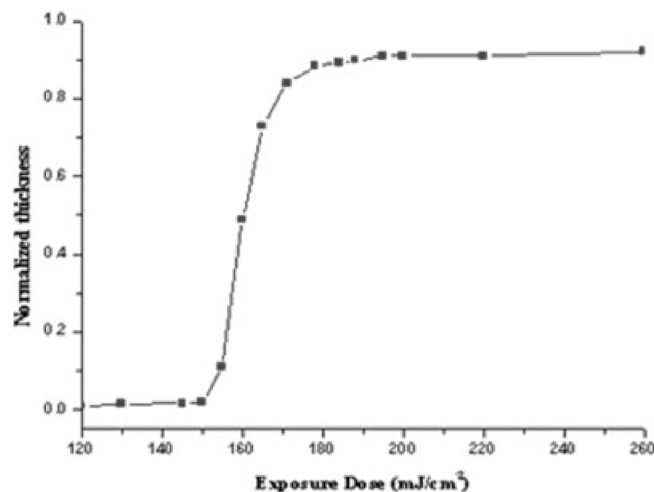


Figure 7 Sensitivity curve of the photoresist film of succinylated PHS/benzoguanamine-formaldehyde/TPST.

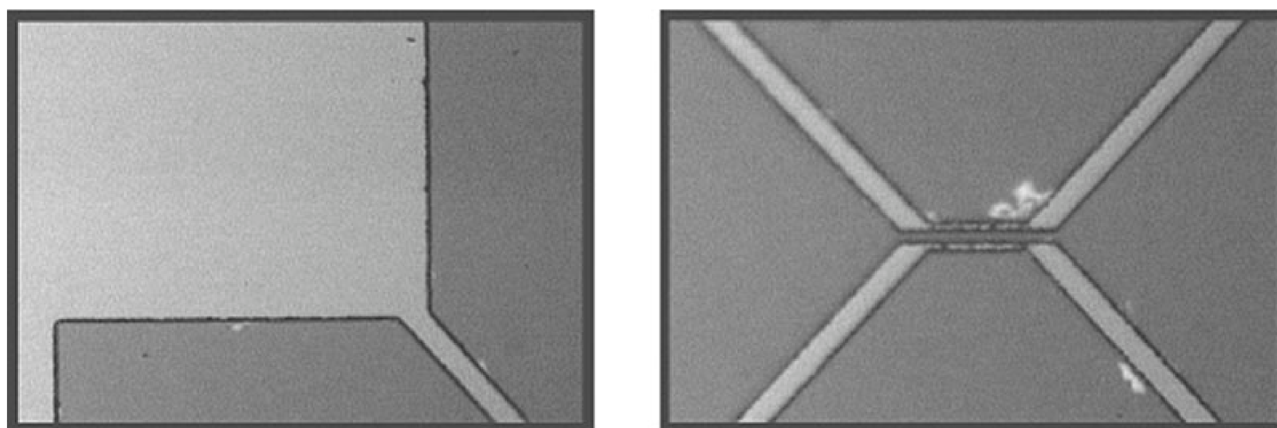


Figure 8 OM pictures of patterns of Succ-PHS/benzoguanamine-formaldehyde/TPST.

However, the normalized peak intensity was found to decrease due to the aromatic ester linkage. Moreover, the peak associated with the carboxyl moiety of succinyl group was shifted from $\sim$1713 to 1700 cm^{-1}. The recorded DSC curves, shown in Figure 5(a), for the casting Succ-PHS formulated with benzoguanamine-formaldehyde and PAG indicate that the thermal curing occurred at 125–150°C. However, the thermogram of the resist after UV irradiation revealed that the curing temperature dropped down because of the catalytic reaction of the photogenerated acids [Fig. 5(b)]. As shown in Figure 6, the thermogram showed that the resist decomposes at $\sim$ 350°C, before UV irradiation; however, after UV irradiation and posttreatment of the cured resist, it does not possess a definite thermal decomposition value.

The residue film of the photoresist showed a normalized thickness upon variation in the exposure dose. With the crosslinker, benzoguanamine-formaldehyde, the yield of the pattern was increased until 30 s of irradiation; after 30 s the yield was saturated and remained constant. The response curve of the crosslinker, benzoguanamine-formaldehyde, is shown in Figure 7. Finally, the negative pattern of the resist was confirmed by OM (Fig. 8) and SEM (Fig. 9) analysis. As shown in Figures 8 and 9, there was no line edge roughness and good resolution, but a little scum at the bottom of the pattern because of conditions that were not optimized and the poor environment of the irradiation tool. The final resolution of the resist showed 15 μm for the benzoguanamine crosslinker. The combination given in this work shows a good result on the image formation induced by the promoted activities of acid generated from the PAG via exposure. Therefore, with this newly synthesized copolymer, PAG, and the selected crosslinker in a proper ratio, a negative tone photoresist material is suggested for a photolithographic procedure. In this work we carried out the experiments only for i-line exposure evaluation in order to study the high-resolution negative tone resist for a high-density interconnection (HDI) print circuit board and micro-BGA. This chemically amplified resist based on Succ-PHS having narrow polydispersity showed proper sensitivity and resolution of the i-line illumination.

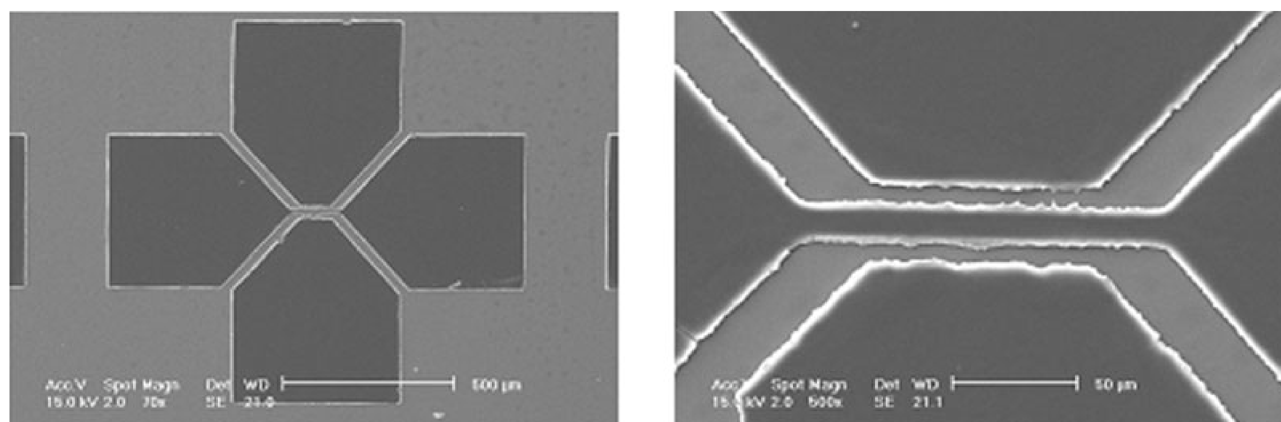


Figure 9 SEM pictures of patterns of Succ-PHS/benzoguanamine-formaldehyde/TPST.

CONCLUSION

We synthesized a poly(hydroxystyrene) containing a succinyl flexible sidechain by ATRP with controlled molecular weight and narrow polydispersity by using (PEBr)/CuBr/Cu(0)/2,2′-bipyridine as the initiating system. Succ-PHS showed good resolution for a negative tone image on an i-line photolithographic application. We also proved that the photogenerated acid-catalyzed reaction between the resin and crosslinker afforded high sensitivity.

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