polymer papers

Cationic chemistry and chemically amplified resist materials for microlithography: synthesis and applications of copolymers of 4-(1-hydroxy-1-methylethyl)styrene and styrene or 4-hydroxystyrene

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Two new copolymers based on 4-(1-hydroxy-1-methylethyl)styrene and styrene or 4-hydroxystyrene have been designed and prepared for use as ultrahigh resolution resist materials in microlithography. The tertiary benzylic alcohol moieties contained in these copolymers undergo acid-catalysed dehydration in a process that proceeds via a stabilized carbenium intermediate, leading to the eventual crosslinking of the copolymers. Resist formulations incorporating these copolymers are readily obtained through the use of a photoacid generator such as triphenylsulfonium hexafluoroantimonate. Irradiation of a film of the resist with deep-u.v. light or an electron beam results in the liberation of protons within the exposed areas of the polymer film. Subsequent heating of the exposed film provides the activation energy that is necessary for the dehydration and crosslinking steps to proceed. The design of the new copolymers is such that no swelling of the crosslinked polymers is seen upon solvent development of the resist images as the polarity of the crosslinked areas is changed drastically as a result of the dehydration step. The resists show extremely high sensitivities to both deep-u.v. and electron-beam radiation and are useful as imaging materials.

(Keywords: chemical amplification; negative resist; microlithography)

INTRODUCTION

The design of polymers that can be used as resist material has changed considerably in recent years as new chemically amplified resists have found acceptance in microelectronics manufacturing[1–3]. Of particular interest are the polymers based on the acid-catalysed thermolysis concepts first studied more than a decade ago by Fréchet and co-workers[4–6]. Probably the best known chemically amplified resists to date are based on poly(4-t-butyloxycarbonyloxystyrene)[4–7] or analogous structures[8–12] for which radiation-generated acid causes loss of the 4-t-butyloxycarbonyl (t-BOC) protecting groups in a catalytic process that results in chemical amplification. As a result of the loss of the t-BOC groups, the polarity of the polymer changes drastically and image development can be achieved either with aqueous base to obtain a positive-tone image, or with an organic solvent such as anisole to achieve negative-tone imaging. It is particularly noteworthy that high quality negative-tone images free of any swelling can be obtained from this resist. This is because a large difference in polarity exists between the exposed and unexposed areas of the film as a result of the loss of the t-BOC groups. The unexposed t-BOC protected polymer is soluble in anisole, while the deprotected polymer has no affinity for this solvent[13].

Electrophilic aromatic substitution has also been used to design highly sensitive resist materials[14–21]. This design, which also relies on acid photogenerated *in situ*, involves the formation of carbenium moieties from species containing several electrophilic groups, followed by their alkylation of the aromatic rings of a matrix polymer in a process that not only amounts to crosslinking, but is also chemically amplified. Chemical amplification arises as the photogenerated proton that is consumed in the formation of the carbenium species is later generated as each aromatic substitution also liberates a proton.

This paper explores the use of novel copolymers containing side-chain functionalities that can be modified via an acid-catalysed process, thereby affording chemical amplification. A review of the use of photogenerated acid and base in polymer curing and imaging has appeared recently[13].

RESULTS AND DISCUSSION

During the study[22,23] of new comb-shaped copolymers containing poly(isobutylene) side-chains, it was noticed that copolymers containing 4-(1-hydroxy-1-methylethyl)-styrene units had a strong tendency to crosslink in the presence of acid catalysts. This crosslinking reaction results from the dehydration of the tertiary benzylic alcohol groups of the 4-(1-hydroxy-1-methylethyl)styrene moieties to afford a reactive carbenium intermediate that

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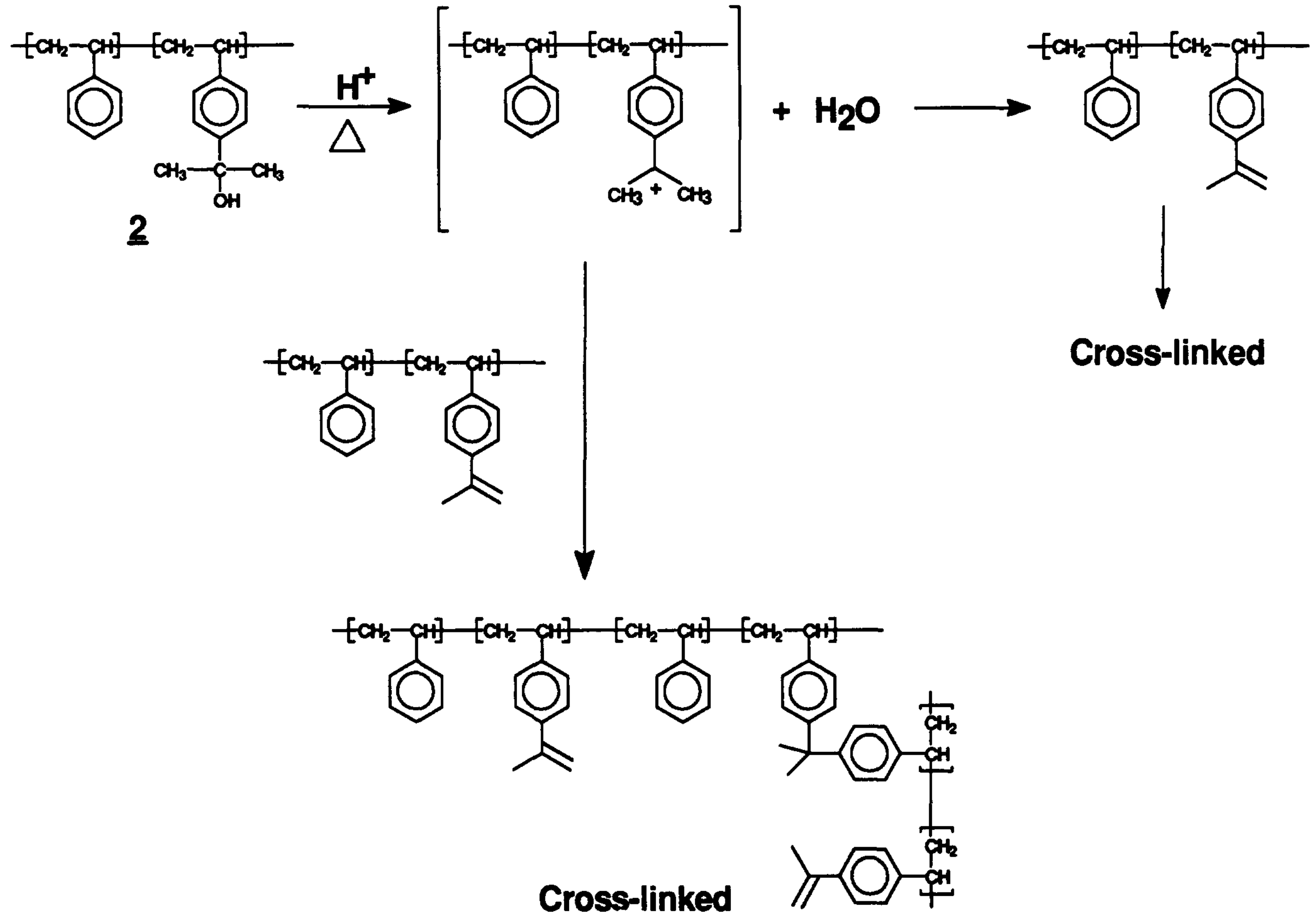
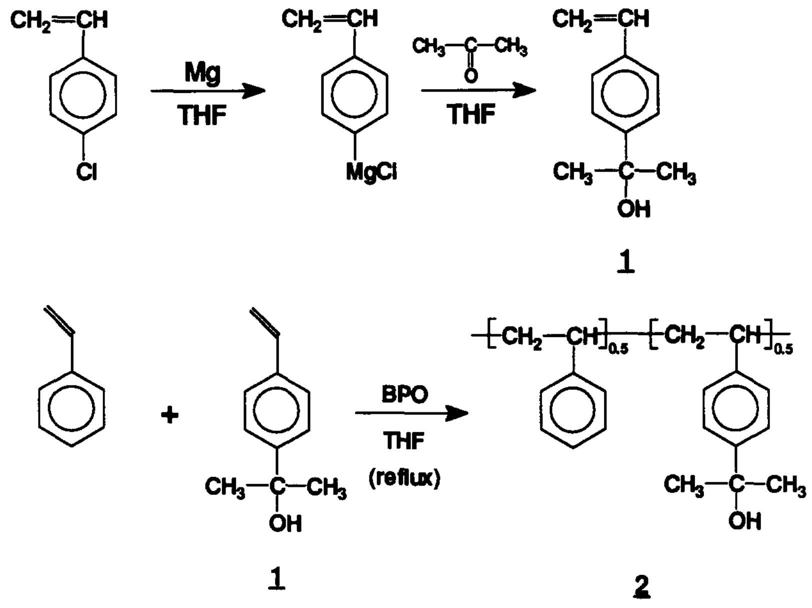
can react further, either via an elimination–polymerization process, or through a series of successive electrophilic aromatic substitution reactions[24,25] (*Scheme 1*). Regardless of the reaction pathway, the overall process results in the insolubilization of the polymer, suggesting that this chemistry could be used to formulate a high sensitivity negative-tone resist material that would be free of swelling.

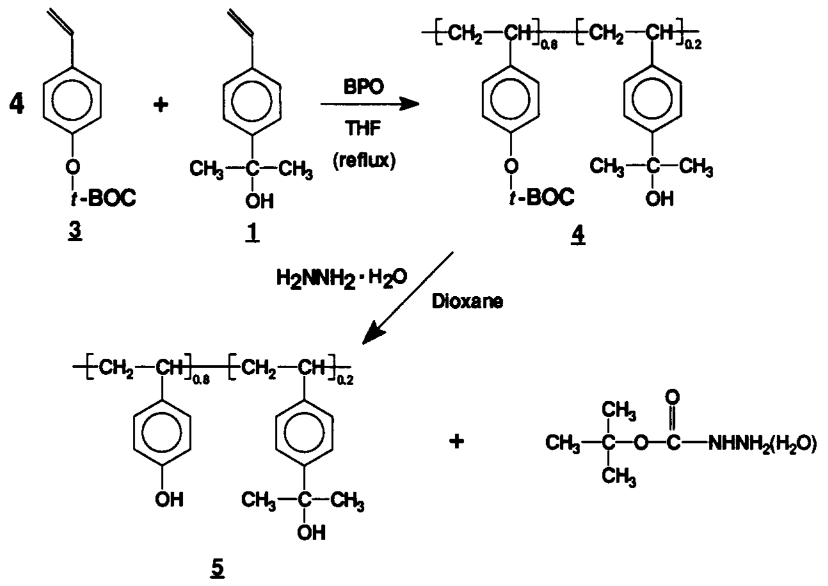
Copolymer **2** is readily obtained by free-radical copolymerization of styrene and 4-(1-hydroxy-1-methylethyl)styrene[22,23,26] **1** using benzoyl peroxide as initiator (*Scheme 2*). The copolymer is soluble in organic solvents but not in the type of aqueous developers that are most desirable for modern microlithography. Therefore a second copolymer, **5**, incorporating a significant percentage of 4-hydroxystyrene units instead of styrene,



Scheme 1



Scheme 2



Scheme 3

was also prepared, as shown in *Scheme 3*. In view of the relatively low stability of 4-hydroxystyrene itself, commercially available t-BOCstyrene[7] **3** was used in the copolymerization with monomer **1** to afford the t-BOC protected copolymer **4**. The ratio of monomers **3** to **1** was kept high at 4:1 to ensure that the final copolymer **5** would dissolve readily in aqueous base. Since acid could not be used to remove the t-BOC protecting groups of **4**, as a crosslinking side-reaction would also occur, we selected hydrazinolysis as the deprotection reaction. This reaction, which proceeds cleanly in dioxane, leads to the quantitative deprotection of **4** into **5** with the formation of t-BOC hydrazine as a by-product. Monitoring of the reaction by *FT*i.r. spectrometry confirms the complete removal of the t-BOC groups as the strong carbonyl peak near $1760\,\mathrm{cm}^{-1}$ disappears completely after hydrazinolysis, as shown in *Figure 1*. The transformation of **4** into **5** is also confirmed by ^{13}C n.m.r. spectrometry with the disappearance of the sharp methyl and quaternary carbon signals of the t-butyl groups at 28.3 and 83.2 ppm, respectively, as well as the carbonyl carbon at 152.6 ppm.

As expected, the glass transition temperature of copolymer **5** ($T_g = 171°C$) is significantly higher than that of copolymer **2** ($T_g = 98°C$) due to the presence of a large proportion of 4-hydroxystyrene units in **5**. Both copolymers were prepared with relatively modest molecular weights, $M_n = 21\,000$ and $34\,000$ and $M_w = 41\,000$ and $66\,000$, respectively, for copolymers **2** and **4**, as measured by g.p.c. with universal calibration provided by a viscometric detector. The molecular weight of **5** is easily deduced from that of **4**; direct measurements on **5** were avoided due to the tendency of phenolic polymers to clog g.p.c. columns.

Resist formulations were prepared from copolymers **2** and **5** with 5 wt% triphenylsulfonium hexafluoroantimonate[27] in 3-methoxypropyl acetate. Given the molecular weights of the copolymers selected for this study, the solutions were prepared at concentrations of about 20 wt%, and films of about $1.0\,\mu m$ in thickness were spin-coated onto silicon, quartz or sodium chloride discs. Imaging experiments on silicon wafers were preceded by thorough spectroscopic studies of the photoinitiated crosslinking process using films spin-coated onto NaCl or quartz substrates. *Figure 2* shows the changes in i.r. spectra that were observed for a resist formulated from copolymer **2** and onium salt after exposure to 254 nm u.v. light at a dose of $1\,\mathrm{mJ\,cm}^{-2}$ followed by baking at 130°C for 5 min. Dehydration is confirmed by the disappearance of the very large hydroxyl band near $3400\,\mathrm{cm}^{-1}$, while formation of the new conjugated vinyl group is confirmed by the appearance of a sharp C=C band at $1627\,\mathrm{cm}^{-1}$. Despite the high percentage of 4-(1-hydroxy-1-methylethyl)styrene units in the copolymer, dehydration is essentially quantitative. This dehydration process occurs as a result of the photogeneration of protons[26] within the exposed areas of the polymer film. The protons catalyse the dehydration, which occurs only when thermal activation is provided by heating to 130°C in the post-exposure bake step. This is confirmed by a control experiment in which no change is observed upon heating a film of **2** to 130°C in the absence of acid. The purely thermal dehydration of **2** only occurs at a temperature exceeding 200°C. Additional monitoring of the crosslinking reaction can be achieved by u.v. spectrometry.

Figure 3 shows the changes in the u.v. spectrum for a resist formulated from **2** after exposure (254 nm, $1\,\mathrm{mJ\,cm}^{-2}$) and post-bake (130°C, 5 min). The acid-catalysed thermal dehydration process is accompanied by a very large increase in absorbency of the polymer film at the exposure wavelength (254 nm). This large change in absorbency results from the formation of a conjugated vinyl group as water is evolved from **2** (*Scheme 1*). Since copolymer **5** only contains 20 mol% of 4-(1-hydroxy-1-methylethyl)styrene units (compared to 50 mol% for copolymer **2**) the increase in its film absorbency upon exposure (254 nm, $1\,\mathrm{mJ\,cm}^{-2}$) and post-bake (120°C, 5 min) is much less pronounced (*Figure 4*). However, it must be emphasized that these changes in absorbency of the polymer films upon image development do not have any effect on the imaging process itself. While an increase in absorbency during exposure to radiation would be deleterious, because light

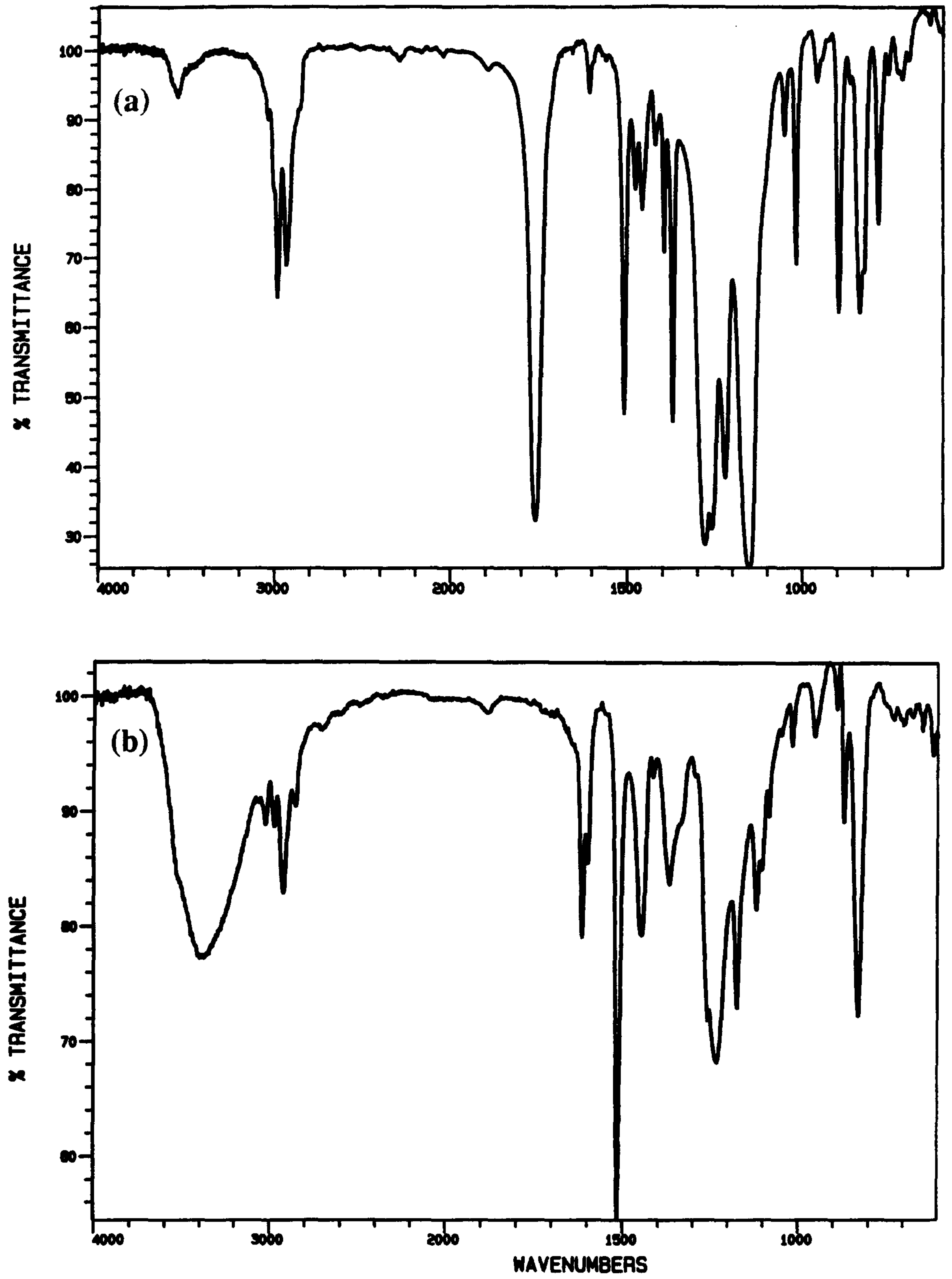


Figure 1 I.r. spectra of copolymer **4** (a) and of copolymer **5** (b) after removal of the t-BOC groups

penetration through the polymer film would be impaired, the increase in absorbency observed in this instance only occurs *after* exposure. Formation of the conjugated vinyl groups that are responsible for the high absorbency of the film is only achieved during the post-exposure bake step. Therefore, this change in u.v. absorption is of no concern in terms of the suitability of polymers **2** and **5** for application as deep-u.v. resists.

Imaging and sensitivity of the resists derived from 2 and 5

Sensitivity measurements at 254 nm were carried out on 1 μm thick films of resists derived from copolymers **2** and **5**, each containing 5 wt% of onium salt, spin-coated onto silicon wafers. Since **2** does not contain any free phenolic group, development of the negative-tone image it affords upon exposure to deep-u.v. radiation and subsequent post-bake at 130°C for 5 min requires the use

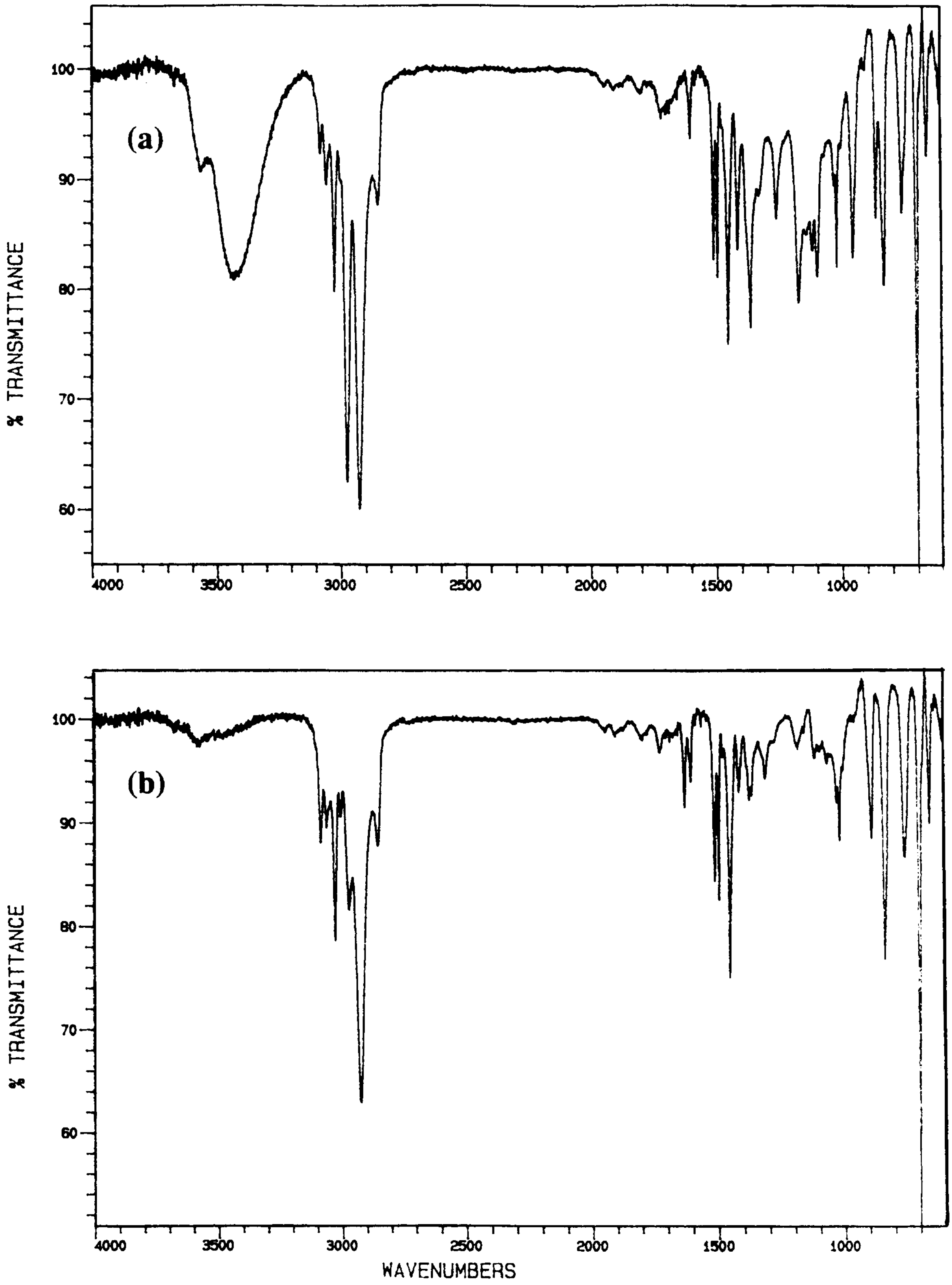


Figure 2 I.r. spectra of copolymer **2** containing 5 wt% onium salt: (a) before exposure; (b) after exposure to 1 mJ cm^{-2} of u.v. light at 254 nm followed by post-baking at 130°C for 5 min

of organic solvents. The developer of choice was found to be 2-propanol, since it afforded rapid development with no observable swelling of the crosslinked image. While many negative-tone resist materials are subject to extensive swelling during development, the design of resists based on **2** is such that swelling can be avoided by an appropriate choice of developer. As we have demonstrated earlier with a resist based on the photo-Fries rearrangement of poly(4-formyloxystyrene), the significant change in polarity that occurs upon the complete acid-catalysed thermal dehydration of **2** is key to this lack of swelling. In addition to becoming crosslinked, the exposed areas of the polymer film become extremely non-polar and have no affinity for the 2-propanol used to develop the unexposed areas of the film.

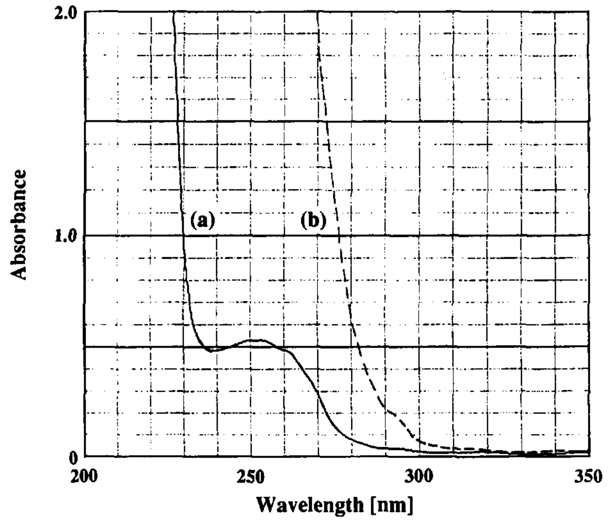


Figure 3 U.v. spectra of copolymer 2 containing 5 wt% onium salt: (a) before exposure to u.v. light; (b) after exposure to 1 mJ cm^{-2} of u.v. light at 254 nm followed by post-baking at 130°C for 5 min

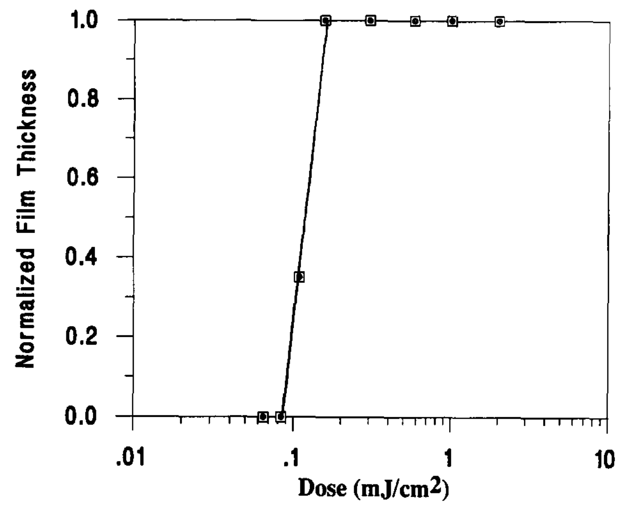


Figure 5 Sensitivity curve for copolymer 2 containing 5 wt% onium salt using 254 nm u.v. light

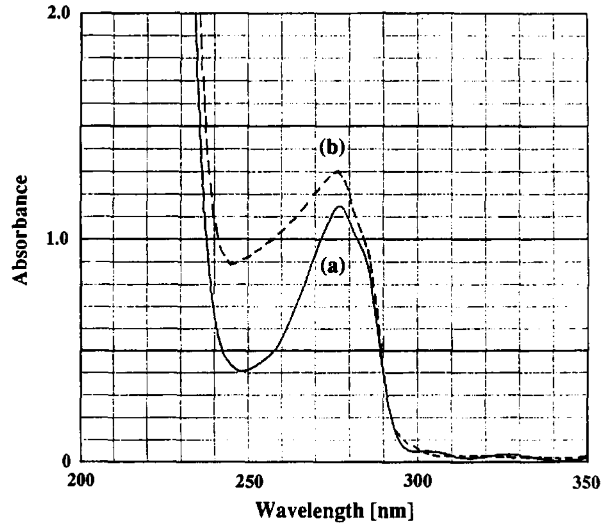


Figure 4 U.v. spectra of copolymer 5 containing 5 wt% onium salt: (a) before exposure to u.v. light; (b) after exposure to 1 mJ cm^{-2} of u.v. light at 254 nm followed by post-baking at 120°C for 5 min

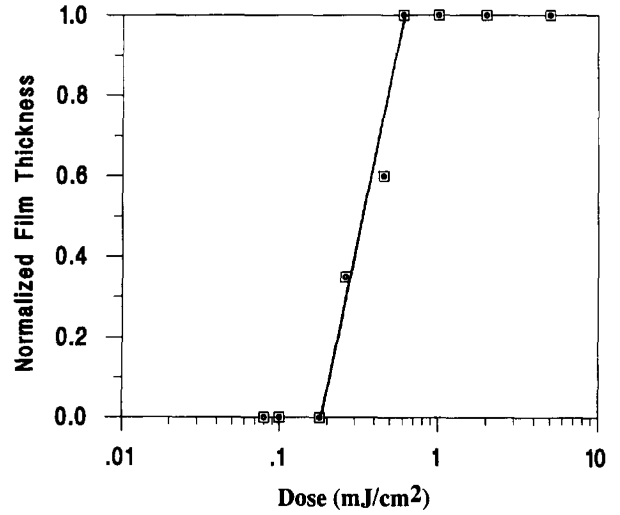


Figure 6 Sensitivity curve for copolymer 5 containing 5 wt% onium salt using 254 nm u.v. light

The sensitivity curve for the resist formulated with 2 and 5% onium salt is shown in *Figure 5*. As can be seen in this figure, the sensitivity of the resist at 254 nm is extremely high: 0.15 mJ cm^{-2} with a contrast of about 4. The corresponding resist formulated from 5 and 5% onium salt is best developed using aqueous base (MF312:H_2O, 45:55) since the polymer contains free phenolic groups. Again, no swelling is observed and the resist also shows high sensitivity (*Figure 6*) with a deep-u.v. exposure dose of 0.6 mJ cm^{-2} at 254 nm and a lower contrast of 1.5. Under E-beam exposure with films 0.55 μm thick, the same resist formulated with copolymer 5 showed a sensitivity of 2.0 μC cm^{-2} at 20 kV (*Figure 7*) while the resist derived from 2 showed an E-beam sensitivity that exceeded the limits of our instrumentation (sensitivity is better than 0.12 μC cm^{-2}).

Figure 8 shows a scanning electron micrograph of a negative-tone image obtained from resist 2 after exposure to 0.3 mJ cm^{-2} at 254 nm and development in 2-propanol. The undercut profile of this contact printed

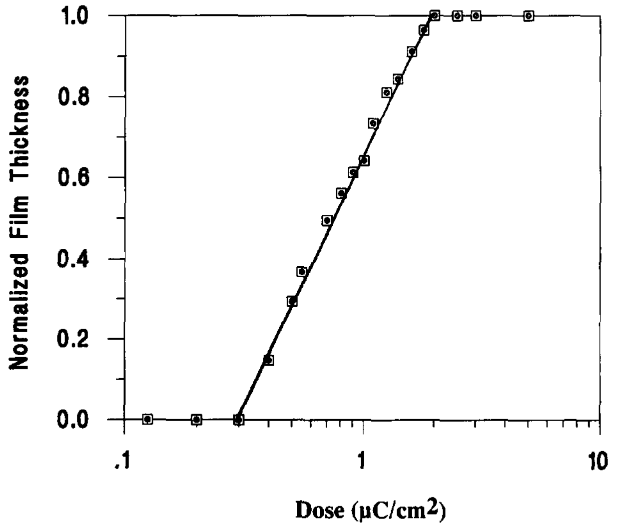


Figure 7 Sensitivity curve for copolymer 5 containing 5 wt% onium salt using E-beam radiation

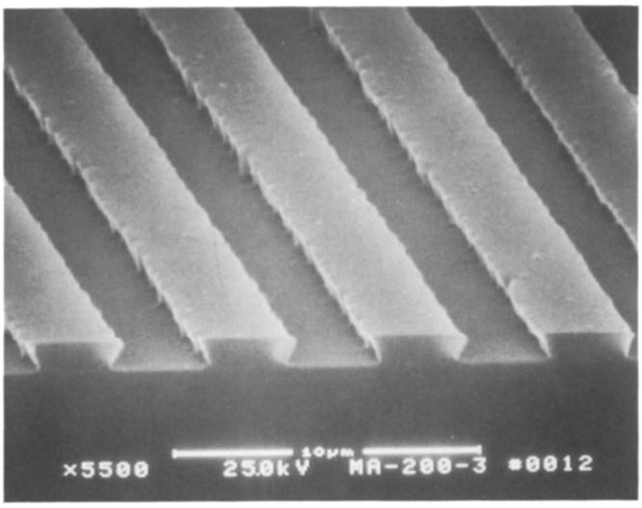


Figure 8 Scanning electron micrograph of a negative-tone image obtained from copolymer **2** and 5 wt% onium salt, using exposure to 0.3 mJ cm^{-2} of u.v. light at 254 nm and development

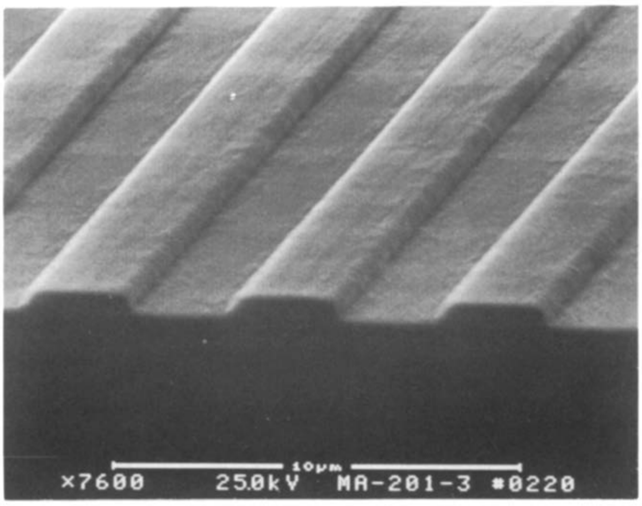


Figure 9 Scanning electron micrograph of a negative-tone image obtained from copolymer **5** and 5 wt% onium salt, using exposure to 1.9 μC cm^{-2} of E-beam radiation and development

image is due to the difference in extent of crosslinking at the top and bottom of the resist layer at the very low exposure dose. *Figure 9* is also a negative-tone image obtained from **5** after E-beam exposure at a dose of 1.9 μC cm^{-2} at 20 kV and development in aqueous base.

EXPERIMENTAL

Materials

Styrene, 4-chlorostyrene, benzoyl peroxide (BPO) and hydrazine monohydrate were purchased from Aldrich. The monomer 4-t-butyloxycarbonyloxystyrene[7], **3**, was obtained from Eastman Kodak and used without further purification. The photoacid generator, triphenylsulfonium hexafluoroantimonate, was prepared as described in the literature[27]. 3-Methoxypropyl acetate was obtained from Arco. The developer, MF312, an aqueous solution of tetramethylammonium hydroxide, was obtained from Shipley Co.

Instrumentation

I.r. spectra were obtained on a Nicolet FTIR/44 spectrometer. ^{1}H n.m.r. spectra were recorded on solutions in $CDCl_3$ or acetone-d_6 on a Bruker AF300 spectrometer with the solvent proton signal as the standard. ^{13}C n.m.r. spectra were recorded on solutions in acetone-d_6 on a Bruker AF300 spectrometer with the solvent carbon signal as the standard. A Nicolet 9430 spectrometer was used to obtain u.v. spectra. D.s.c. was performed using a Mettler DSC30 with a heating rate of 10°C min^{-1}. Molecular weights were determined by g.p.c. on a Nicolet 9560 liquid chromatograph using tetrahydrofuran (THF) at 40°C as the mobile phase at a flow rate of 1.0 ml min^{-1} (3 PLGel columns: 500 Å, 1000 Å and mixed C). Molecular weights were measured using universal calibration (in line viscosity detector from Viscotek, and r.i. detector) based on polystyrene standards.

Preparation of 4-(1-hydroxy-1-methylethyl)styrene[21,26] 1

To a dried 500 ml flask containing 50 ml of freshly distilled THF and 20.00 g of dry magnesium turnings, was added dropwise a solution of 27.60 g (0.20 mol) distilled *p*-chlorostyrene in 100 ml of dry THF. The formation of the Grignard reagent was initiated by addition of a small crystal of iodine and a few drops of methyl iodide. The addition of *p*-chlorostyrene was performed at such a rate that the reaction was running smoothly. After the addition, the solution was heated to reflux for 1 h. The solution was cooled to room temperature and an excess of dry acetone (30 ml) was added dropwise. After completion of the addition, the mixture was stirred under argon overnight. The work-up of the reaction was carried out by pouring the mixture into 1 l of saturated NH_4Cl solution and extracting twice with ether. The combined organic phases were washed with a small amount of water, then dried over $MgSO_4$, filtered and evaporated. The amount of crude mixture recovered was 31.60 g. The crude product was purified by flash chromatography of silica gel with CH_2Cl_2 as eluent, to give 20.03 g (61.8% yield) of a transparent, viscous liquid.

^{1}H n.m.r. (δ values in $CDCl_3$): 1.60 (6H, s, methyl); 1.94 (1H, bs, OH); 5.23, 5.74 (2H, d, vinyl) and 6.74 (1H, q, vinyl); 7.36–7.48 (4H, ABq, ArH).

I.r. (NaCl): ν_{max} (cm^{-1}): 3600–3250, 2976, 1630, 1512, 1401, 1364, 1258, 1171, 1096, 842.

Preparation of copolymer 2 from 1 and styrene

The copolymerization was carried out in a 200 ml, round-bottom, three-necked flask equipped with a condenser, an argon gas inlet and a magnetic stirrer. After the required amounts of the two monomers (4.0 and 2.6 g, respectively) in 99 ml of THF and 1.0 mol% (0.12 g) benzoyl peroxide had been added, the mixture was left stirring for 1 h prior to being refluxed for 24 h. The polymerization mixture was allowed to cool, then concentrated and poured dropwise into an excess of hexane to precipitate the copolymer. The polymer was dried for 30 h *in vacuo*. Purification of the resulting copolymer was accomplished by two reprecipitations from acetone using hexane as the non-solvent. The copolymer was then dried *in vacuo* for 48 h to afford 4.5 g of purified copolymer.

G.p.c.: $M_n = 21\,000$; $M_w = 41\,000$.

^{1}H n.m.r. (δ values in acetone-d$_6$): 1.18–2.32 (CH_3, backbone), 6.32–6.96 (ArH styrene), 6.86–7.56 (Ar'H).

I.r. (KBr): ν_{max} (cm^{-1}): 3600–3150, 2973, 2924, 1494, 1361, 1169, 1096, 830, 700.

Preparation of copolymer 4 from 1 and 3

This polymer was prepared as described above from 3.0 g of **1** and 16.3 g of **3** in 290 ml THF with 0.22 g benzoyl peroxide. After work-up and purification as above, 12.5 g of purified copolymer was obtained.

G.p.c.: $M_n = 34\,000$; $M_w = 66\,000$.

^{1}H n.m.r. (δ values in acetone-d$_6$): 1.25–2.28 (CH_3, backbone) 6.32–7.59 (aromatic).

I.r. (KBr): ν_{max} (cm^{-1}): 3610–3470, 2981, 1758, 1508, 1395, 1278, 1151, 895, 836.

Removal of the t-BOC protecting groups of copolymer 4 and its conversion to copolymer 5

Copolymer **4** (2.5 g) and dioxane (50 ml) were placed in a 100 ml, three-necked flask equipped with a nitrogen gas inlet. Hydrazine monohydrate (1.4 ml) was added to the flask and the solution was left stirring under nitrogen for 20 h at room temperature. The resultant reaction mixture was added dropwise to the solution, which consists of 2 M HCl (30 ml) and 75% aqueous dioxane (60 ml), to precipitate the copolymer. The polymer was filtered and washed thoroughly with water. Further purification was done by two reprecipitations from acetone using water as the non-solvent. The copolymer was then dried *in vacuo* for 72 h.

^{1}H n.m.r. (δ values in acetone-d$_6$): 1.15–2.32 (CH_3, backbone), 6.12–6.88 (ArH of 4-hydroxystyrene), 7.07–7.48 (Ar'H), 7.80–8.23 (OH).

I.r. (KBr): ν_{max} (cm^{-1}): 3650–3100, 2919, 1613, 1513, 1447, 1231, 1190, 829.

I.r. studies, u.v. studies and imaging experiments

The solutions of photoacid generator and copolymer in 3-methoxypropyl acetate were filtered through a 0.5 mm Teflon filter and were subsequently used to cast films onto standard sodium chloride, quartz and silicon wafers. The films were baked at 110°C for 3 min. Film thicknesses (about $1.0\,\mu m$ for deep u.v. studies, and $0.55\,\mu m$ for E-beam studies) were measured by using a Tencor Alpha Step 200. U.v. exposure was performed at 254 nm using an Optical Associate Inc. exposure tool with an Oriel narrow bandpass filter. Post-exposure baking was done at 100–130°C for 1–5 min. Development was achieved by dipping the wafers in 2-propanol or aqueous base (MF 312 in water 45:55) developer. E-beam exposures were carried out on a Cambridge Instrument EBMF-10.5/CS at 20 kV; development conditions in aqueous base were as above. Deep-u.v. sensitivity curves were determined using a chromium on quartz multidensity resolution filter (Ditric Optics) to produce a range of doses impinging on the resist film. For *Figure 5*, a prebake lasting 3.0 min at 110°C was followed by exposure at 254 nm and post-bake at 130°C for 5 min and development in 2-propanol for 14 s. For *Figure 6*, a prebake lasting 3.0 min at 110°C was followed by exposure at 254 nm and post-bake at 120°C for 5 min and development in MF-312:H_2O (45:55) for 105 s. For *Figure 7*, the dose was controlled directly by the E-beam instrument and conditions were analogous to those of *Figure 6*, except for the post-exposure bake at 100°C for 1 min.

CONCLUSION

The new copolymers described in this study significantly extend the concept of acid-catalysed chemical amplification, first demonstrated with poly(t-butyloxycarbonyloxystyrene), as it was initially thought that only superacid would effectively catalyse such processes with the catalytic chain lengths of 800–1200 demonstrated by McKean *et al.*[28]. In fact, the presence of water in the reaction medium is clearly not a problem. Therefore protonated water is the strongest acid present in our system and the key step[29,30] appears to be the ease with which the carbenium intermediate species can be formed by protonation of the starting material. Although we have not measured the catalytic chain length of our system, the very high sensitivity, and the fact that complete loss of water is seen, suggest that it is similar in magnitude to that measured by McKean *et al.*[28] for the less sensitive poly(t-butyloxycarbonyloxystyrene) based resists. We are currently conducting a detailed mechanistic study of a family of chemically amplified resists, because a thorough understanding of the various steps involved in the process will facilitate the design of highly efficient materials.

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