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Synthesis and polymerization of t-BOC protected maleimide monomers: *N*-(t-butyloxycarbonyloxy)maleimide and *N*-[*p*-(t-butyloxycarbonyloxy)phenyl]-maleimide

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Two t-butyloxycarbonyl (t-BOC) protected maleimide monomers, *N*-(t-butyloxycarbonyloxy)maleimide (t-BOCOMI) and *N*-[*p*-(t-butyloxycarbonyloxy)phenyl]maleimide (t-BOCOPMI), have been synthesized and polymerized. The t-BOC group was used to protect the hydroxy groups of the starting *N*-substituted maleimides, *N*-hydroxymaleimide (HOMI) and *N*-(*p*-hydroxyphenyl)maleimide (HOPMI). t-BOCOMI and t-BOCOPMI were copolymerized with styrene derivatives (X-St) to obtain the t-BOC protected polymers P(t-BOCOMI/X-St) and P(t-BOCOPMI/X-St) in high conversions. P(t-BOCOMI/St) and P(t-BOCOPMI/St) were cleanly deprotected by heating the polymers to 110 and 175°C, respectively. The deprotection temperature of the copolymers of t-BOCOMI (ca. 100°C) is the lowest among the known t-BOC protected polymers. Deprotection of P(t-BOCOMI/X-St) and P(t-BOCOPMI/X-St) produced the corresponding polymers having HOMI and HOPMI structures, respectively, and resulted in large changes in physical properties. The deprotected polymers have very high glass transition temperatures (above 250°C) and good solubility in aqueous base solutions, whereas the t-BOC polymers are only soluble in organic solvents. P(t-BOCOMI/St) was found to have desirably low ultra-violet absorption and high sensitivity in resist formulations.

(Keywords: t-BOC maleimide monomers; synthesis and polymerization; *N*-protected polymaleimides)

INTRODUCTION

During the past decade, chemically amplified resists have attracted a great deal of attention because of their high sensitivity and versatility in lithographic applications[1,2]. In the chemical amplification process, the deprotection reaction, catalysed by acids generated photochemically, is considered to be the key chemistry. The typical acid-labile protecting group is the t-butyloxycarbonyl (t-BOC) group, which is readily removable by acid-catalysed thermolysis. Poly[*p*-(t-butyloxycarbonyloxy)styrene] (*p*PBOCSt) has been investigated in detail as a prototype of t-BOC protected polymers[3,4] and successfully applied with some modifications to practical lithography[5,6]. Recently Ito and coworkers[7] reported the synthesis of poly[*m*-(t-butyloxycarbonyloxy)styrene] (*m*PBOCSt) and described much-improved properties. The protected polymers, *p*PBOCSt and *m*PBOCSt, are transformed into the corresponding polymers having *p*- and *m*-hydroxystyrene (HOSt) units by the deprotection of the side-chain t-BOC groups with concurrent evolution of carbon dioxide and isobutylene. t-Butyl methacrylate is a commercial t-BOC monomer and its terpolymers were reported to be useful resist materials, since they produce methacrylic acid polymers when deprotected[8]. The large polarity changes caused by the deprotection of such polymers generate large changes in polymer solubilities and thermal properties, which are required for practical resist applications.

In some advanced lithographic processes, resist polymers are required to have high glass transition temperatures (T_g) above 200°C. Incorporation of the maleimide (MI) units advantageously provides an avenue to high T_g. Thus, thermally stable copolymers consisting of *N*-substituted maleimide-styrene (MI-St)[9] and *N*-(*p*-hydroxyphenyl)maleimide-styrene (HOPMI-St)[10,11] were synthesized. The t-BOC group has been introduced on both imide NH of MI units and phenolic OH of HOPMI units through reactions carried out on the preformed maleimide copolymers[9,12,13]. However, these t-BOC modified copolymers could limit the practical usefulness owing to the difficulties in synthetic

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control of the protection reactions on the polymers because the protected copolymers are not prepared directly by copolymerizations of the corresponding t-BOC protected MI monomers.

Therefore, we have studied the synthesis and polymerization of variously *N*-substituted (protected) MI monomers. Previously, we have reported the syntheses and polymerizations of functional maleimide monomers such as *N*-(t-butyloxycarbonyl)maleimide (t-BOCMI)[14,15], *N*-(t-butoxy)maleimide (t-BuOMI)[16] and *N*-(*p*-toluenesulfonyloxy)maleimide (TsOMI)[17,18]. These *N*-substituted maleimides were usually prepared via the retro-Diels-Alder reactions based on inexpensive starting materials. All of the reported t-BOC protected MI polymers were found to have sufficiently high T_g values, above 200°C, after the thermal or acidolytic deprotection in the side-chains. In this work, the facile syntheses and copolymerizations of two t-BOC protected MI monomers, *N*-(t-butyloxycarbonyloxy)maleimide (t-BOCOMI) (**5**) and *N*-[*p*-(t-butyloxycarbonyloxy)phenyl]maleimide (t-BOCOPMI) (**7**), are reported and the characteristics of the deprotection reactions are discussed.

EXPERIMENTAL

Materials and instruments

Furan, phenylchloroformate, di-t-butyl dicarbonate (DTBDC), maleic anhydride, *p*-aminophenol, styrene (St), *p*-methylstyrene (MeSt) and *p*-chlorostyrene (ClSt) were purchased from Aldrich Chemical Co. *p*-Acetoxystyrene (AcOSt), *p*-(t-butyloxycarbonyloxy)styrene (t-BOCSt) and *p*-trimethylsilylstyrene (SiSt) were kindly donated by Hoechst Celanese Corp., Eastman Kodak Co. and Korea Kumho Petrochemical Co., respectively. The styrene monomers (X-St) were purified by distillation. The radical initiator *N*,*N*′-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other chemicals were purified by conventional methods. Tetrahydrofuran (THF) and dioxane solvents were spectrophotometric grade. Commercial tetramethylammonium hydroxide (TMAH) solutions were used as the developer in photoimaging experiments.

^{1}H n.m.r. spectra were taken on a JEOL PMX-60 SI spectrometer or a Varian Gemini 300 MHz spectrometer in deuteriochloroform using tetramethylsilane (TMS) as an internal standard. ^{13}C n.m.r spectra were also taken with a Varian Gemini spectrometer in deuteriochloroform. Infra-red spectra were recorded on a Polaris *FT*-i.r. spectrophotometer from Mattson Instrument Co., and mass spectra were taken on a JEOL JMS-DX 303 spectrometer. Elemental analysis was done with a Perkin-Elmer model 240C Elemental Analyzer. Thermal analysis was performed on a Du Pont model 910 DSC and model 951 TGA at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The solution viscosities of polymers were measured with a Cannon-Fenske viscosity tube (No. 50) or an Ubbelohde viscometer tube mounted to an automatic measuring apparatus from Schott-Gerate GmbH at 25°C in dioxane.

Synthesis of N-*(t-butyloxycarbonyloxy)maleimide (t-BOCOMI) (5)*

N-Hydroxymaleimide (HOMI) (**4**) was prepared according to the known procedure[19] as follows. *N*-(Phenyloxycarbonyloxy)maleimide was obtained in a yield of 78% by thermolysis of its furan adduct at 150°C. A solution of 42.26 g of *N*-(phenyloxycarbonyloxy)maleimide in 500 ml of methanol was refluxed to produce HOMI (**4**) in a yield of 62% (12.60 g) after recrystallization: m.p. 125°C (lit.[19] m.p. 125–126°C; Aldrich Chemical Catalog m.p. 133–135°C). To a solution of HOMI (11.31 g, 0.10 mol) in 50 ml of THF were added 21.88 g (0.10 mol) of DTBDC and pyridine (8.00 g, 0.10 mol). The resulting solution was stirred for 1 h at room temperature, and then THF and pyridine were removed under reduced pressure. Water (50 ml) was added and the resulting mixture was extracted three times with dichloromethane and dried over anhydrous magnesium sulfate. The solvent was stripped off and the solid product was obtained as yellowish crystals. Recrystallization from benzene and n-hexane (1 : 10 by volume) gave the desired t-BOCOMI (**5**) as colourless needle crystals, in a yield of 40.0% (8.30 g); m.p. 84°C.

^{1}H n.m.r. (300 MHz, in $CDCl_3$), δ (ppm): 1.60 (s, 9H, t-Bu), 6.65 (s, 2H,–CH=CH–). ^{13}C n.m.r. (300 MHz, in $CDCl_3$), δ (ppm): 27.5 (Me), 87.9 (t-Bu), 132.6 (C=C), 150.2 (carbonyl of t-BOC), 164.1 (carbonyl of imide). I.r. (KBr), $\bar{\nu}$ (cm^{-1}): 1805, 1785 and 1745 (carbonyl of imide and carbonate), 1380 (t-Bu), 1050 (C–O–C), 820 (olefinic CH). M.s.: 198 (M–CH_3, 4), 140 (20), 96 (7), 57 (100). Elemental analysis: calculated for $C_9H_{11}NO_5$, C 50.74, H 5.13, N 6.58; found, C 50.70, H 5.13, N 6.61.

Synthesis of N-*[*p*-(t-butyloxycarbonyloxy)phenyl]-maleimide (t-BOCOPMI) (7)*

By direct preparation from HOPMI. *N*-(*p*-Hydroxyphenyl)maleimide (HOPMI) (**6**) was prepared by the reaction of maleic anhydride and *p*-aminophenol according to the known procedure; m.p. 187°C (lit.[20] m.p. 184°C). To a solution of **6** (19.76 g, 0.10 mol) in a mixture of pyridine (40 ml) and THF (160 ml) was added 25.00 g (0.11 mol) of DTBDC. After stirring for 1 h at room temperature, the solution was poured into an excess of water and the precipitate was filtered and dried. Recrystallization from methanol gave the desired t-BOCOPMI (**7**) as pale-yellow needles in a yield of 90% (27.10 g); m.p. 142°C.

^{1}H n.m.r. (300 MHz, in $CDCl_3$), δ (ppm): 1.53 (s, 9H, t-Bu), 6.79 (s, 2H,–CH=CH–), 7.4–7.2 (q, 4H, phenyl). ^{13}C n.m.r. (300 MHz, in $CDCl_3$), δ (ppm): 28.1 (Me), 84.0 (t-Bu), 134.2 (C=C), 121.9, 126.9, 128.7, 151.9 (aromatic), 150.2 (carbonyl of t-BOC), 163.3 (carbonyl of imide). I.r. (KBr), $\bar{\nu}$ (cm^{-1}): 1750 and 1710 (carbonyl of imide and carbonate), 1380 (t-Bu), 1050 (C–O–C), 820 (olefinic CH). M.s., 189 (80), 82 (14), 57 (100). Elemental analysis: calculated for $C_{15}H_{15}NO_5$, C 62.28, H 5.23, N 4.84; found, C 62.38, H 5.36, N 4.86.

By imidization of t-BOC maleamic acid. *p*-(t-Butyloxycarbonyloxy)aniline (**8**) was prepared by the reaction of *p*-aminophenol with DTBDC in THF[3,21]. To a solution of **8** (22.40 g, 0.11 mol) in acetone (200 ml) was added 11.00 g (0.11 mol) of maleic anhydride, and the resulting mixture was stirred for 3 h at room temperature. The solution was then poured into an excess of water. The crude product (**9**) precipitated as a white powder in a yield of 87% (28.87 g); m.p.

171°C. The t-BOC maleamic acid (**9**) (28.60 g, 0.09 mol) and sodium acetate (3.82 g, 0.05 mol) in acetic anhydride (300 ml) were allowed to react for 4 h at 80°C. The solution was then poured into water and the precipitates were filtered, dried and recrystallized from methanol to obtain the t-BOCOPMI (**7**) in a yield of 74% (19.27 g); m.p. 142°C.

Polymerization

All polymerizations were performed in dioxane with AIBN as an initiator under nitrogen atmosphere. The radical polymerizations of t-BOCOMI and t-BOCOPMI with styrene monomers (X-St) (**10**) were conducted at 50 or 55°C under conditions as described in *Table 1*. The polymers were isolated by precipitation in methanol. The polymers were fully characterized by spectroscopy and the thermal deprotection of the side-chain t-BOC groups was investigated by t.g.a. and d.s.c. analysis.

Copolymerization of t-BOCOMI (5) with styrene. In a 100 ml reaction flask were placed 4.46 g (20.9 mmol) of t-BOCOMI, 2.13 g (20.4 mmol) of styrene and 133 mg of AIBN (0.80 mmol, 2 mol%) in 13 ml of dioxane. After the polymerization was performed for 2 h at 50°C, the product was diluted with dioxane and precipitated by adding slowly to 1 litre of methanol. The white powdery alternating copolymer P(t-BOCOMI/St) (**11**) (X=H) was obtained in a conversion of 83% (5.47 g) after drying at 30°C *in vacuo*. The inherent viscosity of the polymer was 1.00 dl g^{-1} in dioxane at 25°C.

Copolymerization of t-BOCOPMI (6) with styrene. In a 100 ml reaction flask were placed 5.79 g (20.0 mmol) of t-BOCOPMI, 2.08 g (20.0 mmol) of styrene and 131 mg of AIBN (0.80 mmol, 2 mol%) in 39 ml of dioxane. The mixture was heated for 5 h at 55°C. The product was diluted with dioxane and precipitated by slow addition to 1 litre of methanol. The white powdery alternating copolymer P(t-BOCOPMI/St) (**12**) (X=H) was obtained in a conversion of 85% (6.70 g). The inherent viscosity of the polymer was 0.62 dl g^{-1} in dioxane at 25°C.

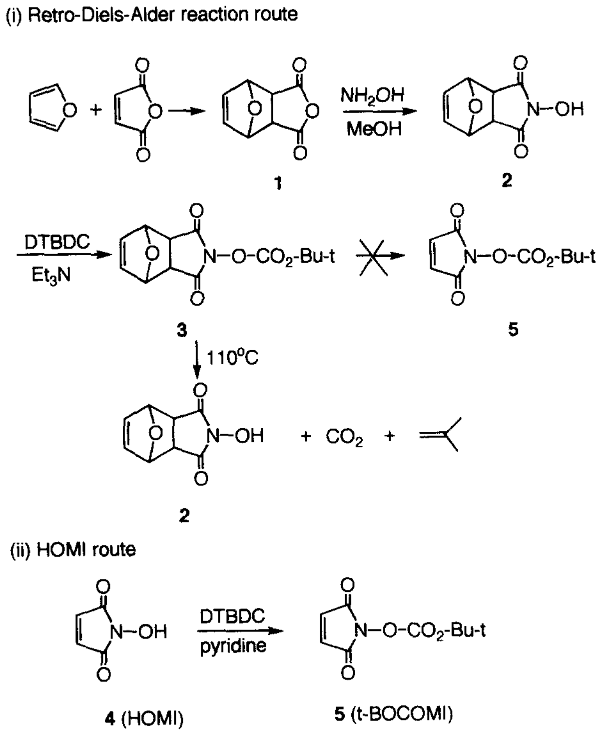
Resist evaluation

The resist solutions were prepared by dissolving the t-BOC polymers at 20 wt% and a photoacid generator at 10 wt% to the polymer in cyclohexanone and were spin-coated to make films. After baking to remove solvent, the films were imagewise-exposed at 260 nm with an OAI Exposure System as previously described[12,15,16]. Negative- and positive-tone images were obtained by developing with appropriate developers after the post-exposure bake treatment.

RESULTS AND DISCUSSION

Synthesis of monomers: t-BOCOMI (5) and t-BOCOPMI (7)

The reverse Diels–Alder reaction is known to be a useful method for the preparation of *N*-substituted functional maleimides[14,16,17,19]. We attempted a retro-Diels–Alder reaction to obtain the t-BOCOMI (**5**) monomer as described in *Scheme 1(i)*. The t-BOC protected adduct **3**, t-BOCOMI/furan, was obtained by reacting the HOMI/furan (**2**) adduct with DTBDC as described for the preparation of t-BuOMI[16]. However, the attempted thermolysis of **3** failed. At about 120°C, deprotection of t-BOC groups occurred to regenerate the adduct **2** instead of producing the desired t-BOCOMI (**5**). The low decomposition temperature of the t-butyl carbonate group of the adduct **3** (ca. 110°C) precludes the desired retro-Diels–Alder reaction. Therefore, the t-BOC group was directly introduced into HOMI (**4**). DTBDC and **4** were allowed to react in the presence of different bases under a variety of conditions. The maleimide is quite unstable to base but using pyridine allowed successful preparation of t-BOCOMI as shown in *Scheme 1(ii)*.

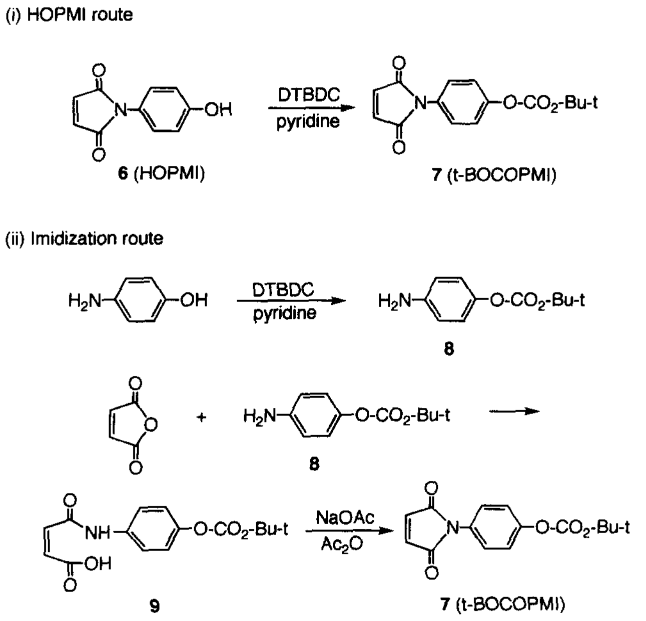


Scheme 1 Synthesis of *N*-(t-butyloxycarbonyloxy)maleimide (t-BOCOMI) (5)

The t-BOC protected MI monomer, t-BOCOPMI (**7**), was synthesized by two different routes as described in *Scheme 2*. In the first route, t-BOCOPMI was prepared directly from HOPMI (**6**) in a high yield of 90% by treatment with pyridine and DTBDC. In this case no side reaction of the maleimide double bond occurred and the reaction proceeded cleanly. In the second route, **7** was prepared by a reaction of a t-BOC protected compound **8** with maleic anhydride followed by imidization as shown in *Scheme 2(ii)*. This route has a lower yield than the former route. In the n.m.r. spectrum, t-BOCOMI has only two singlet peaks at 1.6 ppm for nine t-Bu protons and at 6.7 ppm for two olefinic protons. t-BOCOPMI shows three singlet peaks at 1.5 ppm for nine t-Bu protons, 6.8 ppm for two olefinic protons and 7.4–7.2 ppm for four aromatic protons. The structures of t-BOCOMI and t-BOCOPMI were confirmed by ^{13}C n.m.r. spectra, i.r. spectra, mass spectra and elemental analysis.

Polymerizations

Radical copolymerizations of the t-BOC protected monomers, t-BOCOMI and t-BOCOPMI, with various styrene monomers were performed. The results are



Scheme 2 Two synthetic routes to *N*-[*p*-(t-butyloxycarbonyloxy)-phenyl]maleimide (t-BOCOPMI) (7)

Table 1 Radical copolymerization of t-BOCOMI and t-BOCOPMI with styrenes

t-BOC polymer[a] **11, 12**	AIBN[b] (mol%)	M/S[c] (g ml^{-1})	Time (h)	Conversion (%)	Inherent viscosity[d]
P(t-BOCOMI/St)	2	0.51	2	83	1.00
P(t-BOCOMI/St)	2	0.50	1	74	1.09
P(t-BOCOMI/St)	1	0.93	1.5	87	1.64
P(t-BOCOMI/MeSt)	4	0.90	2	82	1.24
P(t-BOCOMI/ClSt)	2	0.49	3	46	1.07
P(t-BOCOMI/t-BOCSt)	2	0.52	2	81	1.04
P(HOMI/St)[e]	2	0.50	4	99	0.19
P(t-BOCOPMI)[f]	2	0.73	9	80	–
P(t-BOCOPMI/St)	4	0.50	2	93	0.46
P(t-BOCOPMI/St)	2	0.20	5	85	0.62[g]
P(t-BOCOPMI/St)	1	0.25	4	83	0.77
P(t-BOCOPMI/MeSt)	4	0.50	3	93	0.65
P(t-BOCOPMI/AcOSt)	4	0.50	3	77	0.56
P(t-BOCOPMI/ClSt)	4	0.50	3	86	0.51
P(t-BOCOPMI/t-BOCSt)	4	0.50	3	88	0.71
P(t-BOCOPMI/SiSt)	4	0.50	3	85	0.94
P(HOPMI/St)[e]	4	0.50	2	75	0.51
P(HOPMI/MeSt)[e]	1	0.50	6	81	0.63

[a] Copolymerizations were performed in 1 : 1 molar feed ratio at 50°C for t-BOCOMI and at 55°C for t-BOCOPMI in dioxane: St, styrene; MeSt, *p*-methylstyrene; ClSt, *p*-chlorostyrene; AcOSt, *p*-acetoxystyrene; t-BOCSt, *p*-(t-butyloxycarbonyloxy)styrene; SiSt, *p*-trimethylsilylstyrene

[b] Mole per cent of the initiator AIBN to the combined monomers

[c] Ratio of the weight of two monomers to the volume of dioxane

[d] Inherent viscosities (dl g^{-1}) measured at a concentration of 0.20 g dl^{-1} in dioxane at 25°C

[e] Copolymerization of HOMI or HOPMI with St or MeSt at 55°C for comparison

[f] Homopolymerization of t-BOCOPMI at 60°C for 9 h gave P(t-BOCOPMI) with $\bar{M}_w$ of 67 000 (*MWD* 2.65) by g.p.c measurement in THF

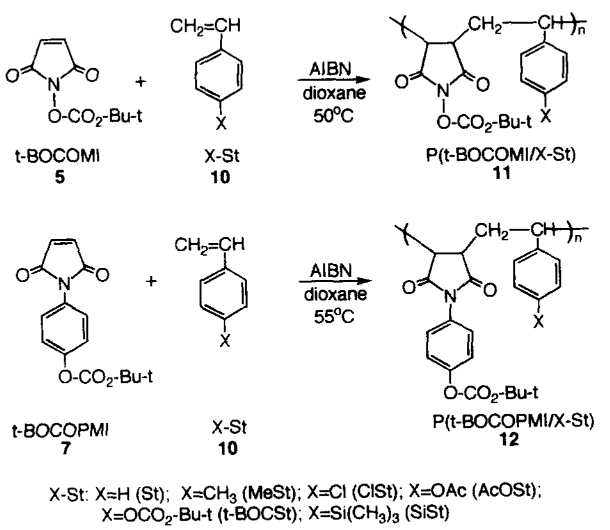
[g] This sample has $\bar{M}_w$ of 313 000 (*MWD* 3.50) by g.p.c measurement in THF

summarized in *Table 1*. Both monomers were readily copolymerized with styrene monomers **10** (X-St), such as St, MeSt, ClSt, AcOSt, t-BOCSt and SiSt, in high conversion within 3 h (*Scheme 3*). The molecular weight of the copolymers was controlled by adjusting the amounts of initiator and solvent used in the copolymerizations. The homopolymerization of t-BOCOMI was sluggish and gave rather low-molecular-weight products with adventitious deprotection of t-BOC groups. However, the homopolymerization of t-BOCOPMI gave high-molecular-weight polymer P(t-BOCOPMI) without accompanying deprotection.

The copolymers, poly(t-BOCOMI-*co*-X-St), i.e. P(t-BOCOMI/X-St) (**11**) and poly(t-BOCOPMI-*co*-X-St) i.e. P(t-BOCOPMI/X-St) (**12**), were confirmed to have alternating structures based on the proton n.m.r. spectra and elemental analyses (*Scheme 3*). It is well known that a nearly alternating structure is generated when an electron-poor MI monomer and an electron-rich styrene monomer are copolymerized[22]. Poly(*N*-hydroxymaleimide-*alt*-styrene) (P(HOMI/St)) and poly[*N*-(*p*-hydroxyphenyl)maleimide-*alt*-styrene] (P(HOPMI/St)) were also prepared from a direct copolymerization of HOMI or HOPMI and styrene in 1 : 1 molar feed ratio for a comparison study.

Thermal properties and deprotection studies

The alternating copolymer P(t-BOCOMI-*alt*-St), i.e. P(t-BOCOMI/St) (**11**) (X=H), is stable up to 80°C by t.g.a., and between 90 and 120°C it undergoes a precipitous mass loss corresponding to the complete thermal deprotection of the t-BOC groups. A plateau followed by decomposition of the main chain above 310°C is observed as depicted in *Figure 1*. The alternating copolymer P(t-BOCOPMI/St) (**12**) (X=H) exhibited a comparable thermogram as shown in *Figure 1*, except that the onset of mass loss occurred at about 170°C. The t-BOC protected copolymers P(t-BOCOMI/X-St) (**11**) and P(t-BOCOPMI/X-St) (**12**) were converted to



Scheme 3 Radical copolymerization of t-BOCOMI or t-BOCOPMI with styrene derivatives (X-St)

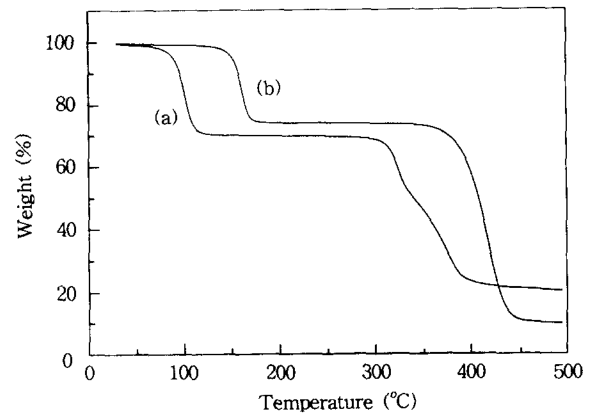
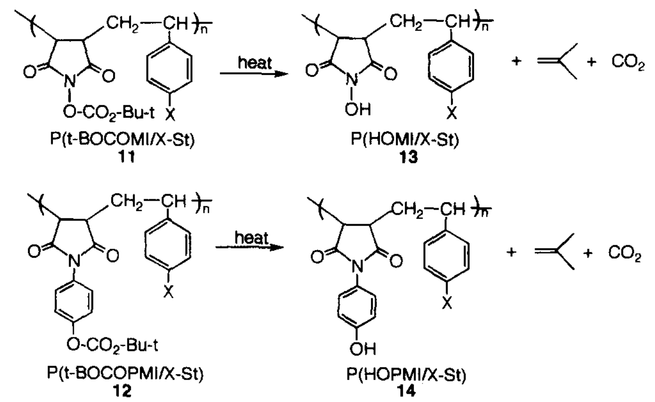


Figure 1 T.g.a. thermograms of P(t-BOCOMI/St) (a) and P(t-BOCOPMI/St) (b) in a nitrogen stream at a heating rate of 10°C min^{-1}



Scheme 4 Thermal deprotection of the t-BOC copolymers to the corresponding copolymers of HOMI and HOPMI

P(HOMI/X-St) (**13**) and P(HOPMI/X-St) (**14**), respectively, by thermal deprotection of the side-chain t-BOC groups, releasing isobutene and carbon dioxide as described in *Scheme 4*. The deprotection temperature of P(t-BOCOMI/St), at about 100°C, is the lowest reported among the t-BOC protected polymers.

The mass loss from the alternating copolymer P(t-BOCOMI/St) observed in a t.g.a. thermogram (*Figure 1*) was 31%, which is the same as the theoretically calculated mass loss due to the evolution of carbon dioxide and isobutene by the deprotection of the t-BOC groups. Two consecutive measurements of thermograms by d.s.c. give information on the deprotection of the polymers[12,14]. The thermograms of (t-BOCOMI/St) reveal an endothermic event corresponding to the deprotection of t-BOC groups at 111°C in the first run and a glass transition at 260°C in the second run as shown in *Figure 2*. In these measurements, the first run was stopped at 150°C, then the same sample was cooled to room temperature, and the second run was performed. The glass transition temperature observed in the second run corresponds to that of the deprotected polymer having the structure of P(HOMI/St) (**13**) (X=H) and was confirmed to be identical to that of the polymer obtained by the direct copolymerization of the corresponding monomers, HOMI and St. The copolymer of *N*-(t-butoxy)maleimide (P(t-BuOMI/X-St)) is also known to give P(HOMI/X-St) by the deprotection of t-Bu groups but deprotection requires very high temperatures (about 270°C)[16]. The mass loss of the alternating copolymer P(t-BOCOPMI/St) was 25%, in good agreement with the theoretical mass loss (*Figure 1*). D.s.c. analysis of P(t-BOCOPMI/St) gave a large endothermic peak at 175°C due to the deprotection of t-BOC groups. In a previous report the t-BOC blocked HOPMI-St copolymer showed the endothermic event at 150°C[12]. The lower deprotection temperature may be ascribed to incomplete protection of P(HOPMI/St) by a polymeric reaction in that case.

The thermal deprotection temperatures (T_{dp}) of the t-BOC protected polymers P(t-BOCOMI/X-St) (**11**) and P(t-BOCOPMI/X-St) (**12**), T_{g} values of the deprotected copolymers P(HOMI/X-St) (**13**) and P(HOPMI/X-St) (**14**), and the onset decomposition temperatures (T_{dc}) of the deprotected copolymers measured in nitrogen atmosphere are summarized in *Table 2*. The homopolymer P(t-BOCOPMI) revealed T_{dp} at 170°C with the mass loss of 34% and T_{dc} at about 380°C without showing T_{g}. The deprotection of the t-BOC groups was observed at about 115 and 175°C for P(t-BOCOMI/X-St) and P(t-BOCOPMI/X-St), respectively. The amounts of the mass loss of the two alternating t-BOC copolymers **11** and **12** during the thermal deprotection agree well with theory (*Table 2*). The deprotected polymers P(HOPMI/

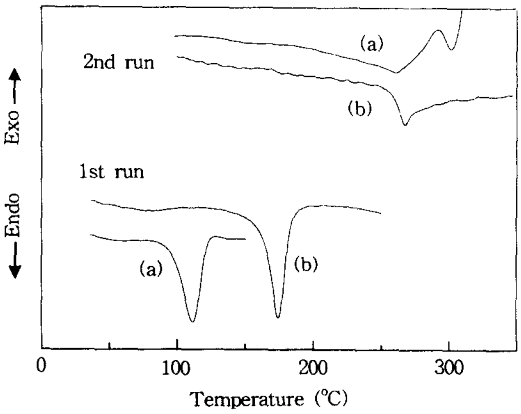


Figure 2 D.s.c. analysis of P(t-BOCOMI/St) (a) and P(t-BOCOPMI/St) (b) in a nitrogen stream at a heating rate of 10°C min^{-1}: first run, deprotection of t-BOC side-chains; second run, deprotected polymers

Table 2 Thermal properties of the t-BOC protected copolymers[a]

t-BOC polymer **11, 12**	Deprotected Polymer **13, 14**,	Mass loss[b]		T_{dp} (°C)	T_g (°C)	T_{dc} (°C)
		Calc.	Found			
P(t-BOCOMI/St)	P(HOMI/St)	31.5	31	111	260	310
P(t-BOCOMI/MeSt)	P(HOMI/MeSt)	30.2	30	118	–	340
P(t-BOCOMI/ClSt)	P(HOMI/ClSt)	28.5	28	113	270	310
P(t-BOCOMI/t-BOCSt)[c]	P(HOMI/HOSt)	46.2[e]	46[e]	110–140	275	340
P(HOMI/St)[d]	–	–	–	–	260	310
P(t-BOCOPMI)[f]	P(HOPMI)	34.6	34	170	–[f]	380
P(t-BOCOPMI/St)	P(HOPMI/St)	25.0	25	175	265	370
P(t-BOCOPMI/MeSt)	P(HOPMI/MeSt)	24.0	24	174	255	420
P(t-BOCOPMI/ClSt)	P(HOPMI/ClSt)	23.0	24	174	260	400
P(t-BOCOPMI/AcOSt)	P(HOPMI/AcOSt)	22.0	23	176	250	400
P(t-BOCOPMI/t-BOCSt)[c]	P(HOPMI/HOSt)	39.0[e]	39[e]	171	280	420
P(t-BOCOPMI/SiSt)	P(HOPMI/SiSt)	21.0	21	183	260	370
P(HOPMI/St)[d]	–	–	–	–	265	370

[a] Thermal analysis at a heating rate of 10°C min^{-1} under nitrogen. T_{dp} = deprotection temperature of the t-BOC groups measured by d.s.c. in the first run (cf. *Figures 2, 3* and *4*); T_g = glass transition temperature of the deprotected polymers measured by d.s.c. in the second run (cf. *Figure 2*); T_{dc} = onset decomposition temperature measured by t.g.a.

[b] Measured in wt% by t.g.a. (cf. *Figure 1*)

[c] t-BOCSt units are converted to *p*-hydroxystyrene (HOSt)

[d] Authentic alternating copolymers obtained from the copolymerization of HOMI or HOPMI with St for comparison

[e] The combined mass loss of both t-BOC groups (cf. *Figures 3* and *4*)

[f] The deprotected homopolymer P(HOPMI) showed no T_g

X-St) are more thermally stable than P(HOMI/X-St) analogues.

In a previous study P(t-BuOMI/t-BOCSt) exhibited the characteristic two-step deprotection behaviour associated with t-BOCSt (at 185°C) and t-BuOMI (at 252°C) and gave the deprotected polymer structure of P(HOMI/HOSt)[16]. In this study, two t-BOCSt copolymers, P(t-BOCOMI/t-BOCSt) and P(t-BOCOPMI/t-BOCSt), displayed a combined deprotection behaviour with broad endothermic peaks in the d.s.c. analysis as shown in *Figures 3* and *4* along with a single combined mass loss in t.g.a. analysis. Particularly, P(t-BOCOMI/t-BOCSt) exhibits its broad endothermic peak in the region of 110 to 140°C. The t-BOCSt units in the copolymers are deprotected at lower temperatures than that of the homopolymer (about 190°C)[3,4]. The deprotected copolymers, P(HOMI/HOSt) and P(HOPMI/HOSt), have high T_g values at about 275°C.

The thermal deprotection was easily followed by infra-red spectral changes using a film of P(t-BOCOMI/St) on a sodium chloride plate as shown in *Figure 5*. The protected polymer has absorption bands at 2940 cm^{-1} for t-Bu and at 1815, 1790 and 1745 cm^{-1} for the carbonyls of imide and carbonate groups, but the deprotected polymer P(HOMI/St) obtained from P(t-BOCOMI/St) shows only strong absorption bands at 3250 cm^{-1} for *N*-hydroxy groups and 1790 (weak) and 1715 cm^{-1} (strong) for imide carbonyl groups. The i.r. spectrum of the deprotected polymer was found to be identical to that of the authentic copolymer of P(HOMI/St). Thermal deprotection of P(t-BOCOPMI/St) was accompanied by the disappearance of the strong carbonyl absorption bands at 1760 and 1710 cm^{-1} and the appearance of bands at 1770 (weak) and 1700 cm^{-1} (strong) and a new broad absorption band at 3500 cm^{-1} due to the phenol groups.

N-Hydroxysuccinimides[23] have pK_a values as high as 6 to 7 and are more acidic than either succcinimides or

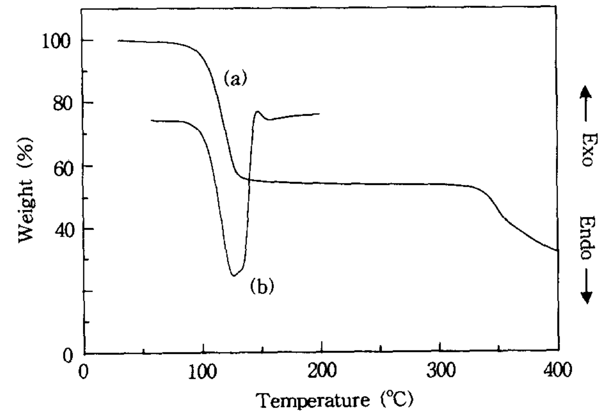


Figure 3 Thermograms, (a) t.g.a. and (b) d.s.c., showing the deprotection of P(t-BOCOMI/t-BOCSt)

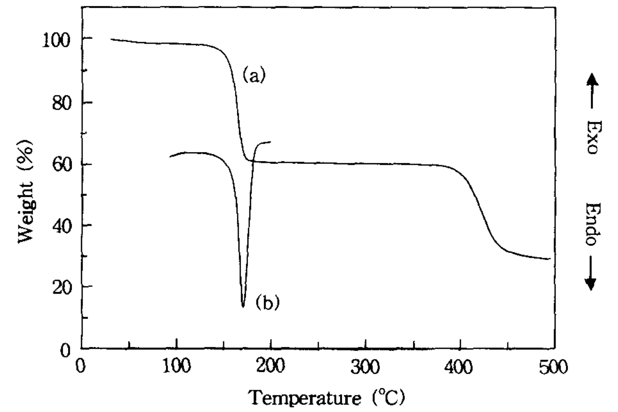


Figure 4 Thermograms, (a) t.g.a. and (b) d.s.c., showing the deprotection of P(t-BOCOPMI/t-BOCSt)

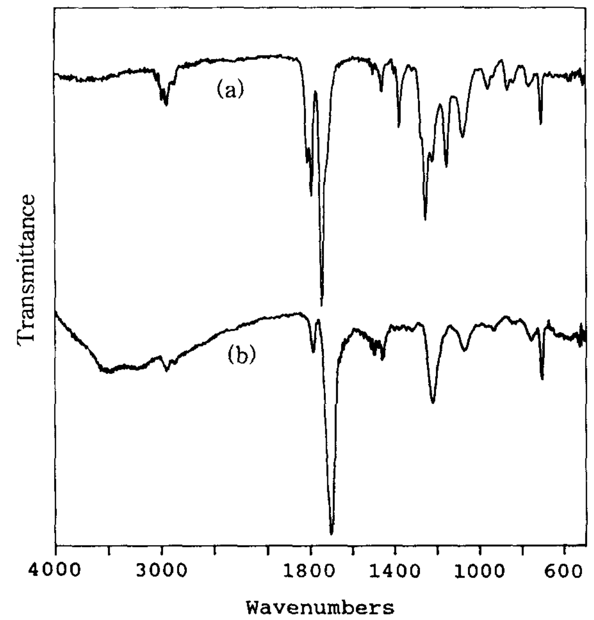


Figure 5 Infra-red spectra of P(t-BOCOMI/St) before (a) and after (b) deprotection of t-BOC groups

phenols, which have pK_a about 10. The acidity of the *N*-hydroxysuccinimides is clearly associated with the low thermolysis temperature. Even very low concentration of deprotected monomer units (resulting, for example, from hydrolysis) can effectively catalyse the thermolysis of the protecting groups. In *Table 3*, the thermal deprotection behaviours of the protected polymaleimides are summarized. The well known t-BOC polymer, poly(t-BOC-styrene) (*p*PBOCSt) has T_{dp} at about 190°C with the mass loss of 45%[3].

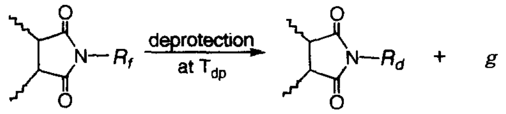
Solubility change

The t-BOC protected copolymers undergo very dramatic changes in solubility when deprotected as summarized in *Table 4*. P(t-BOCOMI/X-St) (**11**) and P(t-BOCOPMI/X-St) (**12**) are, for example, very soluble in common organic solvents such as chloroform, anisole, 2-ethoxyethyl acetate and dioxane but insoluble in aqueous alkaline solutions. The deprotected polymers, P(HOMI/X-St) (**13**) and P(HOPMI/X-St) (**14**), are soluble in aqueous base solutions, dioxane and DMF but insoluble in common organic solvents such as chloroform, anisole and 2-ethoxyethyl acetate. In the special case of the silicone-containing polymer P(t-BOCOPMI/SiSt), somewhat different solubility behaviour is observed. The deprotected polymer P(HOPMI/SiSt) is quite soluble in both organic solvents and aqueous base (*Table 4*).

Resist evaluation

All of the t-BOC copolymers are white powders with good film-forming properties. P(t-BOCOMI/St) shows very low absorption in the deep u.v. region with optical density (*OD*) of 0.13 μm^{-1} at 250 nm, whereas P(t-BOCOPMI/St) has rather high absorption at 250 nm with *OD* over 0.5 μm^{-1}. Low absorption ($OD <$ $0.4 \mu m^{-1}$) is desirable for practical lithography. Only the preliminary evaluation of the resist properties of P(t-BOCOMI/St) is discussed here. The resist evaluation of P(t-BOCOPMI/St) was previously reported[12,13]. The acid-catalysed thermolysis of the t-BOC groups on P(t-BOCOMI/St) in the presence of 10 wt% *p*-toluenesulfonic acid begins at about 60°C. In the preliminary resist evaluation, resist films of P(t-BOCOMI/St) containing 10 wt% triphenylsulfonium hexafluoroantimonate as a photoacid generator (PAG) were imagewise-exposed to 250 nm light in contact mode. Negative-tone images were successfully obtained from the copolymer by developing with anisole after post-exposure bake (PEB) treatment at 70°C for 3 min on a hot plate. Positive-tone images were obtained by developing with an aqueous 2.38 wt% TMAH solution. A detailed resist evaluation of selected t-BOC polymers among those listed in this report is in progress, and a full account of the results will be reported elsewhere.

Table 3 Thermal deprotection behaviour of protected polymaleimides[a]



Protected polymaleimide, R_f	Deprotection temperature[b], T_{dp} (°C)	Mass loss (wt%)	Deprotected polymaleimide, R_d	Byproducts, g	Ref.
CO_2-Bu-t (t-BOCMI)	152	33	H	$CH_2{=}C(CH_3)_2 + CO_2$	14
OCO_2-Bu-t (t-BOCOMI)	111	31	OH	$CH_2{=}C(CH_3)_2 + CO_2$	This work
OCO_2-$CH(CH_3)_2$ (iPOCMI)	235	28	OH	$CH_2{=}CHCH_3 + CO_2$	24
O-Bu-t (t-BuOMI)	283	21	OH	$CH_2{=}C(CH_3)_2$	16
$C_6H_4OCO_2$-Bu-t (t-BOCOPMI)	175	25	C_6H_4-OH	$CH_2{=}C(CH_3)_2 + CO_2$	This work
t-Bu[c] (t-BuMI)	300	34	H	$CH_2{=}C(CH_3)_2$	25

[a] All of the polymaleimides have alternating structures with styrene in both the protected and deprotected forms, except the homopolymer of t-BuMI

[b] T_{dp} measured by d.s.c.

[c] Homopolymer of t-BuMI

Table 4 Solubility comparison[a] between P(t-BOCOMI/St) and P(HOMI/St), and between P(t-BOCOPMI/SiSt) and P(HOPMI/SiSt)[b]

Solvent	P(t-BOCOMI/St)	P(HOMI/St)	P(t-BOCOPMI/SiSt)	P(HOPMI/SiSt)
Acetone	++	–	++	+
Chloroform	++	–	++	+
Hexane	–	–	–	–
Toluene	–	–	++	+
Anisole	++	–	++	+
Chlorobenzene	++	–	++	+
Cyclohexanone	++	–	++	+
Methyl isobutyl ketone	+	–	++	++
2-Ethoxyethyl acetate	++	–	++	+
N,*N*-Dimethylformamide	++	++	++	+
Tetrahydrofuran	++	+	++	+
Dioxane	++	+	++	+
Methanol	–	–	–	+
4 wt% KOH (aq)	–	++	–	+
4 wt% NaOH (aq)	–	++	–	++
0.3 N TMAH (aq)[c]	–	++	–	+

[a] Remark: ++, very soluble; +, soluble; –, insoluble

[b] The alternating copolymer P(HOMI/St) and P(HOPMI/SiSt) obtained by thermal deprotection of P(t-BOCOMI/St) at 110°C and P(t-BOCOPMI/SiSt) at 190°C, respectively

[c] Tetramethylammonium hydroxide (2.38 wt%)

CONCLUSIONS

t-BOCOMI (**5**) and t-BOCOPMI (**7**) were synthesized and radically copolymerized with various substituted styrenes (X-St) to give new t-BOC protected acid-labile polymers P(t-BOCOMI/X-St) (**11**) and P(t-BOCOPMI/X-St) (**12**), respectively, that incorporate the maleimide structure. P(t-BOCOMI/X-St) and P(t-BOCOPMI/X-St) were cleanly converted to the *N*-hydroxymaleimide copolymers P(HOMI/X-St) and *N*-(*p*-hydroxyphenyl)maleimide copolymers P(HOPMI/X-St) by thermal deprotection of the t-BOC groups. The deprotected polymers P(HOMI/X-St) and P(HOPMI/X-St) have high T_g values above 260°C and good solubility in aqueous base solutions, and t-BOC polymers are useful in the formulation of chemically amplified resists.

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