Synthesis and polymerization of *N*-(*tert*-butyloxycarbonyl)maleimide and facile deprotection of polymer side-chain t-BOC groups

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A new t-BOC protected monomer, *N*-(*tert*-butyloxycarbonyl)maleimide (t-BOCMI) **3** was synthesized by thermolysis in a high yield and a new kind of t-BOC protected polymer was prepared by radical copolymerization. t-BOCMI and styrene derivatives (X-St) were readily copolymerized to obtain alternating copolymers of P(t-BOCMI/X-St) **5** in high conversions. The t-BOCMI units of the t-BOC protected copolymers were converted to the maleimide (MI) units by heating at about 150°C or above, releasing 2-methylpropene and carbon dioxide. The facile deprotection of the side-chain t-BOC groups from the protected copolymers was attained to bring about a large polarity change. The deprotected copolymers P(MI/Y-St) **6** have very high glass transition temperatures (T_gs) of about 250°C and good solubility in aqueous base solutions, whereas the t-BOC polymers P(t-BOCMI/X-St) are only soluble in organic solvents. The t-BOC protected maleimide polymers were found to have specific properties for application as chemically amplified resist materials such as alkaline solubility, high T_g and facile deprotection.

(Keywords: *N*-(*tert*-butyloxycarbonyl)maleimide; t-BOC protected maleimide polymers; poly[*N*-(*t*-butyloxycarbonyl)-maleimide)-*co*-styrene]; deprotection; thermal stability; resist materials)

INTRODUCTION

The concept of chemical amplification as applied to the microlithographic process has yielded several new resist systems with high sensitivities[1–4]. In the chemically amplified process, an initial photochemical event generates a catalyst (typically an acid), which promotes a cascade of chemical reactions with a gain mechanism.

Among the various chemically amplified resist systems, the polymer side-chain deprotection system has attracted much attention because of its high resolution capability along with high sensitivity while retaining main-chain integrity. Such examples are poly[*p*-(*t*-butyloxycarbonyloxy)-styrene] (PBOCSt)[5,6], poly(*t*-butyl *p*-vinylbenzoate) (PTBVB)[7], and certain polymethacrylates[8], which are easily converted upon thermolysis to poly(*p*-hydroxystyrene) (PHOSt), poly(*p*-vinylbenzoic acid) (PVBA) and poly(methacrylic acid), respectively. The deprotected polymers show a remarkable change in polarity after deprotection of the side-chains. When films of the protected polymers containing photoacid generators are exposed to high energy irradiation, acid forms in the exposed areas; this acid catalyses the side-chain deprotection and allows the development of images in either positive or negative mode through a differential dissolution process. Among the various protecting groups, the *t*-butyloxycarbonyl (t-BOC) group is successfully utilized in chemical amplification resist systems, providing highest sensitivity[3,4].

One of the properties required of resist polymers is thermal stability of patterned resist images for advanced lithographic processes. Thus the resist polymers which have a high glass transition temperature (T_g), above 200°C, have been examined. One common synthetic technique to improve thermal stability of resist polymers is to incorporate a maleimide unit into copolymers[9]. Therefore, the novel resist design concept has been applied to imaging of high temperature polymers such as a maleimide–styrene copolymer[10] and a *N*-(*p*-hydroxyphenyl)maleimide–styrene copolymer[11]. The t-BOC group was introduced to protect imide NH in the former and phenolic OH in the latter copolymer through post-reactions on both the maleimide copolymers. Several kinds of protected maleimide copolymers were also studied in an effort to increase the thermal deprotection temperatures[12]. All of the reported maleimide copolymers were found to have a sufficiently high T_g, above 200°C, after deprotection of the side-chains. However, these copolymers were not prepared by direct copolymerizations of the corresponding monomers but by polymeric reactions which could limit the practical usefulness because of the difficulty in synthetic control of the protection reactions.

Since the introduction of the novel PBOCSt resist system, many new resist systems have been reported based on the chemical amplification concept employing side-chain deprotection[1–3]. So far, these resist polymers have been mainly derived from protection of the phenolic or carboxylic functional groups. Therefore extensive effort was made to find a type of t-BOC protected

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polymer other than those with phenol and carboxyl groups. In this paper, we report a new t-BOC protected polymer system derived from the maleimide structure which could be useful as a thermally stable resist. A novel t-BOC protected monomer *N*-(*tert*-butyloxycarbonyl)-maleimide (t-BOCMI) was successfully synthesized and copolymerizations were carried out. A change in specific properties of the t-BOC maleimide copolymers was attained by the facile deprotection of the side-chain t-BOC groups.

EXPERIMENTAL

Materials and instruments

Maleimide (MI), *N*-phenylmaleimide (PMI), di-*t*-butyl dicarbonate (DTBDC), styrene (St), *p*-methylstyrene (MeSt), and *p*-chlorostyrene (ClSt) were purchased from Aldrich Chemical Co. *p*-Trimethylsilylstyrene (SiSt), *p*-(*t*-butoxycarbonyloxy)styrene (t-BOCSt) and *p*-acetoxystyrene (AcOSt) were kindly donated by Korea Kumho Petrochemical Co., Eastman Kodak Co. and Hoechst Celanese Corp, respectively. The styrene monomers (X-St) and methyl methacrylate (MMA) were purified by distillation. Other chemicals were purified by conventional methods.

^{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 as an internal standard. ^{13}C n.m.r. spectra were also obtained with a Varian gemini spectrometer in deuteriochloroform. Infra-red spectra were recorded on an Alpha-Centauri *FT*i.r. spectrophotometer (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 analyser. Thermal analysis was carried out on a Du Pont model 910 DSC and Model 951 TGA at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Solution viscosities of polymers were measured with a Cannon-Fenske viscosity tube (no. 50) or an Ubbelohde viscometer tube mounted on an automatic measuring apparatus (Schott-Gerate GmbH) at 25°C in dioxane. Molecular weights and molecular weight distribution of polymers were determined in tetrahydrofuran at 35°C using a Waters model 150-C ALG/GPC consisting of four μ-styragel columns without calibration. The molecular weights were estimated relative to polystyrene standards.

Preparation of t-BOCMI 3

The maleimide/furan adduct **1**, 3,6-epoxy-1,2,3,6-tetrahydrophthalimide, was prepared by a reaction of maleimide and furan in a high yield of 99% according to the known procedure[13]. To a solution of the adduct (42.40 g, 0.26 mol) in 300 ml of dimethylsulphoxide were added 35.00 g (0.31 mol) of potassium *t*-butoxide at room temperature and the mixture was stirred for 10 min. DTBDC (62.00 g, 0.28 mol) was added to the reaction mixture and stirred for 2 h at room temperature. The mixture was then poured into cold water, filtered, and dried. White powdery t-BOC adduct **2**, *N*-(*t*-butyloxycarbonyl)-3,6-epoxy-1,2,3,6-tetrahydrophthalimide, was obtained in a yield of 81% as sufficiently pure material without recrystallization; m.p. 139°C (decomposed).

2: ^{1}H n.m.r. (60 MHz, $CDCl_3$), δ(ppm) 1.50 (s, 9H, t-Bu), 3.05 (s, 2H, 2–CO–CH–), 5.20 (s, 2H, 2–O–CH–), 6.55 (s, 2H, 2=CH–). I.r. (KBr), $\bar{\nu}$(cm^{-1}) 1810 (sh), 1790 (sh), 1760 and 1720 (imide and ester), 1150 (ether).

A solution of 19.50 g t-BOC adduct **2** in 200 ml toluene was refluxed for 2 h to thermolyse the adduct. Then the solvent was evaporated and the residue was precipitated in cold *n*-hexane to a obtain the solid product. After recrystallization from a solution of toluene and *n*-hexane (1:10 by vol), the desired monomer, t-BOCMI **3**, was obtained as needle-like crystals in a yield of 76% (11.13 g); m.p. 62–63°C.

3: ^{1}H n.m.r. (60 MHz, $CDCl_3$), δ(ppm) 1.60 (s, 9H, t-Bu), 6.70 (s, 2H, 2=CH–). I.r. (KBr), $\bar{\nu}$(cm^{-1}) 3105 (olefinic CH), 2980 (t-Bu), 1800, 1765 and 1720 (imide and ester), 1330, 1250 and 1150 (C–N), 850 (olefinic CH), 700 (C=C). ^{13}C n.m.r. δ(ppm) ($CDCl_3$), 27.83 (Me), 85.24 (t-Bu), 135.08 (C=C), 145.88 (carbonyl of t-BOC), 166.22 (carbonyl of MI); m.s. 182 ($M-CH_3$, 2), 142 (13), 124 (66), 98 (14), 57 (100). Analysis: calculated for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.70; H, 5.60; N, 7.18.

Polymerization

All the polymerizations were carried out in ampoules sealed after freeze–thaw cycles. The t-BOCMI monomer **3** and the comonomers were charged in 1:1 molar ratio with *N*,*N*′-azobis(isobutyronitrile) (AIBN) initiator. Radical polymerizations were conducted under the conditions described in *Table 1*. The polymers were obtained by precipitating into *n*-hexane or methanol. The structure of obtained polymers was 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. Copolymerization of t-BOCMI and styrene in large quantities was carried out according to the following procedure to obtain P(t-BOCMI/St) **5a**. To a 500 ml reaction vessel with a nitrogen inlet and an outlet were added 15.80 g (0.08 mol) of t-BOCMI, 8.30 g styrene (0.08 mol) and 1.10 g AIBN (6.40 mmol, 4 mol%) in 40 ml dioxane. The copolymerization was carried out for 5 h at 55°C. After polymerization, the product was diluted with dioxane and precipitated into 5 l of methanol. The white powdery alternating copolymer P(t-BOCMI/St) was obtained in a conversion of 89% (21.40 g) after drying *in vacuo* at 40°C. The inherent viscosity of the polymer was measured to be 0.94 dl g^{-1} in dioxane.

RESULTS AND DISCUSSION

Synthesis of t-BOCMI 3

t-BOCMI **3** was newly prepared in a high yield by a retro-Diels-Alder reaction, which is a useful procedure for the synthesis of maleimide derivatives[14] as described in *Scheme 1*.

The maleimide/furan adduct **1** was prepared by a Diels-Alder reaction in a quantitative yield. The t-BOC group was introduced to protect the imide NH of the adduct by a reaction with di-*t*-butyl dicarbonate and the t-BOCMI/furan adduct **2** was obtained as a white powder and was sufficiently pure without recrystallization. The t-BOC adduct **2** was thermolysed in refluxing toluene and the target monomer t-BOCMI was obtained as needle-like crystals with m.p. of 62°C. When the adduct **2** was heated above 130°C the decomposition of t-BOC groups occurred instead of the desired thermolysis. In an n.m.r. spectrum, t-BOCMI shows only two singlet peaks at 6.70 ppm for two olefinic protons and at 1.60 ppm for nine protons of a t-BOC group. The

Table 1 Radical copolymerizations of N-(*tert*-butyloxycarbonyl)maleimide **3**

t-BOC polymer[a]	AIBN[b] (mol%)	M/S[c] (g ml^{-1})	Time (h)	Conversion (%)	Inherent viscosity[d] (dl g^{-1})	$\bar{M}_w$[e] × 10^{-3}
P(t-BOCMI)	2	0.50	24	30	0.11	
P(t-BOCMI)[f]	1	–	24	35	0.24	58
P(t-BOCMI/St) **5a**	1	0.33	5	70	1.60	
P(t-BOCMI/St) **5a**	4	0.60	5	89	0.94	268
P(t-BOCMI/St) **5a**	6	0.25	3	92	0.60	193
P(t-BOCMI/t-BOCSt) **5b**	4	1.00	3	89	0.69	326
P(t-BOCMI/AcOSt) **5c**	2	1.00	3	78	1.11	533
P(t-BOCMI/MeSt) **5d**	2	1.00	1	90	1.80	707
P(t-BOCMI/ClSt) **5e**	2	1.00	3	83	1.50	620
P(t-BOCMI/SiSt) **5f**	4	0.50	3	90	0.77	314
P(t-BOCMI/MMA)	2	1.00	24	62	0.53	188
P(t-BOCMI/PMI)	2	2.00	3	56	0.28	50
P(MI/St)[g]	1	0.65	6	68	0.96	214

[a] All the t-BOC copolymers have alternating structures except P(t-BOCMI/MMA) and P(t-BOCMI/PMI) which have 3:7 molar composition. Copolymerizations were carried out in 1:1 molar feed ratio at 55°C in dioxane

[b] The mol% of the initiator AIBN to the total amounts of two monomers

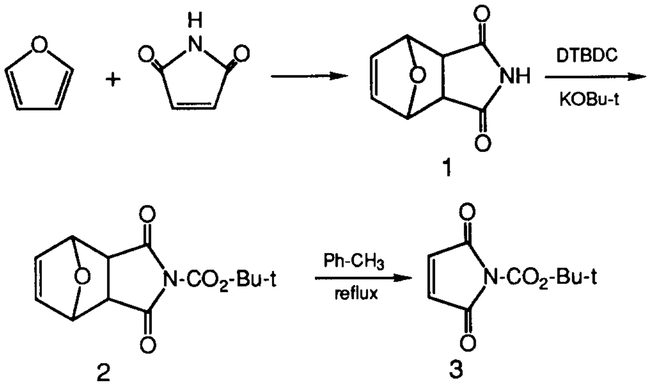
[c] M/S is the ratio of the total weight of two monomers to the volume of dioxane solvent

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

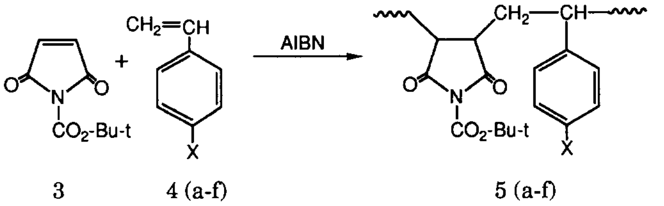
[e] The molecular weights were measured by g.p.c. in THF

[f] Homopolymerization with BPO initiator in bulk at 70°C

[g] P(MI/St) was obtained by copolymerization of maleimide and styrene in 1:1 molar feed ratio



Scheme 1



X=H, **4a** (St), **5a**; X=OCO$_2$-Bu-t, **4b** (t-BOCSt), **5b**; X=OAc, **4c** (AcOSt), **5c**; X=Me, **4d** (MeSt), **5d**; X=Cl, **4e** (ClSt), **5e**; X=SiMe$_3$, **4f** (SiSt), **5f**

Scheme 2

structure of t-BOCMI was confirmed by ^{13}C n.m.r., i.r., mass spectra, and elemental analysis.

Polymerization

Radical copolymerizations of the t-BOCMI monomer with various comonomers were carried out and the results are summarized in *Table 1*. t-BOCMI was readily copolymerized with styrene derivatives **4** (X-St) such as St, t-BOCSt, AcOSt, MeSt, ClSt and SiSt in high conversions in the presence of a radical initiator within 3 h (*Scheme 2*).

For comparison, poly(maleimide-*alt*-styrene), P(MI/St) was directly obtained from a copolymerization of maleimide and styrene in a 1:1 molar feed ratio. However, both the homopolymerization of t-BOCMI and the copolymerization with N-phenylmaleimide (PMI) resulted in rather low conversions and low molecular weights. A copolymerization with MMA gave a moderate yield. The homopolymerization of t-BOCMI was sluggish and the polymers obtained usually had some deprotected maleimide units as a result of adventitious deprotection of t-BOC groups during the polymerization. This poor homopolymerization behaviour of t-BOCMI is ascribable to the bulky side-chain of the t-BOC group with 1,2-disubstitution.

Molecular weights of the t-BOC copolymers **5** were controlled by the amount of the initiator and dioxane solvent used in the copolymerizations. To obtain a large amount of copolymers having suitable molecular weights, some of the copolymerizations were conducted using large quantities of AIBN initiator and the copolymers were used for characterizing the resist properties. Copolymerizations of t-BOCMI with styrene monomers were performed in 1:1 molar feed ratio and the obtained copolymers **5**, poly(t-BOCMI-*co*-X-St), i.e. P(t-BOCMI/X-St), were confirmed to have an alternating structure from the ^{1}H n.m.r. spectral analyses. It is well known that a nearly alternating structure is formed when an electron-poor monomer (t-BOCMI) and an electron-rich monomer (styrene) are copolymerized[15]. However, the copolymers with electron-poor monomers, P(t-BOCMI/MMA) and P(t-BOCMI/PMI), were identified as having 3:7 molar composition.

Thermal deprotection and structural change

In t.g.a. the alternating copolymer P(t-BOCMI-*alt*-St), i.e. P(t-BOCMI/St) **5a**, was found to be stable up to 130°C, but above 150°C it underwent rapid thermal deprotection of the t-BOC groups by releasing carbon dioxide and 2-methylpropene, as shown in *Figure 1*. The t-BOC protected copolymers, P(t-BOCMI/X-St) **5**, were converted to P(MI/Y-St) **6**, by thermal deprotection of t-BOC groups, as shown in *Scheme 3*.

In an earlier paper[10] a t-BOC blocked MI–St copolymer was reported to lose weight above 115°C. The low deprotection temperature is presumably ascribable to insufficient protection by a polymeric reaction in that case. The weight loss of the alternating copolymer P(t-BOCMI/St) **5a** in the t.g.a. thermogram of *Figure 1* was estimated to be 33%, which is the same amount as the theoretically calculated weight loss due to the evolution of carbon dioxide and 2-methylpropene from the copolymer. The d.s.c. thermograms of P(t-BOCMI/St) in *Figure 2* reveal an endothermic event corresponding to the deprotection of t-BOC groups at 152°C (thermal deprotection temperature, T_{dp}) in the first run and show the T_g at 245°C in the second run. In the d.s.c. measurements, the first run was recorded to 200°C, then the same sample was cooled to room temperature and the second run was performed to decomposition. Therefore the T_g observed in the second run corresponds to that of the deprotected polymer **6a** and is confirmed to be identical to that of P(MI/St) obtained by direct polymerization.

The T_{dp} of the t-BOC protected polymers **5**, T_gs of the deprotected copolymers **6**, and the onset decomposition temperatures (T_{dc}) of the deprotected copolymers were measured in nitrogen atmosphere and are summarized in *Table 2*. The weight losses of the alternating t-BOC copolymers **5** during thermal deprotection measured by t.g.a. agreed well with the calculated amounts. An exception was P(t-BOCMI/t-BOCSt) **5b** which exhibited a large weight loss of 48%, because the deprotection of t-BOC groups occurred in both the t-BOC monomer units. Thus the t-BOC polymer **5b** becomes poly(maleimide-*alt*-*p*-hydroxystyrene), P(MI/HOSt) **6b** by removing both t-BOC groups. In summary, t-BOC groups of the copolymers **5** are deprotected at about 150°C or above and the deprotected polymers **6** with free maleimide units have high T_gs of about 250°C, and eventually main-chains of the polymers **6** decompose at about 400°C. But the homopolymer P(t-BOCMI) showed a rather low T_{dp} of 116°C and a smaller weight loss than the theoretical amount due to adventitious deprotection during polymerization. The observed weight loss of the obtained P(t-BOCMI) was 30–40% whereas the theoretically calculated amount is 51%. In addition, P(t-BOCMI) showed no observable T_g even after deprotection in the second d.s.c. run. Two non-styrene copolymers, P(t-BOCMI/MMA) and P(t-BOCMI/PMI), showed weight losses corresponding to their 3:7 molar composition, as shown in *Table 2*.

The polar substituents of the styrene comonomers could increase the deprotection temperatures of the t-BOC polymers **5**. In the deprotected polymers **6**, polar interactions and hydrogen bondings among MI and Y groups are considered to cause the greater increase in T_gs. In particular, the interaction among MI and *p*-hydroxystyrene (HOSt) units in P(MI/HOSt) **6b**, obtained from the side-chain deprotection of P(t-BOCMI/

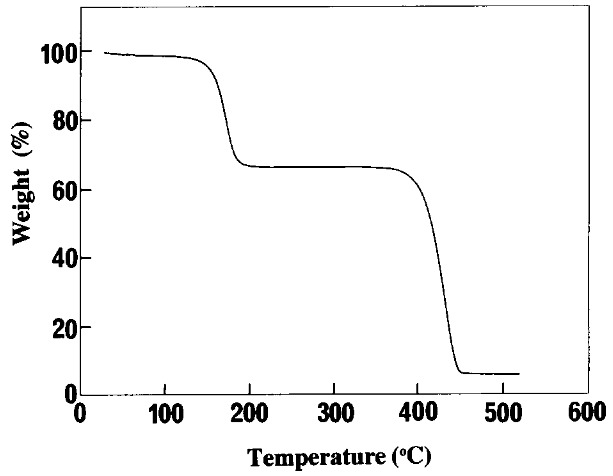


Figure 1 T.g.a. thermogram of P(t-BOCMI/St) in a nitrogen stream at a heating rate of 10°C min^{-1}

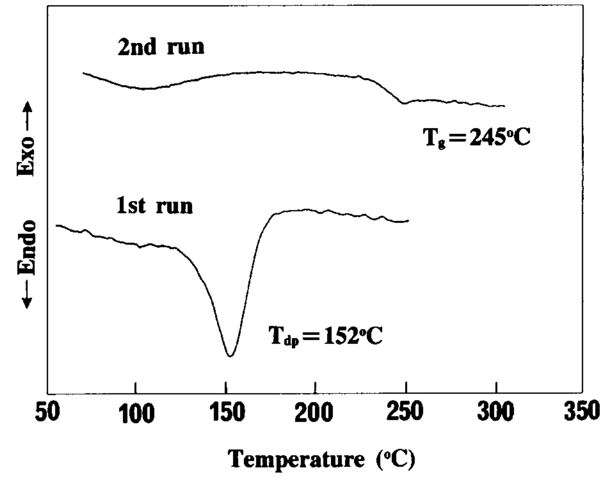
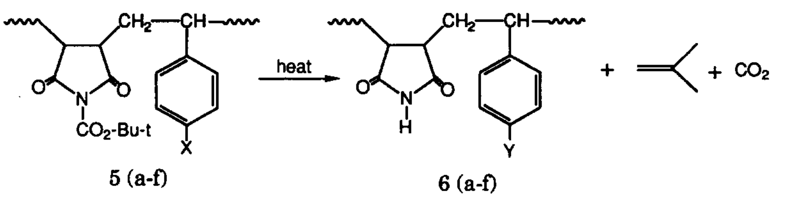


Figure 2 D.s.c. analysis of P(t-BOCMI/St) in a nitrogen stream at a heating rate of 10°C min^{-1}: first run, deprotection of t-BOC side-chains; second run, deprotected polymers



Y = H (6a), OH (6b), OAC (6c), Me (6d), Cl (6e), SiMe$_3$ (6f)

Scheme 3

Table 2 Thermal properties of the t-BOC protected copolymers

t-BOC polymer	Deprotected polymer[a]	Weight loss[b] (%)	T_{dp}[c] (°C)	T_g[d] (°C)	T_{dc}[e] (°C)
P(t-BOCMI)	P(MI)	35	116	–[g]	400
P(t-BOCMI/St) **5a**	P(MI/St) **6a**	33	152	245	370
P(t-BOCMI/t-BOCSt) **5b**	P(MI/HOSt)[f] **6b**	48	170	280	380
P(t-BOCMI/AcOSt) **5c**	P(MI/AcOSt) **6c**	28	152	–[g]	370
P(t-BOCMI/MeSt) **5d**	P(MI/MeSt) **6d**	32	162	252	370
P(t-BOCMI/ClSt) **5e**	P(MI/ClSt) **6e**	30	155	260	370
P(t-BOCMI/SiSt) **5f**	P(MI/SiSt) **6f**	26	166	260	370
P(t-BOCMI/MMA)	P(MI/MMA)	23	150	180	330
P(t-BOCMI/PMI)	P(MI/PMI)	20	130	–[g]	400
P(MI/St)	–	–	–	245	370

[a] After deprotection of t-BOC groups of the original polymers, t-BOCMI units are converted into maleimide units
[b] Measured in wt% by t.g.a.
[c] T_{dp} is the deprotection temperature measured in the first d.s.c. run (cf. *Figure 2*)
[d] T_g is the glass transition temperature of the deprotected copolymer measured in the second d.s.c. run (cf. *Figure 2*)
[e] T_{dc} is the onset decomposition temperature of main-chains measured by t.g.a.
[f] t-BOCSt units are converted to *p*-hydroxystyrene (HOSt) by evolving carbon dioxide and 2-methylpropene[6]
[g] No detection of T_g

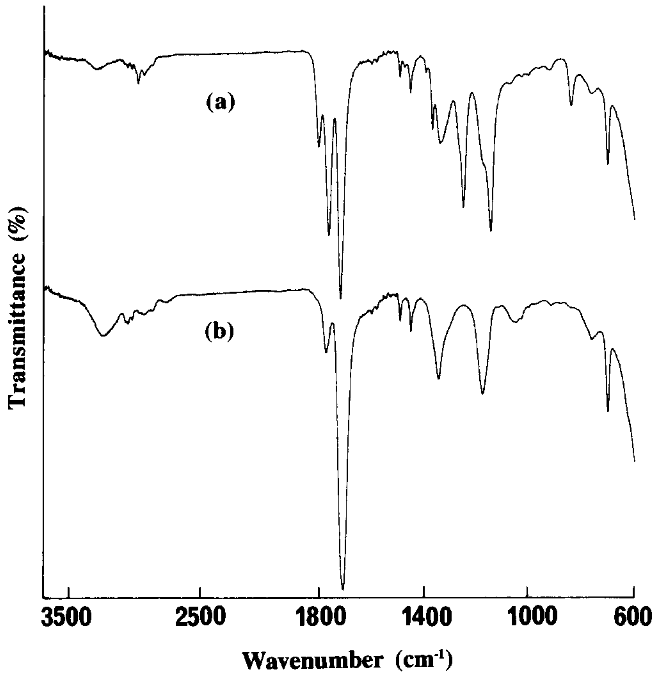


Figure 3 I.r. spectra of P(t-BOCMI/St) (a) before and (b) after thermolysis

t-BOCSt) **5a**, shows a pronounced effect on the increase of T_g to as much as 280°C.

The thermal deprotection behaviour was easily followed by i.r. spectral change using a film of P(t-BOCMI/St) **5a** on a sodium chloride plate, as shown in *Figure 3*. The starting protected polymer has strong absorption bands at 2980 cm^{-1} for *t*-butyl and at 1800, 1770 and 1720 cm^{-1} for carbonyls of imide and ester groups, but the deprotected polymer P(MI/St) **6a** obtained by heating above 150°C shows strong absorption bands at 3450 cm^{-1} for imino groups and 1700 cm^{-1} for imide groups due to the deprotection of t-BOC groups. The i.r. spectrum of the deprotected polymer was found to be identical to that of P(MI/St), which was directly obtained by a radical copolymerization of maleimide and styrene.

Table 3 Solubility[a] of P(t-BOCMI/St) **5a** and P(MI/St) **6a**

Solvent	P(t-BOCMI/St)	P(MI/St)[b]
Acetone	+ +	+
Chloroform	+ +	–
Hexane	–	–
Toluene	+	–
Chlorobenzene	+ +	–
Anisole	+ +	–
Cyclohexanone	+ +	+
Methyl isobutyl ketone	+ +	–
2-Ethoxyethyl acetate	+ +	–
N,N'-dimethylformamide	+ +	+ +
Tetrahydrofuran	+ +	+
Dioxane	+ +	+
Methanol	–	–
0.7 N KOH (aq)	–	+ +
1.0 N NaOH (aq)	–	+ +
0.3 N TMAH[c] (aq)	–	+ +

[a] + +, very soluble; +, soluble; –, insoluble
[b] The alternating copolymer P(MI/St) **6a** was obtained by thermal deprotection of P(t-BOCMI/St) **5a** at 170°C
[c] Tetramethylammonium hydroxide

All the t-BOC copolymers are white powders having a good film-forming property. The t-BOC protected copolymers show considerable change in solubility after deprotection due to the large polarity change, as described in *Table 3* for **5a** and **6a**. P(t-BOCMI/St) **5a** is very soluble in common organic solvents such as chloroform, toluene, chlorobenzene, and dimethylformamide (DMF) but insoluble in aqueous alkaline solutions and methanol. The deprotected polymer P(MI/St) **6a** is soluble in aqueous base solutions, dioxane, and DMF but insoluble in common organic solvents such as chloroform, toluene and chlorobenzene. The solubility of **6a** in aqueous base solutions is of the utmost importance for practical application as resist materials. However, the deprotected polymer P(MI/SiSt) **6f** was found to have different solubility behaviour as it is insoluble in the aqueous bases mentioned in *Table 3*. The polymer **6f** is also insoluble in some organic solvents such as toluene, anisole and chlorobenzene whereas the t-BOC polymer, P(t-BOCMI/SiSt) **5f** is very soluble in the same organic solvents.

The acidolytic deprotection of t-BOC groups of P(t-BOCMI/St) in the presence of *p*-toluenesulphonic acid was observed at 100°C or lower, which indicates the applicability of the polymer as a chemically amplified resist along with thermal stability and alkaline development. In particular, P(t-BOCMI/SiSt) **5f**, which exhibits a high T_g of 260°C after deprotection, is considered to be a candidate as a silicon-containing t-BOC resist system. Various silicon-containing polymers were extensively investigated as promising resist materials for enhancing reactive-ion etching resistance in microlithographic processes[16]. The preliminary lithographic evaluation of some of the t-BOCMI copolymers was reported earlier[17]. The resist evaluation of the selected t-BOC polymers in the presence of acid generators is in progress and full accounts will be published elsewhere.

CONCLUSIONS

As a new t-BOC protected monomer, t-BOC maleimide (t-BOCMI) **3** was synthesized by a retro-Diels-Alder reaction in high yield, and radical copolymerizations of t-BOCMI were carried out to obtain a new kind of t-BOC protected polymer based on the maleimide structure. The t-BOCMI copolymers with styrene derivatives, P(t-BOCMI/X-St) **5**, were readily converted to the free maleimide copolymers P(MI/Y-St) **6** by thermal deprotection of the side-chain t-BOC groups at about 150°C or above. Upon deprotection, the deprotected polymers P(MI/Y-St) have high T_gs at about 250°C along with good solubility in aqueous base solutions. The new t-BOC protected maleimide copolymers were found to possess specific requirements such as alkaline solubility, high T_gs and facile deprotection for application as thermally stable, sensitive deep u.v. resist materials for imaging of $<0.5\,\mu$m patterns based on the chemical amplification concept.

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