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Synthesis of Polymers Having *N*-Hydroxymaleimide Units by Thermolysis of *N*-(Isopropyloxycarbonyloxy)maleimide Polymers

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N-(Isopropyloxycarbonyloxy)maleimide (iPOCMI) has been synthesized and polymerized to give both the homopolymer and copolymers with substituted styrenes. These polymers were readily deprotected by thermolysis of the isopropyloxycarbonyl (iPOC) groups to provide the corresponding *N*-hydroxymaleimide (HOMI) polymers. The homopolymer and styrenic copolymers of iPOCMI were radically obtained in higher conversion and higher molecular weight than those obtained by direct polymerizations of *N*-hydroxymaleimide. The homopolymer of iPOCMI was transformed into poly(*N*-hydroxymaleimide)(PHOMI) by thermolysis of iPOC groups at 205 ℃ with concurrent release of propene and carbon dioxide. The copolymer of iPOCMI and styrene was thermally deprotected to the copolymer of HOMI and styrene at 235 ℃. The mass loss was 28% and the T_g of the resulting copolymer was 250 ℃. The thermal deprotection readily provided the desired, polar HOMI polymers which have T_gs above 240 ℃. The deprotection was accompanied by large changes in aqueous base solubility.

Introduction

A novel technology based on the "chemical amplification" concept has been established that affords a desired modification of polymer properties by thermal and photochemical acidolytic deprotection of side-chains.[1] Among the protecting groups that have been studied for this purpose, the *tert*-butyloxycarbonyl (*t*-BOC) group has been particulary useful in conjuction with phenolic polymers for application to the design of highly sensitive photoimaging systems.[2,3] Our continuing search for novel polymeric photoresist materials which can provide high resolution images possessing high thermal stability and aqueous base developing capabilities, led us to study maleimide (MI) polymers by virtue of their unique thermal stability and polar functionality.[4] Polymers with succinimide structures in the main-chain can be obtained by radical copolymerization of maleimide monomers. In particular, the polymers and copolymers of *N*-hydroxymaleimide **1** (HOMI) are potential candidates for this application because they bear highly acidic *N*-hydroxy functional groups. For example,[5] *N*-hydroxysuccinimide **2** and *N*-hydroxy-3,4-dimethylsuccinimide **3** are known to have pK_a values of 6.0 and 7.2, respectively, whereas those of succinimide (N-H) and phenol (O-H) derivatives are about 10.

1   **2**   **3**
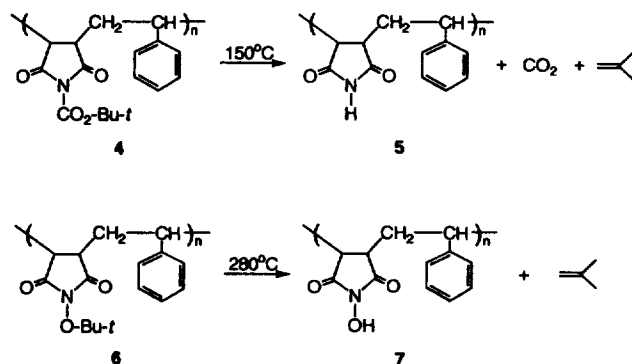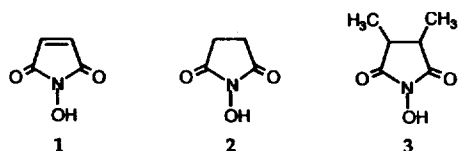
Scheme 1.

The HOMI monomer **1** is a 1,2-disubstituted ethylene and has an active hydrogen. Hence, it is not surprising that we were not able to obtain high molecular weight polymers by direct free radical polymerization of **1**. Otsu and coworkers[6,7] reported the synthesis of high molecular weight polymers from 1,2-disubstituted ethylenic monomers *via* a protection-thermal deprotection scheme. They obtained poly(fumaric acid) by heating poly(di-*t*-butyl fumarate) at 180 ℃[6] and polymaleimide by thermolysis of poly(*N*-*t*-butylmaleimide) at 330 ℃.[7] In previous articles we have reported functional polymaleimides which have excellent photoimaging properties and high glass transition temperatures (T_g).[8~11] Two parent functionalized polymaleimides were converted to the aqueous alkali soluble polymers by thermal deprotection (Scheme 1).

The copolymer **4** of *N*-(*tert*-butyloxycarbonyl)maleimide (*t*-BOCMI) and styrene is cleanly converted to poly(maleimide-co-styrene) **5** by thermolysis of *t*-BOC groups[8] whereas the copolymer **6** of *N*-(*tert*-butoxymaleimide) (*t*-BuOMI) and styrene is cleanly converted to poly(*N*-hydroxymaleimide-co-styrene) **7** by thermolysis deprotection of *t*-Bu ether groups.[9]

In this paper, we report the successful synthesis and characterization of *N*-hydroxymaleimide polymers by a protection-thermolysis deprotection scheme. We have found that the more thermally stable isopropyloxycarbonyl (iPOC) group is required to protect the *N*-hydroxy groups of HOMI polymers in place of the well-known *t*-BOC protecting group.

Experimental

Materials and Instruments. Di-*t*-butyl dicarbonate (DTBDC), *N*-hydroxymaleimide (HOMI), *N*-phenylmaleimide (PMI), and three (isopropyl, phenyl, benzyl) chloroformates were purchased from Aldrich Chemical Co. and were used as received. A *t*-BOC monomer, *p*-(*t*-butyloxycarbonyloxy)styrene (*t*-BOCSt) was kindly donated by Eastman Kodak Co. Dried tetrahydrofuran (THF) and dioxane were used as a solvent for the polymerizations.

Melting points were measured with a digital melting point apparatus using capillary tubes. Infrared spectra were obtained with an IBM IR/32 FTIR spectrophotometer. NMR spectra were recorded on a Varian EM 390 (90 MHz) for routine measurements and a Bruker WP200 (200 MHz) for carbon-13 and high resolution measurements. NMR spectra were taken in deuteriochloroform except the copolymers of *N*-hydroxymaleimide which were taken in dioxane-d8, and TMS was used as an internal standard. UV spectra were recorded on a Hewlett-Packard Model 8450A UV/VIS spectrophotometer. Mass spectra were obtained with a Hewlett-Packard 5995 A GC/Mass spectrometer. Molecular weights of polymers were measured by a Waters Model 150-C GPC equipped with μ-styragel columns in THF. Solution viscosities of the polymers were measured at 25 ℃. Thermal analysis was performed with a DuPont 951 and 1090 Thermal Analyzer at a heating rate of 10 ℃/min in DSC runs and 5 ℃/min in
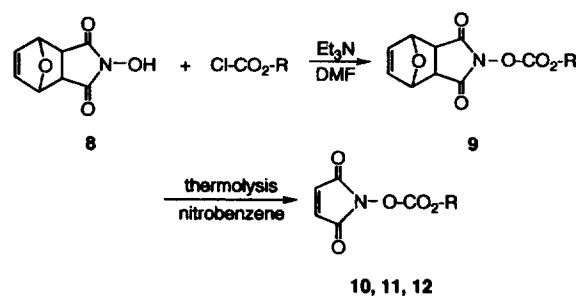
R = CH(CH₃)₂ for iPOCMI 10

R = Ph for PhOCMI 11

R = CH₂Ph for CBzMI 12

Scheme 2.

TGA runs under inert atmosphere.

Preparation of *N*-(Isopropyloxycarbonyloxy)maleimide (iPOCMI) 10. The iPOCMI monomer **10** was prepared by a retro-Diels-Alder reaction according to the known procedure (Scheme 2).[12] The furan/*N*-hydroxymaleimide (furan/HOMI) adduct **8**, *N*-hydroxy-3,6-epoxy-1,2,3,6-tetrahydrophthalimide, was prepared by reacting the adduct obtained from furan and maleic anhydride with hydroxylamine in a yield of 95%. The furan/iPOCMI adduct **9** (R=CHMe₂), *N*-(isopropyloxycarbonyloxy)-3,6-epoxy-1,2,3,6-tetrahydrophthalimide was obtained in a yield of 96% (51.5 g) by a reaction of the adduct **8** with isopropyl chloroformate and triethylamine in *N,N*-dimethylformamide (DMF).

9 (R=CHMe₂), mp 129-130 ℃ (lit.[12] 134-135 ℃); NMR (CDCl₃) δ (ppm) 6.50 (s, 2H, -CH=CH-), 5.30 (s, 2H, -CH-O-CH-), 4.94 (heptet, 1H, -CHMe₂), 2.87 (s, 2H, 2-CH-CO), 1.37 (d, 6H, 2CH₃).

A solution of 32.1 g of the furan/iPOCMI adduct **9** in nitrobenzene was heated to 155 ℃ for 30 min under reduced pressure. The solid residue was recrystallized in an ethanol-isopropanol mixture (1 : 1 by vol) to afford 11.1 g (47% yield) of iPOCMI **10**, mp 70-72 ℃ (lit.[12] 77-78 ℃); NMR (CDCl₃) δ (ppm) 6.80 (s, 2H, -CH=CH-), 4.93 (heptet, 1H, -CHMe₂),

Table 1. Polymerizations of HOMI (**1**), PhOCMI (**11**) and CBzMI (**12**)[a]

Polymer entry	Monomer M1	Monomer M2	M/S[b] (g/mL)	Reaction time (h)	Yield (%)	Mol. Wt.[c] $\overline{M}_w$	Mol. Wt.[c] $\overline{M}_w/\overline{M}_n$	Thermal data[d] T_g (℃)	Thermal data[d] T_d (℃)
P-1	HOMI	—	0.53	27	100	[η]=0.09 (in MeOH)	—	—	300
P-2	HOMI	styrene	0.62	9	63	[η]=0.57 (in NMP)	—	245	340
P-3	PhOCMI	styrene	0.31	2	90	[η]=0.96 (in THF)	—	190	300
P-4	CBzMI	—	0.63	27	94	7,900	2.41	140	310
P-5	CBzMI	styrene	0.70	2	86	—[e]	—	155	310
P-6	CBzMI	PMI	0.85	8	94	35,900	2.55	240	320
P-7	—	PMI	1.16	8	100	52,400	3.22	250[f]	380

[a]Polymerization conditions: 1 to 1 molar monomer feed ratio with 2 mol% AIBN at 58 ℃ in dioxane. [b]The ratio of the combined weight of monomers to the volume of dioxane. [c]Molecular weights measured by GPC in THF. The intrinsic viscosities (dl/g) measured in different solvents (methanol, *N*-methylpyrrolidone, THF) at 25 ℃. [d]Refer to Table 3 for measurements of T_g and T_d. P-1 shows no T_g. [e]High mol. wt. polymer, insoluble in THF. [f]Ref. 18.

1.38 (d, 6H, 2CH₃); IR (KBr) v̄ (cm⁻¹) 3110 (olefinic C-H), 1808, 1784 and 1742 (all for carbonyls), 1250 (carbonate).

Preparation of N-(Phenyloxycarbonyloxy)maleimide (PhOCMI) 11. To an ice-cooled solution of the furan/ HOMI adduct **8** (46.7 g, 0.26 mol) in 150 mL of DMF and triethylamine (26.3 g, 0.26 mol) was added dropwise phenyl chloroformate (40.7 g, 0.26 mol). The solution was stirred for 2 h at room temperature and the precipitated ammonium salt was filtered off, and the filtrate was poured into 2 L of water to precipitate the product. The white powdery adduct (furan/PhOCMI) **9** (R=Ph) was obtained in a yield of 91% (71.3 g), mp 135 ℃ (lit.[12] mp 135 ℃). In a round bottomed flask, 60.1 g of the furan/PhOCMI adduct **9** was heated at 150 ℃ for 1.5 h under reduced pressure. The yellowish solid residue was recrystallized from a solution of acetone and *n*-hexane (1 : 10 by vol) to afford 45.6 g (98% yield) of PhOCMI **11**, mp 98 ℃ (lit.[12] mp 98 ℃); NMR (CDCl₃) δ (ppm) 7.30 (s, 5H, phenyl), 6.80 (s, 2H, -CH=CH-); IR (KBr) v̄ (cm⁻¹) 3100 (olefinic C-H), 1820, 1785 and 1740 (all for carbonyls).

Preparation of N-(Benzyloxycarbonyloxy)maleimide (CBzMI) 12. CBzMI was similarly prepared by the retro-Diels-Alder reaction procedure with a yield of 73% (14.5 g) in thermolysis of a furan/CBzMI adduct **9** (R=CH₂Ph) at 150 ℃ in nitrobenzene, mp 89 ℃ (lit.[12] 103-104 ℃); NMR (CDCl₃) δ (ppm) 7.40 (m, 5H, phenyl), 6.44 (s, 2H, -CH=CH-), 5.08 (s, 2H, -CH₂Ph).

Polymerization. All of the polymerizations were performed in dioxane with *N,N'*-azobisisobutyronitrile (AIBN) as a radical initiator. The radical polymerizations were conducted at 55 ℃ under conditions as described in Table 1. Copolymerizations with styrene monomer were run at 1 to 1 molar feed ratio. The polymers were isolated by precipitation in methanol. The polymers were fully characterized by spectroscopy, and TGA and DSC analysis. Molecular weights of the polymers were measured by GPC in THF and inherent viscosities of some polymers were measured with viscosity tubes in dioxane at 25 ℃.

Results and Discussion

Synthesis of O-Substituted N-Hydroxymaleimide Monomers. For the purpose of incorporating HOMI units into polymer chains, three O-substituted HOMI monomers were chosen to synthesize as described in Scheme 2. Three possible protecting groups, isopropyloxycarbonyl (iPOC), phenyloxycarbonyl (PhOC), and benzyloxycarbonyl (CBz) groups were introduced on the furan/HOMI adduct **8**. The three

R = Ph for P-3
R = CH₂Ph for P-5
R = CH(CH₃)₂ for P-10
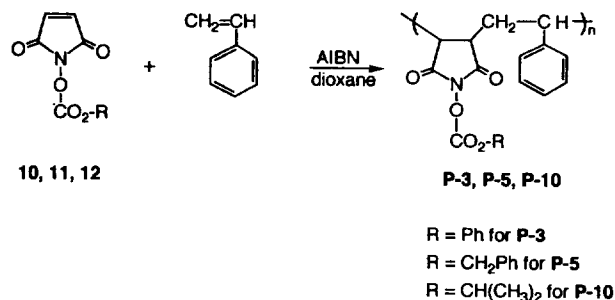
Scheme 3.

monomers, iPOCMI **10**, PhOCMI **11**, and CBzMI **12** were prepared from the corresponding adducts **9** by a retro-Diels-Alder reaction according to the procedure of Akiyama and coworkers.[12] To obtain free HOMI, the protecting group was removed from PhOCMI by refluxing in methanol.

Polymerization. The results of radical polymerizations of HOMI, PhOCMI, and CBzMI monomers using AIBN as a radical initiator are summarized in Table 1 along with thermal analysis data of the resulting polymers. *N*-Phenylmaleimide (PMI) was used as a different kind of maleimide monomer. These maleimide derivatives belong to the class of 1,2-disubstituted, electron deficient ethylene monomers which are known to be reluctant to undergo radical homopolymerization. However, many substituted-maleimide monomers are relatively reactive in radical polymerizations compared to maleic anhydride which is hardly polymerizable.[13~15] It is interesting that PMI undergoes radical polymerization readily to produce a high molecular weight poly(*N*-phenylmaleimide) **P-7** with a quantitative conversion.

Two homopolymers, poly(*N*-hydroxymaleimide) (PHOMI) **P-1** and poly(CBzMI) **P-4**, were obtained in very high conversions but with fairly low molecular weights based on solution viscosity and GPC measurements. The copolymer **P-2** obtained from HOMI and styrene also gave rather low molecular weight products. The propensity to produce low molecular weight polymers in the homo- and copolymerizations of HOMI is ascribed partly to the acidic *N*-hydroxy functionality and to the 1,2-disubstitution. Therefore, *O*-protected *N*-hydroxymaleimides were synthesized and polymerized to obtain high molecular weight polymers and subsequently deprotected by thermolysis to provide *N*-hydroxy groups. The copolymerization reactions of the protected maleimides with styrene in 1 to 1 molar feed ratio are shown in Scheme 3. The copolymerizations of PhOCMI and CBzMI gave fairly high molecular weight polymers in high conver-

Table 2. Polymerizations of iPOCMI (10) at 58 ℃ in Dioxane[a]

Polymer entry	Comonomer	M/S (g/mL)	AIBN (mol%)	Reaction time (h)	Yield (%)	Mol. Wt.	
						M̄ᵥᵥ	M̄ᵥᵥ/M̄ₙ
P-8	homopolymer	1.00	2.0	24	80	12,600	1.90
P-9	homopolymer	1.00	1.0	24	73	−	−
P-10	styrene	1.02	4.0	3	95	68,200	1.97
P-11	PMI	1.25	2.0	8	90	19,000	2.75
P-12	*t*-BOCSt[b]	0.84	4.0	3	96	577,000	1.74

[a] Refer to Table 2 for M/S and Mol. Wt. [b] *p*-(*t*-Butyloxycarbonyloxy)styrene

sions within two hours (Table 1). The polymers of PhOCMI were known to convert to PHOMI in refluxing methanol,[16] but the deprotection of CBz groups from the polymers P-4 and P-5 was found to be somewhat difficult and inefficient. Hydrogenolysis of the CBzMI polymer P-5 with a catalyst system of palladium on carbon and aminolysis of P-5 and P-10 were unsuccessfully attempted. The modification of the CBzMI polymers P-4 and P-5 in solution with hydrogen bromide gas was possible, but the reaction was difficult to control.

The third monomer *N*-(isopropyloxycarbonyloxy)maleimide 10 (iPOCMI) was successfully employed in both polymerization and subsequent deprotection which were investigated in more detail. The results of the polymerizations of iPOCMI are summarized in Table 2. The homopolymerization of iPOCMI resulted in high conversions, but the molecular weights were low partly due to the 1,2-disubstitution and chain transfer of the iPOC groups. Copolymerizations of iPOCMI with styrene gave very high molecular weight polymers P-10 and P-12 in short periods of time. The copolymerizations of the three maleimide monomers 10, 11 and 12 with styrene in 1 to 1 molar feed ratio were observed to be very fast because the polymerization solutions were very viscous within 15 min after initiation of the polymerizations.

The composition of the copolymers P-2, P-3, P-5, P-10, and P-12 was determined to be 1 to 1 by carbon-13 NMR, high resolution proton NMR spectra and elemental analysis. The tendency toward an alternating structure is ascribed to the well known charge-transfer polymerization system derived from the electron deficient maleimide monomers and the electron rich styrene monomers.[17] It was reported that the copolymerization of *N*-phenylmaleimide and styrene gives an exactly alternating copolymer, irrespective of monomer feeds ratio.[18] The iPOC maleimide polymers have three absorption bands associated with carbonyl groups, two from the imide and one from the carbonate group at about 1810, 1790 and 1740 cm⁻¹, respectively. The copolymers of HOMI show a broad hydroxyl absorption at about 3200 cm⁻¹ and two carbonyl absorption bands at about 1780 and 1710 cm⁻¹. The copolymers of CBzMI have two carbonyl absorption bands at 1790 cm⁻¹ (weak) and 1720 cm⁻¹ (strong).

Solubility of Polymers. Poly(*N*-hydroxymaleimide) is soluble in methanol, warm water, warm NMP, and aqueous base solutions, but insoluble in many organic solvents. The homo- and copolymers of substituted maleimides are very soluble in common organic solvents such as acetone, THF, chloroform, and cyclohexanone, but insoluble in methanol, toluene, and aqueous base solutions. The copolymer of HOMI, P-2 is soluble in aqueous base solutions and a few organic solvents such as THF, dioxane, warm acetone, and DMF, but insoluble in common organic solvents such as chloroform, anisole, toluene and methanol. The good solubility of the homo- and copolymers of *N*-hydroxymaleimide in aqueous base solutions is ascribed to the acidic *N*-hydroxysuccinimide functionality in the polymer chains.

Thermal Properties. In the case of *t*-BOC protected polymers, thermal deprotection quantitatively generates phenol and imide functionalities below 200 °C, releasing only isobutene and carbon dioxide.[2,3,8,11] However, the iPOC protected HOMI polymers undergo thermal deprotection at higher temperatures, about 210 °C and generate the *N*-hydroxy
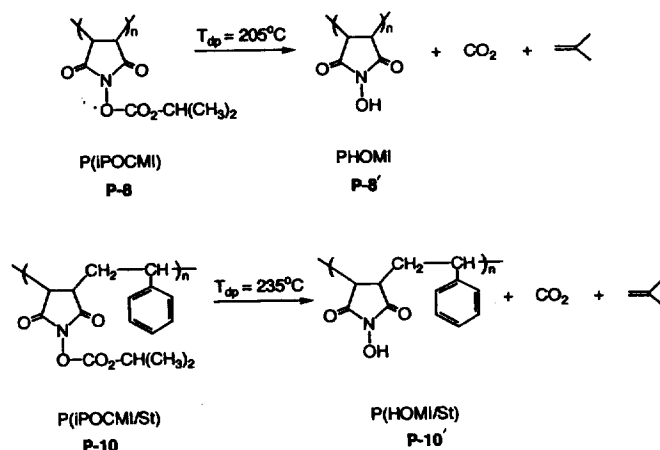
Scheme 4.
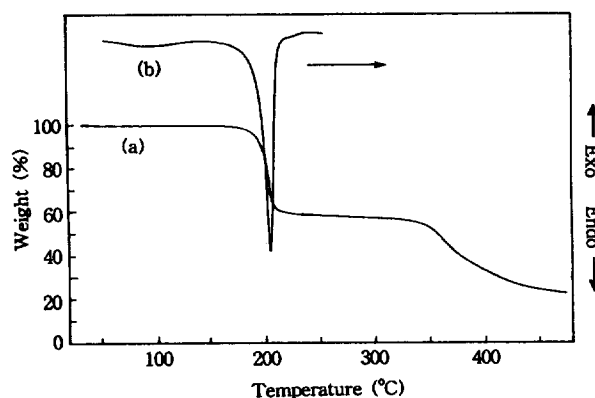
Figure 1. Thermograms of (a) TGA and (b) DSC for poly(iPOCMI) **P-8** showing thermal deprotection (T_{dp}) at 205 °C with mass loss of 43%.
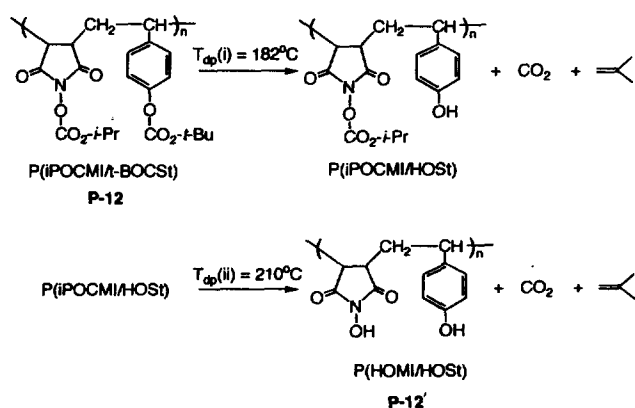
functionality, propene and carbon dioxide as shown in Scheme 4. Thermal analyses of the iPOCMI polymers confirm the complete deprotection of iPOC groups. In thermogravimetric analysis (TGA), the iPOC polymers show a precipitous mass loss above 200 °C, and then a stable plateau that persists until onset of decomposition of the polymer. A thermogram of the homopolymer of iPOCMI, P-8 shows a mass loss of 43% at about 200 °C, and then a plateau that persists until main-chain decomposition at about 340 °C as shown in Figure 1. The observed mass loss (43%) agrees well with the calculated amount based on the evolution of propene and carbon dioxide by deprotection of iPOC groups. The deprotection temperature (T_{dp}) of the iPOC protected polymers, the glass transition temperature (T_g) of the deprotected polymers with HOMI structure, and the onset decomposition temperature (T_d) of polymer main-chains are listed in Table 3 along with the amount of the mass loss observed during the deprotection.

The thermal deprotection of the iPOC polymers and the thermal behavior of the subsequent (deprotected) polymers were verified by DSC analyses. The DSC analyses were carried out by two consecutive runs as described in the previous reports.[8-11] First, the iPOC polymers were heated up to 250 °C only to bring about the deprotection of iPOC side-
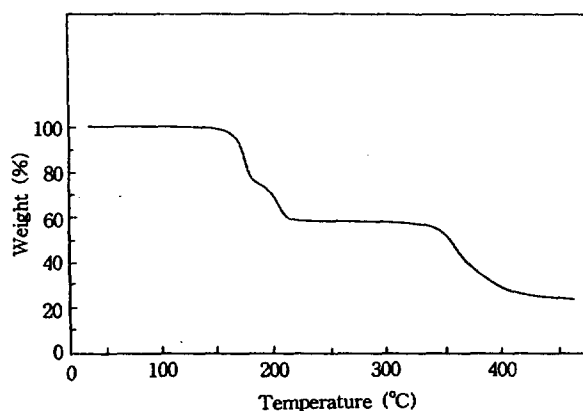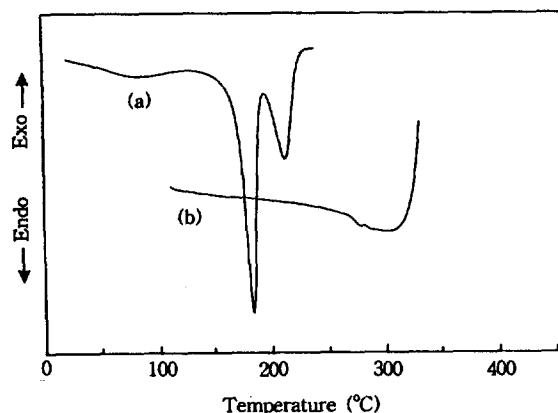
Table 3. Thermal Analysis of iPOCMI Polymers[a]

Polymer entry	T_{dp} (°C)	Mass loss (wt%) calcd	Mass loss (wt%) found	Deprotected polymer	T_g (°C)	T_d (°C)
P-8	205	43.2	43	PHOMI	—[b]	340
P-10[c]	235	28.4	28	P(HOMI/St)	250	340
P-11	215	23.1	22	P(HOMI/PMI)	—[b]	370
P-12[d]	(i) 182	(i) 22.8	(i) 23	(i) P(iPOCMI/HOSt)	—	—
	(ii) 210	(ii) 21.6	(ii) 21	(ii) P(HOMI/HOSt)	270	340

[a] N-Hydroxymaleimide (HOMI), styrene (St), N-phenylmaleimide (PMI), p-hydroxystyrene (HOSt); T_{dp} = deprotection temperature measured by the first DSC run.; T_g = glass transition temperature of deprotected polymer measured by the second DSC run; T_d = onset decomposition temperature of deprotected polymer measured by TGA. [b] The deprotected polymer shows no T_g. [c] Polymer **P-10** has T_g at 175 °C measured by DSC before deprotection. [d] Polymer **P-12** exhibits two-step deprotection behavior: the first deprotection for t-BOC groups and the second one for iPOC groups.

Scheme 5.

Figure 2. A TGA thermogram of P(iPOCMI/t-BOCSt) **P-12** in a nitrogen stream at a heating rate of 5 °C/min⁻¹.

chains and then cooled down to room temperature. The samples were then heated again until to the polymer decomposition temperature. A DSC thermogram of the iPOC homopolymer **P-8** is shown in Figure 1. In the first heating, a sharp endothermic peak is observed at 205 °C due to the deprotection of iPOC groups. The deprotected polymer **P-8'** (PHOMI) showed no glass transition in the second DSC run. This was expected from based on thermal analysis of the homopolymer **P-1**, PHOMI which was obtained by direct polymerization of HOMI (Table 1). Thus the iPOCMI homopolymer **P-8** is transformed into the hydroxy-functional polymer **P-8'** (PHOMI) by heating to about 205 °C, that is the deprotection temperature (T_{dp}) of the side-chain iPOC groups as described in Scheme 4. The thermally deprotected polymer from **P-8** was confirmed to be identical to PHOMI by spectral analyses.

The styrene copolymer of iPOCMI, **P-10** showed somewhat higher T_{dp} (235 °C) in DSC analysis with mass loss of 28% (Scheme 4). In the first DSC run, the iPOC copolymer **P-10** shows a T_g at 175 °C. After deprotection the deprotected polymer, P(HOMI/St) **P-10'**, showed a T_g at 250 °C. The deprotected polymer **P-10'** was confirmed to have an identical structure to the copolymer **P-2** obtained by the direct copolymerization of the corresponding monomers, HOMI and styrene. The polymers, **P-2** and the modified polymer **P-10'** showed nearly identical thermal data. The same polymer, **P-10'** was also obtained from the thermal deprotection of t-BuOMI copolymer **6** at 280 °C as mentioned in the introduc-

Figure 3. DSC thermograms of P(iPOCMI/t-BOCSt) **P-12** in a nitrogen stream at a heating rate of 10 °C/min⁻¹: (a) first run for deprotection of both iPOC and t-BOC side-chains; (b) second run for deprotected polymer P(HOMI/HOSt) **P-12'** showing T_g at 270 °C.

tion (Scheme 1).[9] The copolymer of N-phenylmaleimide, **P-11** generated the modified polymer P(HOMI/PMI) by thermal deprotection at 215 °C.

The copolymer **P-12** consisting of two kinds of the protected monomers, iPOCMI and p-(tert-butyloxycarbonyloxy)sty-

rene (*t*-BOCSt), exhibited an interesting thermal deprotection behavior. P(iPOCMI/*t*-BOCSt) **P-12** underwent stepwise thermal deprotection due to sequential loss of the *t*-BOC and iPOC groups as depicted in Scheme 5. The TGA and DSC thermograms of **P-12** reveal the peculiar behavior as shown in Figure 2 and Figure 3, respectively. In the thermogram, the mass loss of 23% and 21% are observed at 182 ℃ and 210 ℃, respectively. The lower temperature mass loss comes from the deprotection of *t*-BOC groups and the higher corresponds to loss of the iPOC groups. The mass loss agrees well with the calculated values. After the deprotection of both groups, the resulting modified polymer **P-12'**, P (HOMI/HOSt) bears both the HOMI and *p*-hydroxystyrene (HOSt) units and exhibits very high T_g of 270 ℃. The glass transition temperature is close to that reported for this polymer but prepared by a different route.[4] This peculiar deprotection behavior is similar to that previously reported for the copolymer P(t-BuOMI/*t*-BOCSt), which also showed a two-step deprotection.[9]

In Table 1 it can be seen that the CBzMI polymers, **P-4** and **P-5**, have T_gs at about 150 ℃ but show no evidence of thermal deprotection of the CBz groups. The homopolymer PHOMI showed no T_g in DSC measurements. The deprotected polymers, P(HOMI/St), P(HOMI/PMI) and P(HOMI/HOSt) obtained from the corresponding polymers **P-10**, **P-11** and **P-12** also have T_gs over 250 ℃ or no measurable T_g. Thus, we conclude that the copolymers of HOMI have very high glass transition temperatures compared to most of the vinyl polymers obtained by radical polymerization.

Evolution of propene and carbon dioxide gases during the thermal deprotection of the side-chain iPOC groups was documented by mass spectrometry. The abundant mass peaks from the iPOC polymers **P-8** and **P-10** were m/e 44 CO_2, 42 for CH_3-CH=CH_2, 41 for CH_2=CH-CH_2, and 39 for C_3H_3 species. In the case of the polymer **P-12**, the most abundant mass peaks in the decreasing order were m/e 56 for CH_2=C $(CH_3)_2$, 44 for CO_2, 42 for CH_3-CH=CH_2, 41 for CH_2=CH-CH_2, and 39 for C_3H_3 species. Thus, the gases evolved in thermolysis of the polymer **P-12** are isobutene, propene and carbon dioxide due to the deprotection of *t*-BOC groups as well as iPOC groups in the side-chains.

Deprotection by Thermolysis. The thermal analysis of the iPOC polymers clearly demonstrates efficiency of thermal deprotection for generating the *N*-hydroxysuccinimide structure in polymer chains. The thermolysis-deprotection process of three iPOC polymers, **P-8**, **P-10** and **P-12** is described in Scheme 4 and Scheme 5. The homopolymer **P-8** and the copolymer **P-12** were subjected to heat in an oven at 210 ℃ for 30 min, and in the case of the copolymer **P-10** treated at 230 ℃ for 30 min. After the thermolysis process, no color changes in the samples were observed and complete deprotection was confirmed by IR absorption spectra. The solution viscosity of the modified polymer **P-8'** was 0.09 dl/g in methanol at 25 ℃, indicating a very low molecular weight polymer comparable to the polymer **P-1** which was prepared directly from the monomer HOMI. In the case of the deprotected polymer **P-10'** the solution viscosity was 1.20 dl/g in NMP at 25 ℃, much higher than the viscosity (0.57 dl/g) of the polymer **P-2** prepared directly from the corresponding monomers, HOMI and styrene. Therefore high molecular weight copolymers having HOMI units can be ob-

tained by the protection and thermolysis-deprotection process. Hydrolysis of the iPOC polymer **P-10** to **P-10'** was possible with *p*-toluenesulfonic acid in refluxing DMF, but the hydrolysis of the CBz polymer **P-5** failed under the same reaction conditions.

The deprotected polymers **P-10'** and **P-12'** show good solubilities in aqueous base solutions, whereas they are less soluble in common organic solvents due to the newly generated *N*-hydroxy functionalities. Preliminary imaging studies of the iPOCMI polymers **P-8** and **P-10** were done with the resist solutions containing 10% triphenylsulfonium hexafluoroantimonate as a photoacid generator. Resist films were spin-coated on silicon wafers, exposed to deep UV, and then post-exposure baked above 150 ℃ for 5 min. Both positive- and negative-tone images were generated when developed with anisole and aqueous base solutions, respectively. This work will be reported elsewhere.

Conclusions

(a) Homopolymers of iPOCMI and copolymers with styrene that were produced by radical polymerizations resulted in very high molecular weights with high conversions.

(b) The thermolysis-deprotection of iPOCMI polymers is a simple, clean and efficient route to polymers having HOMI units. Polymers that incorporate the HOMI monomer have exceptionally high glass transitions at 240 ℃ and are soluble in aqueous base solutions.

(c) Polymers that incorporate the iPOCMI monomer are promising candidates for photoresist application.

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Predissociation of Lower Rovibrational Levels of OH

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A Theoretical Treatment of the Resonances in the Predissociation of Lower Rovibrational Levels of the $A^2\Sigma^+$ State of OH

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An exact quantum mechanical theory is employed to treat predissociation process of the $A^2\Sigma^+$ state of OH. The widths and positions of the lower ($v=2$ and $v=3$) rovibrational levels are calculated. Energy shifts of the resonances from the zeroth order (pure Hund's case (b)) positions are shown to be small for $N \leq 10$, indicating that the $A^2\Sigma^+$ state can be described as case (b) very well for low N. Due to the differential interactions of the $A^2\Sigma^+_{1/2}$ and $A^2\Sigma^+_{-1/2}$ states with $X^2\Pi$ and $2^2\Pi$ states, small splittings between the F_1 and F_2 levels are predicted. Calculated lifetimes of the resonances agree with experimental results reasonably well.

Introduction

The hydroxyl radical (OH) is an important constituent of combustion gas and cometary gas. Many *ab initio* studies have been done on the potential energy curves[1~5] and also on the spin-orbit interactions[2] and transition dipole moments [1~5] between the low-lying electronic states of OH. Photodissociation processes of OH have also been of interest in a number of investigations, because of the astrophysical importance of the molecule. Dalgarno and coworkers,[1,3,5] for example, have done extensive studies on the direct photodissociation processes of the low-lying states of OH. The A-X band system of OH has been studied for a long time[6~8] especially because of the potential use in detecting OH fragments by laser induced fluorescence technique.

Predissociation is one of the dynamic processes[9,10] that result from the breakdown of the Born-Oppenheimer approximation. It is now well known that interactions between the binding and dissociating states basically determine the widths and positions of the resonances (or quasi-bound states) observed in the photodissociation spectra. There have been numerous studies where the relationships between these interactions and the characteristics of the resonances have been investigated. In these works, the widths and shifts of the resonances have been expressed in terms of the matrix elements of the interactions between the wave functions of the binding states and the continuum wave functions of the dissociating states. Continuum wave functions are usually obtained by using methods based on scattering theory. Various levels of approximations have been employed in these methods, the consequences of which are that some of the

interactions, which are expected to play a significant role in the dynamic processes, are not considered. In Yarkony's recent calculations,[2] for example, case (b) limit has been *assumed* for the $X^2\Pi$ and $^4\Pi$ states of OH. In most situations, molecular electronic states do not belong to the pure Hund's cases. These assumptions had to be made because *not* all of the couplings have been included in the formalism. Particular Hund's coupling cases need not be assumed for these states as long as all the nonadiabatic interactions between these states and other states correlating with the dissociation products are included to evaluate the total Hamiltonian. These deficiencies are also evident in Sink *et al.*'s work,[11,12] where asymptotic couplings among the dissociative states have not been included. Many interesting observables such as the population ratios of the photofragments internal states and anisotropy parameters cannot be calculated by employing these approximation methods.

Intensities and line shapes are also very important characteristics of the resonances that cannot be properly calculated by employing approximate schemes where some of the interactions are not incorporated. It is well known[13] that the resonances can exhibit a variety of asymmetric profiles when the continuum states, interacting with discrete states, are optically coupled with the initial states. These asymmetric resonances have recently been observed for the predissociation processes of Cs_2[14,15] and FNO.[16] Theoretical analyses of the photodissociation spectra of these molecules have provided detailed informations on the underlying mechanisms. The quantum interferences between the discrete states and the continuum states, which give rise to these very interesting non-Lorentzian absorption line shapes, can only be pro-