

Thermal conversion of *t*-butyloxycarbonyloxy attached polyamides to polybenzoxazoles

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Summary

A series of *t*-butyloxycarbonyloxy (*t*-hoc-oxy) attached polyamide (*t*-bocPA) as a polybenzoxazole (PBO) precursor was synthesized from poly(*o*-hydroxyamide) (PAOH) and its thermal conversion to PBO was investigated by using FT-IR, TGA and DSC. Most of the protecting group of *t*-bocPA was decomposed at 250 °C and the polymer converted to PBO at 350°C. The thermal reaction for PBO formation was accelerated by the strong acid such as *p*-toluenesulfonic acid. It was revealed that photo-acid generator (PAG) can act not only as an acid generator on UV exposure, but also as a catalyst to lower the temperature of PBO formation.

Introduction

The photosensitive heat resistant (PHR) polymers have been considered as essential materials for the passivation layer and buffer layer of semiconductors (1~4). Since it can be directly patternable, the use of PHR polymers would simplify fabrication process of semiconductor. Thus several PHR polymers have been developed. For instant, as the negative PHR polymers, there are photo-crosslinkable polyamic ester of acrylic acid (3,4), polyamic ester or polyisoimide with photo-base generator (5,6), intrinsically crosslinkable polyimide (7), etc. For positive photopolymers, *o*-nitrobenzyl ester of polyamic acid (8), mixture of poly(hydroxyimide) and naphthoquinone azide derivatives (9), polyimide precursor with 1,4-dihydropyridine derivatives (10), and *t*-boc or tetrahydropyranyl attached poly(hydroxyimide) as an acid sensitive group (11,12), were investigated by various researchers. Recently PBO precursor was introduced as a PHR polymer, which was combined with large amount of naphthoquinone azide (13, 14).

We have been studying positive PHR polymers, *t*-boc attached polyamides mixed with PAG, as a precursor of PBO (15). Besides of the lithographic performance of the polymers, we also studied the thermal conversion of the precursor to PBO, especially effect of acid on the formation of PBO, which is the most important subject for the PHR polymers when they are used as a mixture with PAG. The PBO formation should occur in the unexposed area to preserve and cure the patterned relief of PBO. During PBO formation, the PAG would be decomposed and produce an acid since the temperature of PBO formation is high enough to decompose the PAG. Although the thermal conversions to PBO were reported by several researchers (16~19), there is few literature available for

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the effect of acid on thermal conversion to the PBO from its precursor. Thus we have thoroughly investigated the thermal behavior of the PBO precursor in the presence of acid. In this report, we present the preparation, thermal analysis and catalytic effect of the acid on thermal conversion of the PBO precursor.

Experimental

Materials ; N,N-dimethylacetamide (DMAc) was purified by vacuum distillation over CaH₂. Pyridine was purified by simple distillation with KOH. 2,2'-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6F; Tokyo Kasei, >98%) was purified by recrystallization from H₂O/MeOH and dried at 100°C vacuum oven completely. 3,3'-diamino-4,4'-dihydroxybiphenyl (BP; Tokyo Kasei, >97%), γ -butyrolactone (Tokyo Kasei, >99%) and di-tert-butyl carbonate (t-boc-t-bu; Tokyo Kasei, >95%) were used as received. Isophthalic acid (Junsei Chemical) and 4,4'-oxydibenzoic acid (Tokyo Kasei, >98%) were used also as received.

Measurements ; ¹H-NMR spectra were obtained on a Bruker AMX-300MHz and 500MHz spectrometer using DMSO-*d*₆ or CDCl₃ as a solvent with tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded as KBr pellets on a Bio-Rad Digilab Division FTS-165 FT-IR Spectrophotometer. Inherent viscosity of polymer was measured with a Cannon-Fenske viscometer at a concentration of 0.5g/dL in NMP at 30°C. Thermal analysis was performed with a DuPont model 2950 for TGA and model 2910 for DSC at a heating rate 10°C min⁻¹ under nitrogen atmosphere.

Preparation of diacid chloride ; Isophthaloyl chloride (IPAC) and 4,4'-oxydibenzoyl chloride (ODBC) were synthesized by a conventional chlorination of isophthalic acid or 4,4'-oxydibenzoic acid with excess thionyl chloride, respectively. The crude acid chlorides were purified by vacuum distillation and recrystallization from dried n-hexane several times: Yield, 72% (mp 43~44 °C) and 68% (mp 83~84 °C), respectively, for IPAC and ODBC.

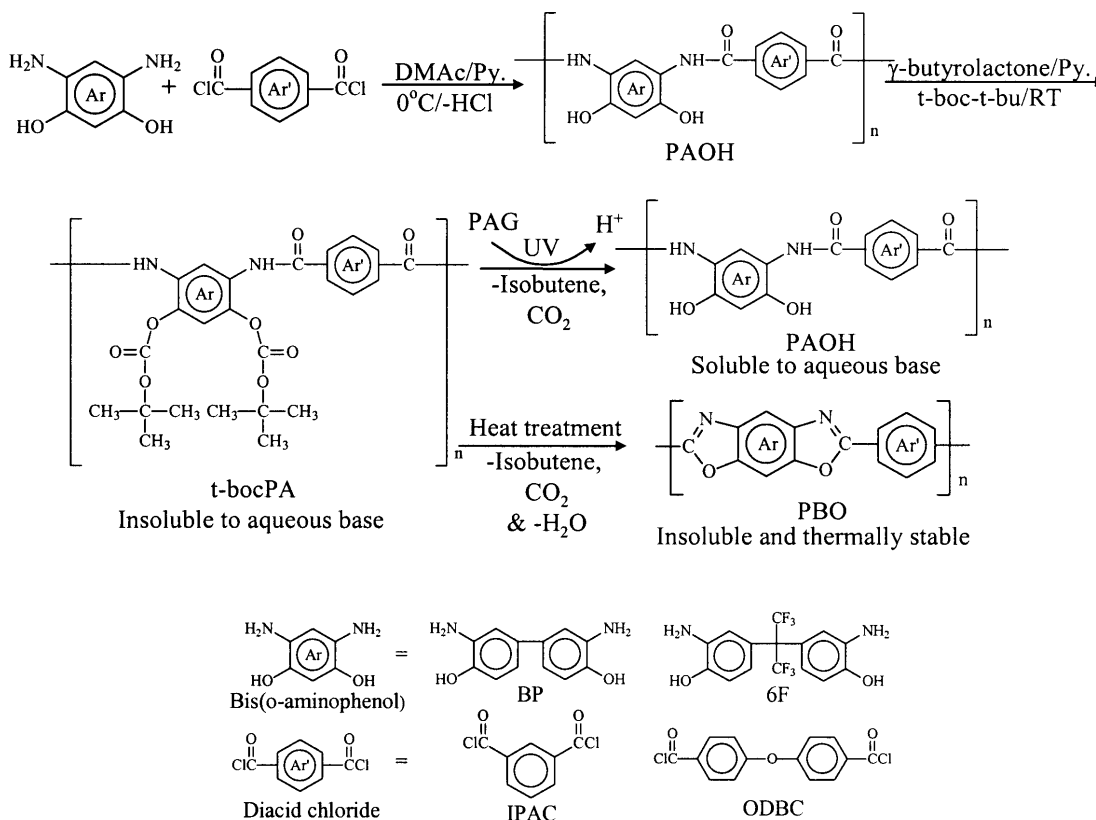
Synthesis of the poly(o-hydroxyamide) (PAOH) ; Polymerizations of poly(o-hydroxyamide)s (PAOH) with high molecular weight were carried out by conventional polycondensation of bis(o-aminophenol) with aromatic acid chloride (14,16). A typical procedure for the polycondensation of PAOH is as follows : To a solution of 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6F; 10 g, 27.3 mmol) and pyridine (8.64 g, 109.2 mmol) in 140mL of DMAc in a 4-neck flask equipped with mechanical stirrer, was added IPAC (5.54 g, 27.3 mmol) slowly. And the mixture was continuously stirred at 0 °C for 4 hr under nitrogen atmosphere. The resulting viscous solution was poured into excess water. The precipitated polymer was filtered and washed several times with water. The white polymeric powder (PAOH-II) was finally dried at room temperature for 72 hr *in vacuo*. The polymerization yield was almost quantitative. ¹H-NMR(DMSO-*d*₆): δ (ppm) 10.34 (s, 2H, OH), 9.77 (s, 2H, amide NH), 8.52 (s, 1H, aromatic H), 8.12(d, 2H, aromatic H), 7.90(s, 2H, aromatic H), 7.64(t, 1H, aromatic H), 7.04(m, 4H, aromatic H). FT-IR (KBr): 3409 cm⁻¹ (NH of amide), 3286 cm⁻¹ (OH of phenolic). 1654 cm⁻¹ (C=O of amide I), 1611 cm⁻¹ (NH of amide II).

Synthesis of the t-boc protected polyamides(t-bocPA) ; Introduction of t-boc group into the PAOH was performed by the reaction with di-tert-butyl carbonate (t-boc-t-bu). A typical synthetic procedure for the preparation of t-bocPA-II from PAOH-II is as follows: To a solution of PAOH-II (10 g, 40.30 mmol of OH equivalent) and catalytic amount of dried pyridine in γ -butyrolactone (90 ml) was added t-boc₂O (17.59 g, 80.60 mmol). The viscous mixed solution was mechanically stirred at room temperature for 3hr. The resulting polymer solution was slowly poured into excess water/methanol mixture in a

Waring blender. The precipitated polymer was washed with water/methanol mixture several times, collected by filtration. And the white polymer powder was finally dried at room temperature for 72 hr *in vacuo*. The yield was almost quantitative. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ (ppm) 9.35(s, 2H, amide NH), 8.78-6.85(m, 10H, aromatic H), 1.37(m, 9H, CH_3 of tert-butyloxy). FT-IR(KBr): 1769cm^{-1} (C=O of carbonate), 1682 cm^{-1} (C=O of amide I), 1607 cm^{-1} (NH of amide II), 1374 cm^{-1} (CH_3 of tert-butyl).

Synthesis of photo-acid generator ; p-Nitrobenzyl-9,10-dimethoxyanthracene-2-sulfonate (NBAS) was prepared by the reaction of 9,10-dimethoxyanthracene-2-sulfonyl chloride and p-nitrobenzyl alcohol in the presence of triethylamine (11). $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 4.11 (s, 3H, methoxy), 4.16(s 3H, methoxy), 5.21 (s, 2H, CH_2 of benzyl), 7.44(d, 2H, H of nitrobenzyl), 7.56~7.64(m, 2H, H of anthracene), 7.74(q, 1H, H of anthracene), 8.10(m, 2H, H of nitrobenzyl), 8.32(q, 2H, H of anthracene), 8.40(q, 1H, H of anthracene), 8.93(q, 1H, H of anthracene). FT-IR (KBr): 1170 and 1369cm^{-1} (SO_3), 1343cm^{-1} (NO_2).

Thermal conversion ; The powder of PAOHs and t-bocPAs were heated to specified temperature for given time and were analyzed by FT-IR for the evaluation of the thermal conversion. For the acid effect on the PBO formation, 0.2g (0.37mmol) of t-bocPAs and 0.019mmol of acids, benzoic acid (BA), p-toluenesulfonic acid (p-TSA), or p-nitrobenzyl-9,10-dimethoxyanthracene-2-sulfonate (NBAS) were mixed in the THF and stirred for 30 minutes in the dark, and then the solvent was evaporated to dryness under reduced pressure at room temperature for 24 hr. The resulted polymer mixtures were analyzed by using DSC and TGA.



Scheme 1. Synthesis and conversion of t-bocPA

Results and Discussion

Polymer Synthesis ; In order to study the PHR polymers, we have prepared polyamides having t-boc group, t-bocPA, which can act as a positive photoresist, when it mixed with PAG. Upon exposure to UV light, the PAG generates acids, which successively de-protect the acid sensitive groups to form phenolic moiety. The de-protected poly(o-hydroxyamide) can be removed by aqueous base solution. And the unchanged t-bocPA at the unexposed area, can be converted to PBO by heat treatment, which is insoluble and thermally very stable. The t-bocPAs, were synthesized by two consecutive reactions as shown in Scheme 1, the polycondensation of polyamides (PAOH)s having hydroxy group at ortho position, and the substitution of t-boc group onto PAOH. The PAOH was prepared by conventional polycondensation reaction from bis(o-aminophenol) and aromatic diacid chloride (16). The polymerization proceeded smoothly and rather quickly at low temperature (0 °C), and reached maximum inherent viscosity within 30 minute of reaction as shown in Figure 1. However, we had polymerized for 4 hr to insure completion of the reaction. The results are summarized in the Table 1.

Table 1. Results of Preparation of PAOH and t-boc PA

PAOH				t-bocPA	
Code	Bis(o-aminophenol)	Diacid chloride	$\eta_{inh}(\text{dl/g})^{1)}$	Code	t-boc content(mol %) ²⁾
I	BP	IPAC	0.69	I	99
II	6F	IPAC	0.76	II	100
III	6F	ODBC	0.69	III	97

1) Inherent viscosity measured at a concentration of 0.5g/dL in NMP at 30 °C.

2) The t-boc content was determined by analysis of FT-IR spectra.

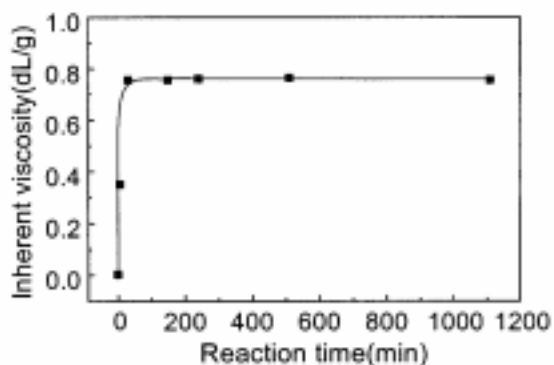


Figure 1. Inherent viscosities of PAOH with reaction time.

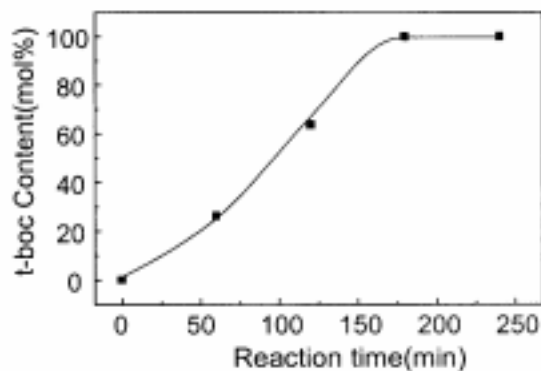


Figure 2, t-boc content of t-bocPA-II with reaction time

The substitution reaction of PAOH to prepare t-boc PA using t-boc-t-bu in the presence of pyridine proceeded straightforward as shown in Figure 2 for t-bocPA-II. The degree of substitution could be adjusted by the reaction time, which can allow us to control the solubility to 2.38 wt% of aqueous TMAH (tetramethylammonium hydroxide) developer for lithographic process. The reaction was completed to 100% in 3 hr.

Solubilities ; The solubilities of the PAOH, t-bocPA and PBO polymers were tested for various solvents and the results are shown in Table 2. Most of them were soluble in the polar aprotic solvent, such as NMP, DMF, DMSO, etc. The solubility of the polymers was increased when the t-boc groups was introduced, and the 100% substituted polymer,

t-bocPA, dissolved even in cyclohexanone, THF, etc. The enhanced solubilities may be originated from the reduced strong polar interaction between OH groups of the polymers and introduction of bulky side group. The polymers (t-bocPA-II, t-bocPA-III) derived from 6F monomer showed better solubility than that of the polymer prepared from BP monomer, owing to the increased flexibility by the kink 6F isopropylidene groups in the polymer backbone. It is interesting that polymer (t-bocPA-III) derived from ODBC was less soluble to the aqueous alkaline developer. The solubility difference of the polymers may be useful to adjust alkaline developing characteristics by copolymerization of the corresponding monomers. All the PBO from PAOH and t-bocPA by heat treatment up to 400°C did not dissolve in any organic solvents we have tested, except H₂SO₄.

Table 2. Solubility of the polymers

Solvent	PAOH			t-bocPA			PBO			Solvent	PAOH			t-bocPA			PBO		
	I	II	III	I	II	III	I	II	III		I	II	III	I	II	III	I	II	III
hexane	-	-	-	-	-	-	-	-	-	acetone	-	+	++	+	++	++	-	-	-
cyclohexanone	-	+	++	++	++	++	-	-	-	DMF ³⁾	+	++	++	++	++	++	-	-	-
toluene	-	-	-	-	+	-	-	-	-	DMAc ⁴⁾	++	++	++	++	++	++	-	-	-
chloroform	-	-	-	-	++	++	-	-	-	NMP ⁵⁾	++	++	++	++	++	++	-	-	-
THF ¹⁾	-	++	++	++	++	++	-	-	-	DMSO ⁶⁾	++	++	++	++	++	++	-	-	-
γ-butyrolatone	-	+	++	++	++	++	-	-	-	water	-	-	-	-	-	-	-	-	-
PGMEA ²⁾	-	+	++	-	++	++	-	-	-	TMAH ⁷⁾	++	++	-	-	-	-	-	-	-
methanol	-	+	-	-	+	+	-	-	-	H ₂ SO ₄	++	++	++	++	++	++	+	+	++

* Solubility: ++, soluble at room temperature; +, partially soluble or swelling; -, insoluble

1) THF: tetrahydrofuran, 2) PGMEA: propylene glycol methyl ether acetate, 3) DMF: N,N-dimethylformamide,

4) DMAc: N,N-dimethylacetamide, 5) NMP: N-methyl-2-pyrrolidone, 6) DMSO: dimethyl sulfoxide,

7) TMAH: 2.38wt% aqueous solution of tetramethyl ammonium hydroxide

Thermal conversion of the polyamides to polybenzoxazole ; The PAOH and t-boc PA can be transformed to PBO by the reaction of amide group with ortho-OH (or its derivatives) at high temperature along with loss of isobutene, carbon dioxide and water.

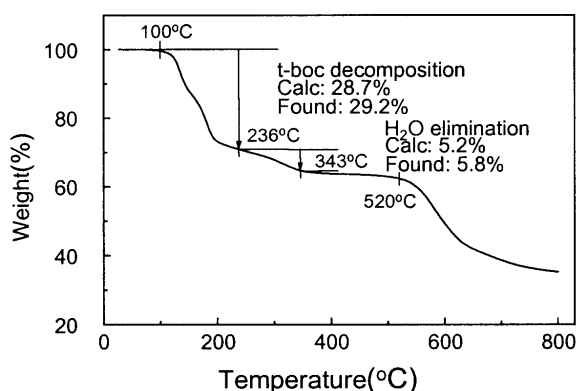


Figure 3. TGA thermogram of t-bocPA-II.

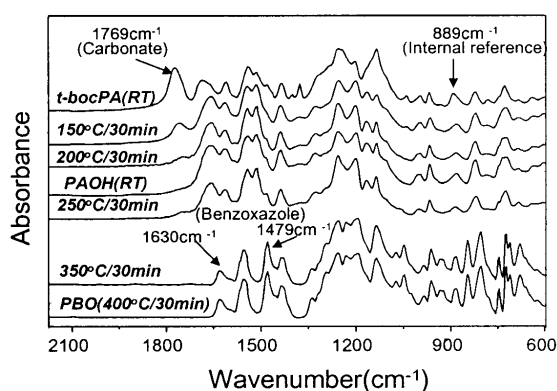


Figure 4. IR spectra of t-bocPA-II with heat treatment

As can be seen from the TGA thermogram of t-bocPA-II (Figure 3), most of the t-boc group was decomposed with 29.2% of weight loss in the range of 100~236 °C, which is relevant to the theoretical value of decomposable t-boc content (28.7%). And subsequent 5.8% of weight loss took place until the temperature reached 343 °C along with thermal

formation of PBO, which is corresponding to dehydration by cyclization reaction between amide and ortho OH group. The decomposition of PBO did not occur until the temperature reached to the 520 °C, which implied that the thermal stability of the PBO derived from t-bocPA-II is as high as that temperature.

We have monitored the thermal PBO formation by examination of FT-IR spectra as shown in Figure 4, which were recorded with temperature and time variation. The IR spectra of the PAOH and PBO were presented for the comparison. The t-bocPA-II had strong carbonyl absorption at 1769 cm^{-1} and PBO had the characteristic benzoxazole absorption at 1630 cm^{-1} and 1479 cm^{-1} . The IR spectra in Figure 4 clearly showed that the decomposition of t-boc group in the polymers took place around 150~200 °C. At 200 °C, 30 minutes of reaction is enough to decompose most of the t-boc group in the t-bocPA, as can be deduced from the resemblance of the IR spectra of PAOH. The PAOH and t-bocPA converted, eventually, to PBO when they were heated to 350 °C for 30 minutes.

To elucidate the detailed thermal conversion rate, careful examination of the IR spectra for the heat-treated sample was performed. The t-boc contents and the PBO formation were determined by observing the intensity of 1769 cm^{-1} (carbonate: -O-COO-) and 1479 cm^{-1} (benzoxazole: -C=N-) relative to the internal reference of 889 cm^{-1} (deformation of aromatic -C-H), respectively.

As shown in Figure 5, the thermal conversion reaction to PBO from PAOH was very sensitive to the reaction temperature. 28% and 39% and 64% of benzoxazole moiety were formed in 30, 60 and 90 min at 250 °C, respectively. While, it took only 5 min and 30 min for 78% and 100% of PBO formation, respectively, at 400 °C.

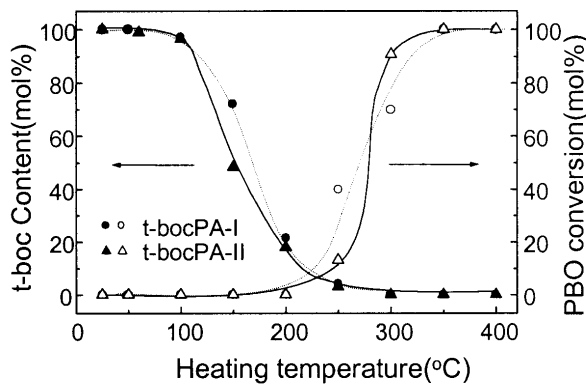
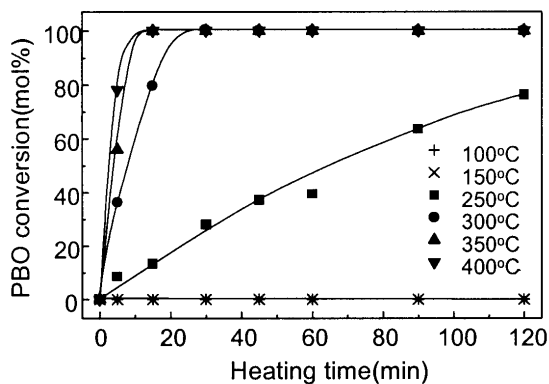


Figure 5. PBO conversion from PAOH-II. Figure 6. Change of t-boc and PBO content of the heat treated t-bocPA for 30 min.

The rate of t-boc-oxy decomposition and PBO formation are shown in Figure 6. The t-boc content of the polymer (t-bocPA-I) decreased abruptly in the range of 150~200 °C and eventually less than 5% of t-boc group remained at 250 °C. Meanwhile, the PBO content increased starting from 200 °C and 100% conversion to PBO was accomplished at 350 °C. The same trend of thermal reaction behavior was also observed in the case of 6F containing t-bocPA-II. However in this case, the PBO formation proceeded faster than that from t-bocPA-I, which is probably due to the flexibility of backbone chain of t-bocPA-II.

To utilize the acid sensitive t-bocPA as a PHR polymer, PAG must be introduced to the polymer mixture. An acid might be generated when the PAG is heated to the decomposition temperature in the dark and the temperature range is usually not as high as that of the PBO formation, 350 °C. Thus the acid exists during the thermal PBO formation. Therefore, the elucidation of acid effect on the thermal reaction is the most important

subject for the acid sensitive PBO precursor when it is mixed with PAG. Relatively to the polymers 5.0 mol % of acids, benzoic acid or p-toluenesulfonic acid were added to the THF solution of the polymers and then dried at room temperature under reduced pressure for 24hr. The effect of acid in the polymer solid mixture on thermal PBO formation could be seen from Table 3 and the DSC thermogram (Figure 7) of typical example with t-bocPA-II. Without any acid in the mixture, the PBO formation was initiated at 234 °C and terminated at 339 °C with maximum rate of reaction at 304 °C. With weak acid, benzoic acid, maximum rate of reaction temperature (T_{max}) and final reaction temperature (T_{final}) were not changed significantly as shown in the Table 3. On the contrary, the PBO formation was strongly affected by the presence of strong acid, p-TSA. The final temperatures of PBO formation (T_{final}) were lowered 45, 61, and 73 °C, respectively for t-bocPA-I, t-bocPA-II and t-bocPA-III with p-TSA. It is very interesting that the T_{final} of the PBO formations were lowered 40, 52 and 56 °C, respectively for t-bocPA-I, t-bocPA-II and t-bocPA-III, when the NBAS, the organic PAG, was added to the precursor polymer as shown in Figure 7 and Table 3.

Table 3. The results of the thermal PBO conversion of t-bocPA in the presence of acids

	t-boc PA-I				t-boc PA-II				t-boc PA-III			
	None ¹⁾	BA ²⁾	p-TSA ³⁾	NBAS ⁴⁾	None	BA	p-TSA	NBAS	None	BA	p-TSA	NBAS
T_{init} (°C)	228	212	167	168	234	217	155	161	235	213	157	172
T_{max} (°C)	304	293	240	213	304	295	245	245	302	295	233	245
T_{final} (°C)	338	331	293	298	339	337	278	287	346	340	273	290

* 5.0mol % of acid respect to polymer was added.

1) None: without any acid in the mixture, 2) BA: benzoic acid, 3) p-TSA: p-toluenesulfonic acid, 4) NBAS: p-nitrobenzyl-9,10-dimethoxyanthracene-2-sulfonate

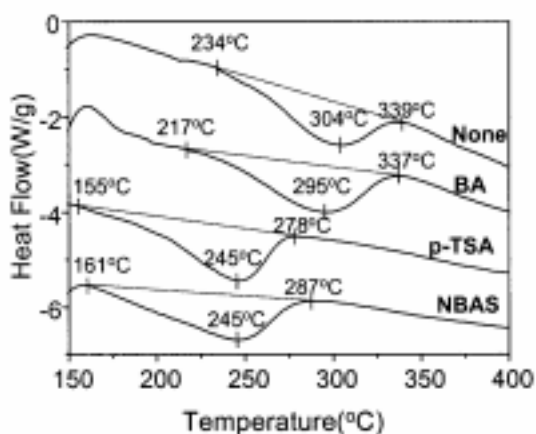


Figure 7. DSC thermogram of t-bocPA-II with various acids

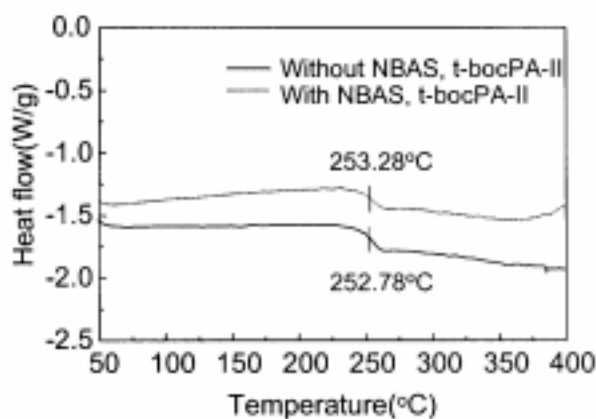


Figure 8. Tgs of Cured PBOs

This decrease of the T_{final} by addition of NBAS implied that the acid (H^+) was generated by thermal decomposition of the PAG (20) and accelerated the thermal formation of PBO. The results of DSC study with PAG suggested that the added PAG could act not only as a photo-acid generator on UV exposure, but also as a catalyst to decrease the PBO formation temperature. The lowering of the reaction temperature for PBO formation is favorable for application of the t-bocPA as a PHR polymer to semiconductor industry, since processing temperature for curing can be reduced as much as 40~56 °C. The addition of NBAS did not significantly affected on the glass transition temperature (T_g)

of the cured PBOs as shown in Figure 8, in which the polymer samples were heated 350 °C for 30 minutes in advance of DSC study.

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20. To insure the acid generation of PAG by thermal decomposition, the solution of NBAS in γ -butyrolactone was heated to 160 °C for 30 min. The corresponding acid, anthracene sulfonic acid (ASA), was isolated and confirmed by NMR, and the yield of ASA were *ca.* 24%. DSC and TGA thermograms of crystalline NBAS showed that it had melting point at 152 °C and decomposed above 192°C.