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High thermal stable thermoplastic–thermosetting polyimide film by use of asymmetric dianhydride (a-BPDA)☆

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Abstract

In order to obtain thermoplastic (before curing) and thermosetting (after curing) polyimides with high T_g for adhesive film, we prepared novel polyimides having phenylethynyl group in the side chain (44% of concentration of curing group) from asymmetric 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA), 3,4′-oxydianiline (3,4′-ODA) or 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) or 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB), and 2,4-diamino-1-(4-phenylethynylphenoxy)benzene (*m*PDAp). Among three kinds of polymer, uncured polyimide of a-BPDA/1,3,4-APB; *m*PDAp had rather high T_g (265 °C, DMA) and thermoplasticity (E' drop$>10^3$ at T_g). After curing reaction of phenylethynyl group, the T_g of the polyimide was increased dramatically (364 °C, DMA). The polyimide derived from 1,3,4-APB having less concentration of curing group (20%) was also prepared to improve further film flexibility and toughness.

Keywords: Asymmetric 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA); Thermoplastics–thermosetting polyimide; Pendent phenylethynyl group

1. Introduction

Aromatic polyimides have been widely investigated for aerospace applications and microelectronics etc. due to their outstanding combinations of mechanical and thermal properties [1–4]. These rigid and symmetric polyimides prefer to form ordered structure because of intermolecular interaction even after glass transition temperature (T_g), resulting in poor solubility and melt fluidity. Therefore, it is normally difficult to consolidate directly in the fully imidized form [5].

It has been reported that the polyimide prepared from asymmetric dianhydride such as asymmetric 2,3,3′,4′-biphenyltetracarboxylic dianhydride (a-BPDA), 2,3,2′,3′-biphenyltetra carboxylic dianhydride (i-BPDA), and 2,3,3′,4′-oxydiphthalic dianhydride represent disordered and amorphous, indicating high T_g and good melt fluidity, being ascribable to its rigid and bent structure [6–8]. The polyimide from a-BPDA and 4,4′-oxydianiline (4,4′-ODA) exhibits T_g at 319 °C and steep drop in storage modulus ($E'>10^3$); meanwhile, the polyimide derived from symmetric 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) and 4,4′-ODA shows lower T_g at 262 °C and smaller E' drop ($E'=10^2$) owing to ordered structure [9,10]. Moreover, phenylethynyl-terminated addition-type imide oligomer (Asymmetric, Aromatic, and Amorphous type imide oligomer; TriA-PI), which is derived from a-BPDA, 4,4′-oxydianiline (4,4′-ODA), and 3-phenylethynylphthalic anhydride (PEPA) demonstrated unusual low melt viscosity (good processability), excellent thermo oxidative stability, and toughness after curing, which improve the difficulty of the consolidation [11,12]. We have been conducting a New Energy and Industrial Technology Development Organization (NEDO) project to develop and evaluate heat-resistant and fiber-reinforced composite for aerospace applications by use of TriA-PI since 2002. The project is also involved in the development of high temperature film type adhesive, required for honeycomb sandwiches and structural components, etc. [13]. Requirements of the uncured polyimide

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for film-type adhesive should be flexible and sustainable in addition to low melt fluidity (high plasticity, E' drop $>10^3$ over T_g), because the film should be molten state sufficiently over T_g. It is also required for the uncured oligomer to be converted and rigidified with much higher T_g (>300 °C), together with toughness. Uncured TriA ($n=4$) shows yellow powder: this is not suitable for this study, although the cured TriA indicates film-like form with toughness probably due to chain extension [14,15]. Film could be formed with increasing the number of molecular weight of TriA; however, cured T_g decreases due to decreasing in the number of endcapped curing unit (increasing repeating unit) in addition to losing thermoplasticity. Introduction of phenylethynyl group as a pendant into the polymer chain should be a good way to prevent the decrease in T_g.

To our knowledge, there are some examples dealing with thermoplastic–thermosetting polyimide; the polyimide from symmetric dianhydride (e.g. s-BPDA), diamine having long distance between amine groups, and reactive endcap (PEPA) represented thermoplasticity in addition to low T_g [16,17]. McGrath et al. reported thermosetting polyimide derived from pyromellitic dianhydride (PMDA) and flexible diamine monomer containing phenylethynyl group as the reactive end cap. The cured T_g (255–264 °C) was slightly low because of flexibility of the main chain owing to keeping thermoplasticity of the polymer during cure reaction [18]. In general, rigid symmetric polyimide such as s-BPDA/*p*-PDA (*p*-PDA = *p*-phenylenediamine) and s-BPDA/4,4′-ODA preferentially produce ordered structure. Flexible diamine monomers have to be introduced into polymer chain in order to exhibit thermoplasticity, e.g. PETI-5 (s-BPDA/1,3,3-APB; 3,4′-ODA/PEPA, uncured $T_g=210$ °C, cured $T_g=270$ °C); however, cured T_g does not increase sufficiently (over 300 °C) [19,20]. We should emphasize again that the polyimide using a-BPDA is expected to have much higher T_g without sacrificing thermoplasticity during cure reaction. This is because the polyimide prepared from a-BPDA is unlikely to form ordered structure due to bent and rotationally hindered structure of a-BPDA, although the polyimide from a-BPDA and 4,4′-ODA indicate high T_g, amorphous, and less plasticity [9–11]. As regards diamine monomers, we employed 3,4′-ODA as diamine monomer: the polyimide from 3,4′-ODA is expected to show rather high T_g and thermoplasticity due to the high flexibility. In this connection, Hergenrother et al. presented the polyimide derived from a-BPDA and 1,3,4-APB or 1,3,3-APB brought rather high T_gs at 248 °C (a-BPDA/1,3,4-APB), 207 °C (a-BPDA/1,3,3-APB) and the thermoplasticity, indicating that the polyimides are unlikely to form locally ordered structure in the molecules [21]. Therefore, we selected a-BPDA as a dianhydride monomer and 3,4′-ODA, 1,3,4-APB, and 1,3,3-APB as diamine monomers. For curing group, 2,4-diamino-1-(4-phenylethynylphenoxy)benzene (*m*PDAp) was introduced as the reactive pendant in the polyimide. The T_gs of the polyimides after curing are expected to increase drastically owing to crosslink reaction and to be almost consistent with or above the T_g of TriA (343 °C) (Scheme 1).

This paper discuss the chemical structure and property relationship of thermoplastic and thermosetting polyimides with high T_g (after curing), introducing phenylethynyl group as the reactive pendant in the polyimide chain.

2. Experimental section

2.1. Starting materials

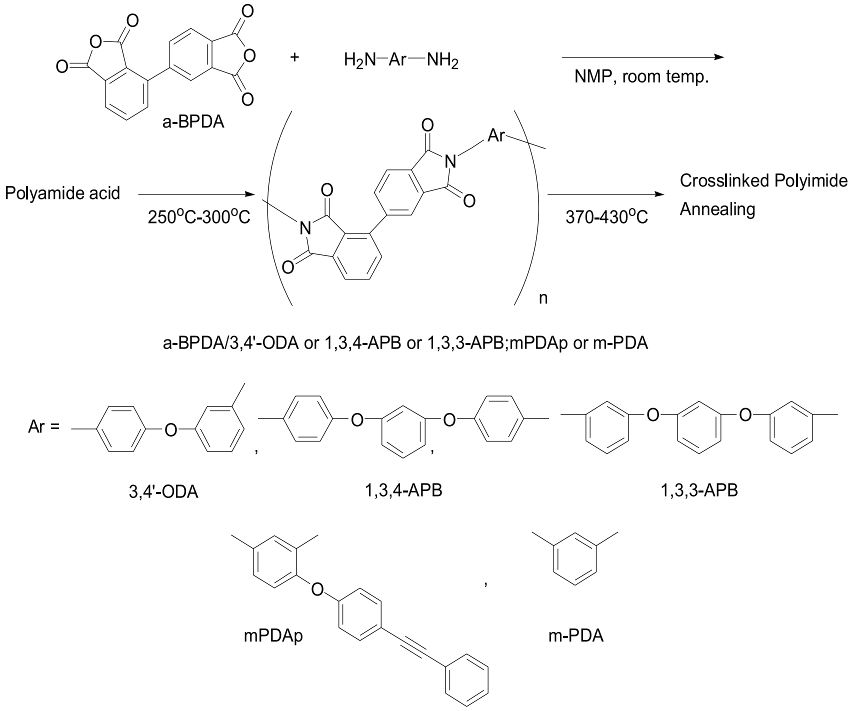
a-BPDA was kindly supplied by UBE Industries, Ltd. and used after heating at 160 °C for 18 h in vacuo for ring closure. 3,4′-ODA was kindly supplied by Wakayama Seika Kogyo, Ltd. and recrystallized from toluene before use. 1,3,4-APB, 1,3,3-APB, and *m*PDAp were kindly supplied by Wakayama Seika Kogyo, Ltd., Mitsui Chemicals, Inc., and Wakayama Seika Kogyo, Ltd., respectively and used as received. *N*-Methyl-2-pyrrolidinone (NMP) was obtained from Tokyo Kasei Kogyo Co., Ltd. and used as received.

2.2. Measurements

Inherent viscosities (η_{inh}) were measured on 0.5 g/dl (w/v) polyamide acid (PAA) in NMP at 30 °C, and the molecular weight was calculated by Mark–Houwink equation [22]. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC-2010 Differential scanning calorimetry at a heating rate of 20 °C/min in a nitrogen atmosphere. Dynamic mechanical analyzer (DMA) was carried out on a RHEOMETRICS SOLIDS ANALYZER RSA II instrument by use of a thin film (23.7 mm length, 5 mm width, and 0.04–0.06 mm thickness) at a heating rate of 5 °C/min and a load frequency of 1 Hz in air. Tensile test was conducted at room temperature using thin film (20 mm length, 3 mm width, and 0.05 mm thickness, rectangular film) on an ORIENTEC CORPORATION TENSILON/UTM-II-20 universal testing instrument composed with AR-6000 recorder. Thermogravimetric analysis (TGA) was performed on a TA instruments SDT 2960 under nitrogen flow at a heating rate of 20–300 °C/min, and then the temperature was hold for 10 min. And the data was collected at a heating rate of 5 °C/min from 50 to 800 °C.

2.3. Synthesis of polyimide

*m*PDAp (0.91 g, 3.02 mmol) and NMP (11 ml, 25 wt%) were placed into a 100 ml of flask equipped with a magnetic stirrer. After dissolution of *m*PDAp, a-BPDA (2.01 g, 6.82 mmol) was added into the flask. The reaction mixture was stirred at room temperature for 1 h, and 3,4′-ODA (0.76 g, 3.78 mmol) was added and the mixture was stirred at ambient temperature for 3 h. The resulting polyamide acid solution was stored in the refrigerator. The



Ar	Phenylethynyl concentration
3,4'-ODA;mPDAp	44%
1,3,4-APB;mPDAp	44%
1,3,3-APB;mPDAp	44%
1,3,4-APB;mPDAp	20%
3,4'-ODA;m-PDA	
1,3,4-APB;m-PDA	
1,3,3-APB;m-PDA	

Scheme 1. Polymerization of thermoplastic–thermosetting polyimides of a-BPDA/3,4′-ODA or 1,3,4,-APB or 1,3,3,-APB; *m*PDAp or *m*-PDA.

polyamide acid (PAA) was doctored on a glass plate and heated on the hot stage at 60 °C for 4 h, and then dried at 60 °C for 12 h in vacuo. The PAA film attached with glass plate was heated at 150 °C for 0.5 h, 200 °C for 0.5 h, 250 °C for 1 h, 300 °C for 10 min for imidization in vacuo. The polyimide film obtained was removed from the glass plate by soaking in water and washed with ethanol, and then dried.

IR (thin film on silicon wafer, cm^{-1}) 1780, 1720 (carbonyl of imide).

2.4. Preparation of cured film

The freestanding uncured polyimide film obtained was heated at 370 °C for 1 h under nitrogen atmosphere. Further heating was necessary depending on the DSC results. To accomplish the curing reaction, it is necessary to heat at 430 °C for 10 min (a-BPDA/3,4′-ODA; *m*PDAp (phenylethynyl concentration = 44%)), 430 °C for 10 min (a-BPDA/1,3,4-APB; *m*PDAp (phenylethynyl concentration = 44%)), 400 °C for 10 min (a-BPDA/1,3,3-APB; *m*PDAp (phenylethynyl concentration = 44%)), and 400 °C for 10 min (a-BPDA/1,3,4-APB; *m*PDAp (phenylethynyl concentration = 20%)).

3. Results and discussion

3.1. Polyimide

As described in Section 1, the polyimide from a-BPDA and 4,4′-ODA has high T_g (319 °C) and less thermoplasticity. In this study, we chose 3,4′-ODA, 1,3,4-APB, and 1,3,3-APB as diamine monomers, having ether linkages at *meta* and *para* positions; the polyimides prepared from these diamines should be thermoplastic possessing rather high T_g.

We synthesized polyimides with the conventional two-step method with the monomer ratios of a-BPDA/3,4′-ODA or 1,3,4-APB or 1,3,3-APB/*m*PDAp = 9/5/4 (phenylethynyl concentration = 44%, mole concentration of *m*PDAp in diamine monomers), which is consistent with the concentration of phenylethynyl group of TriA imide oligomer [11]. In order to compare rheological, thermal, and mechanical properties with and without phenylethynyl group, polyimides derived from *m*-phenylene diamine (*m*-PDA) were also prepared (Table 1, run no 5–7).

The imide reaction was monitored by IR spectroscopy by the appearance of the carbonyl absorption (imide) at 1780 and 1720 cm^{-1}, and thermogravimetric analysis (TGA) by the disappearance of the water produced during imidization. The polyimide films with and without phenylethynyl group were flexible and transparent (Table 2, run 1–3, 5–7). Uncured T_gs of all polyimide film without phenylethynyl group were found to be higher than those with phenylethynyl group, ascribable to the looseness of the molecular packing of the polyimides with pendent phenylethynyl group (Table 2). This phenomenon was observed in other polyimides; the polyimide derived from oxydiphthalic anhydride (ODPA) and 1,4,4-APB or 3-phenyl-1,4-bis(4-aminophenoxy)benzene (PTPEQ) indicate T_gs at 236 °C (ODPA/TPEQ), 212 °C (ODPA/PTPEQ), respectively [19]. T_gs and film properties of the polyimides without pendent phenylethynyl group (runs 5–7, Table 2) might be changed after post heating (370, 400, 430 °C) under equivalent conditions as those of runs 1–3 in Table 2 [21].

The uncured polyimide prepared from 3,4′-ODA has higher T_g (285 °C) than the polyimide derived from 1,3,4-APB (270 °C) due to polymer chain rigidity (less ether linkage unit). The polyimide from 1,3,4-APB possessed higher T_g (270 °C) than that from 1,3,3-APB (223 °C) owing to higher rigidity of the polymer prepared from 1,3,4-APB (ether linkage at *para* position).

3.2. Cure reaction

Regarding to the cure reaction, the decrease in the absorbance of triple bond was not clearly observed by not only IR but also Raman measurement. We conducted to monitor the disappearance of exothermic peak of phenylethynyl group by means of DSC (Figs. 1–3). To prepare the cured films, the polyimide films were heated at 370 °C for 1 h by use of vacuum oven, which is consistent with the curing condition of TriA [11], and further heated depending on the DSC thermogram.

The polyimides derived from 3,4′-ODA and 1,3,4-APB required 430 °C for 10 min for accomplishment of curing reaction, indicating that the exothermic peak of the cured polyimide almost disappeared (Figs. 1 and 2). On the other hand, the curing reaction of the polyimide derived from 1,3,3-APB was accomplished by heating at 400 °C for 10 min (Fig. 3). These findings were speculated from the profiles of DMA (Figs. 5–7) as follows. After steep drop of E' at T_g of the uncured polyimide derived from 3,4′-ODA and 1,3,4-APB, storage moduli (E') in rubbery plateau region increased with increasing temperature (triangle in Figs. 5 and 6), that is, cure reaction gradually progressed. On the other hand, the width of rubbery plateau region of uncured polyimide prepared from 1,3,3-APB (triangle in Fig. 7) widen compared with those from 3,4′-ODA and 1,3,4-APB, and E' did not increase at around 400 °C; the cure reaction could be accomplished under milder condition (400 °C).

3.3. Dynamic tensile property

In the DMA profiles of uncured polyimide films (triangle in Figs. 5–7), there were observed T_gs in the range of 223–279 °C and steep drops in storage modulus (E') more than three orders at T_g, suggesting that the films have excellent thermoplasticity. DMA profiles of cured polyimide films (square in Figs. 5 and 6) derived from 3,4′-ODA and 1,3,4-APB showed high T_g (over 360 °C). T_g of cured polyimide derived from 1,3,3-APB (Fig. 7) indicated slightly lower probably due to flexibility of 1,3,3-APB structure in the polymer.

These cured films including the polyimide from 1,3,3-APB were slightly brittle (Table 2, run 1–3), although the polyimides are evaluated and synthesized by the identical

Table 1
Polyamide acids (PAA) of a-BPDA/3,4′-ODA or 1,3,4-APB or 1,3,3-APB; *m*PDAp or *m*-PDA

Run	Ar	Concentration of phenylethynyl group (%)	Concentration for polymerization (wt%)	η_{inh} (dl/g)	M_w[a]	PAA film
1	3,4′-ODA/*m*PDAp	44	25	0.38	13900	Brittle
2	1,3,4-APB/*m*PDAp	44	25	0.61	25100	Brittle
3	1,3,3-APB/*m*PDAp	44	25	0.45	16900	Brittle
4	1,3,4-APB/*m*PDAp	20	25	0.93	42300	Tough
5	3,4′-ODA/*m*-PDA		20	0.84	37200	Tough
6	1,3,4-APB/*m*-PDA		20	1.07	50400	Tough
7	1,3,3-APB/*m*-PDA		20	0.69	29100	Tough

[a] The molecular weight was calculated by use of the inherent viscosity.

Table 2
Thermal properties of uncured and cured polyimides

Run	Ar;Ar′	Concentration of phenylethynyl group (%)	T_g (°C)			Td$_5$[a] (%)	Form of film	
			DSC Uncured	DMA Uncured	DMA Cured		Uncured	Cured
1	3,4′-ODA/*m*-PDA-P	44	285[b]	279[b]	379[c]	555	Tough	Brittle
2	1,3,4-APB/*m*-PDA-P	44	270[b]	265[b]	364[c]	555	Tough	Brittle
3	1,3,3-APB/*m*-PDA-P	44	223[d]	223[d]	290[e]	540	Tough	Brittle
4	1,3,4-APB/*m*-PDA-P	20	267[b]	260[b]	285[e]	547	Tough	Tough
5	3,4′-ODA/*m*-PDA		313[f]	302[f]	–	547	Tough	–
6	1,3,4-APB/*m*-PDA		289[f]	281[f]	–	547	Tough	–
7	1,3,3-APB/*m*-PDA		250[f]	243[f]	–	533	Tough	–

[a] Td$_5$ indicates 5% weight loss temperature detected by TGA.
Heating conditions for imidization and curing are as follows.
[b] 300 °C for 10 min.
[c] 370 °C for 1 h and 430 °C for 10 min.
[d] 250 °C for 1 h.
[e] 370 °C for 1 h and 400 °C for 10 min.
[f] 300 °C for 1 h.

phenylethynyl concentration as TriA. On the other hand, the cured TriA produced flexible and tough film [11]. This brittleness of the cured films can be speculated as follows: flexible film from TriA, having phenylethynyl group at the molecular ends, was obtained after curing owing to mainly chain extension because phenylethynyl endcaps can be reacted easily without restriction of mobility of the main chain, while pendent phenylethynyl group in the polyimide chain after curing might form branching, cross linking, and cyclic structure in addition to the chain extension, showing brittle film with no flexibility [14,15].

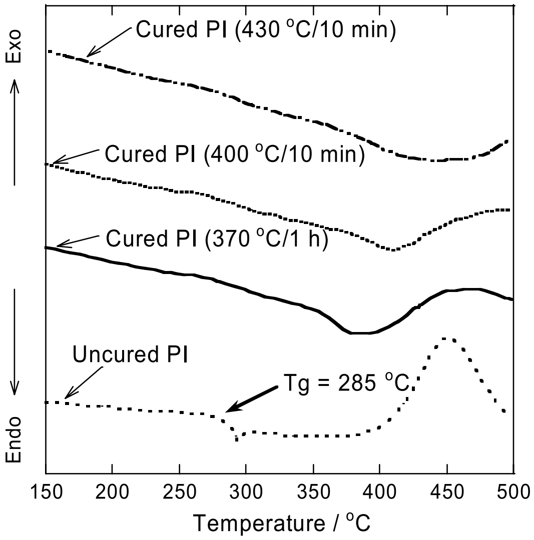


Fig. 1. DSC profiles of uncured and cured polyimide prepared from a-BPDA, 3,4′-ODA, and *m*PDAp (phenylethynyl concentration = 44%). Heating temperature and time were shown in parentheses to prepare cured film.

3.4. Improvement of flexibility

The polyimides mentioned above are containing 44% phenylethynyl concentration, which is consistent with the phenylethynyl concentration of TriA imide oligomer and calculated as two phenylethynyl group in one oligomer ($n = 4$) molecule. As the next attempt, we prepared the polyimide with the 20% of phenylethynyl concentration, which is half concentration of phenylethynyl group of TriA imide oligomer.

The polyimides from 1,3,4-APB exhibited unexpectedly brittle; however, excellent thermal (uncured $T_g = 265$ °C, cured $T_g = 364$ °C) and rheogical properties (drop of E' at

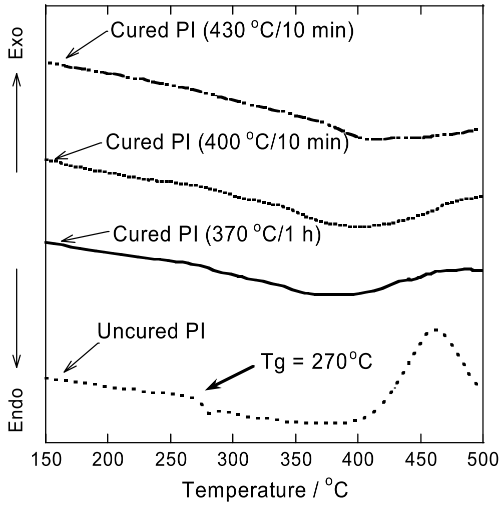


Fig. 2. DSC profiles of uncured and cured polyimide prepared from a-BPDA, 1,3,4-APB, and *m*PDAp (phenylethynyl concentration = 44%). Heating temperature and time were shown in parentheses to prepare cured film.

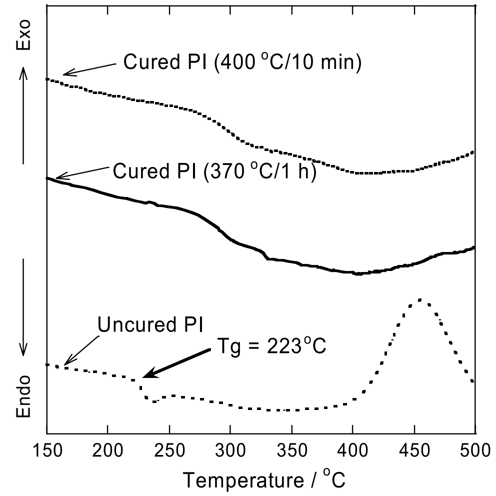


Fig. 3. DSC profiles of uncured and cured polyimide prepared from a-BPDA, 1,3,3-APB, and *m*PDAp (phenylethynyl concentration = 44%). Heating temperature and time were shown in parentheses to prepare cured film.

$T_g > 10^3$). In order to improve the toughness of the cured film without sacrificing high cured T_g, we synthesized polyimide derived from 1,3,4-APB, possessing 20 mol% phenylethynyl group with the monomer ratios of a-BPDA/1,3,4-APB/*m*PDAp = 5/4/1. Toughness of the cured film should be improved due to lower degree of crosslinking than that of the polyimide having phenylethynyl concentration of 44%. The polyimides derived from 1,3,4-APB having 44 and 20 mol% phenylethynyl group are referred to as P-*m*PDAp-44 and P-*m*PDAp-20, respectively. DSC measurement (Fig. 4) indicated heating at 400 °C was required for accomplishment of curing reaction, which is lower postcure temperature than P-*m*PDAp-44 (430 °C). This is probably because the uncured polyimide having less crosslinking units cure easily at lower postcure temperature owing to higher molecular mobility (lower crosslinking density). It is confirmed from DMA that the rubbery plateau of uncured P-*m*PDAp-20 (triangle in Fig. 8) extend to higher temperature. On the other hand, the width of rubbery plateau of uncured P-*m*PDAp-44 (triangle in Fig. 6) was narrow with increasing E' over 300 °C; crosslinked structure was

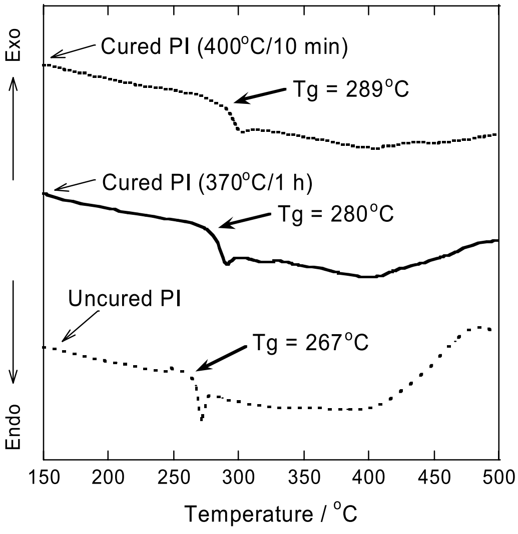


Fig. 4. DSC profiles of uncured and cured polyimide prepared from a-BPDA, 1,3,4-APB, and *m*PDAp (phenylethynyl concentration = 20%). Heating temperature and time were shown in parentheses to prepare cured film.

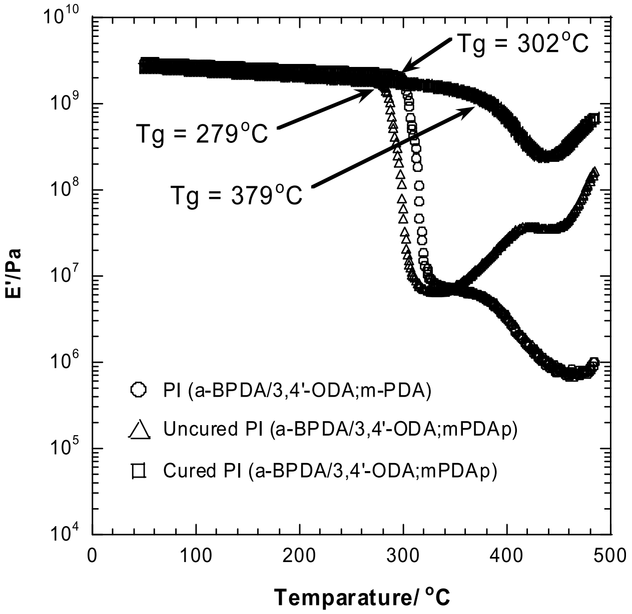


Fig. 5. DMA profiles of uncured and cured polyimide of a-BPDA/3,4′-ODA; *m*PDAp (phenylethynyl concentration = 44%) and a-BPDA/3,4′-ODA; *m*-PDA.

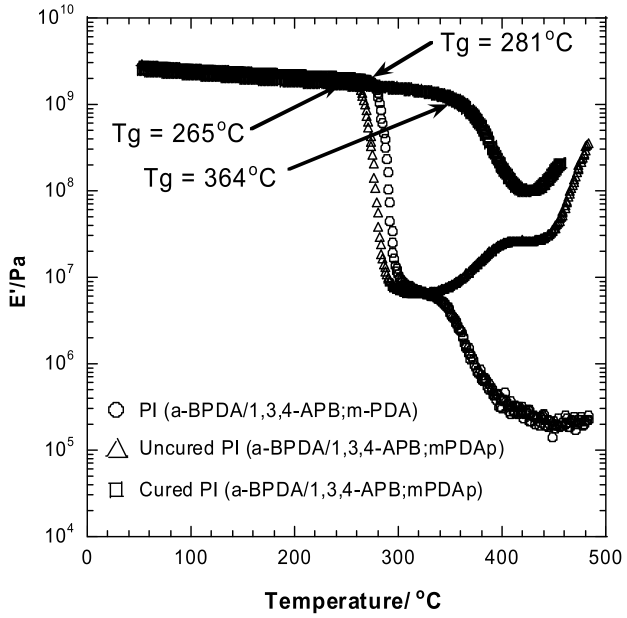


Fig. 6. DMA profiles of uncured and cured polyimide prepared from a-BPDA/1,3,4-APB; *m*PDAp (phenylethynyl concentration = 44%) and a-BPDA/1,3,4-APB; *m*-PDA.

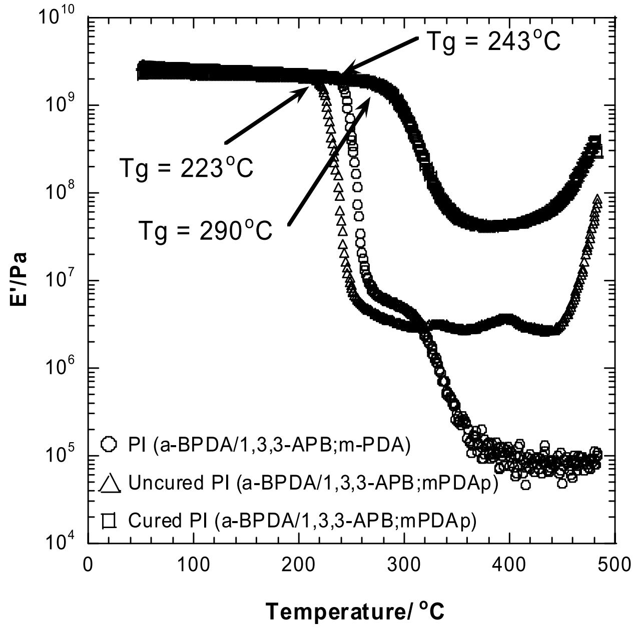


Fig. 7. DMA profiles of uncured and cured polyimide prepared from a-BPDA/1,3,3-APB; *m*PDAp (phenylethynyl concentration = 44%) and a-BPDA/1,3,3-APB; *m*-PDA.

partially formed and higher postcure temperature was necessary to accomplish the cure reaction.

As we expected, not only uncured film but also cured one showed toughness (Table 2, run 4), indicating that the elongation at break of the cured film was remarkably improved to 11.3% (Table 3, run 2). Moreover, the uncured film showed almost the same thermoplasticity as P-*m*PDAp-44; the drop of storage modulus (E') over T_g of P-*m*PDAp-20 is almost consistent with the one of P-*m*PDAp-44 (E' drop over $T_g = 10^3$, Figs. 6 and 8). However, cured T_g of P-*m*PDAp-20 exhibited 285 °C (Table 2, run 4) compared with the T_g at 364 °C of P-*m*PDAp-44 (Table 2, run 2).

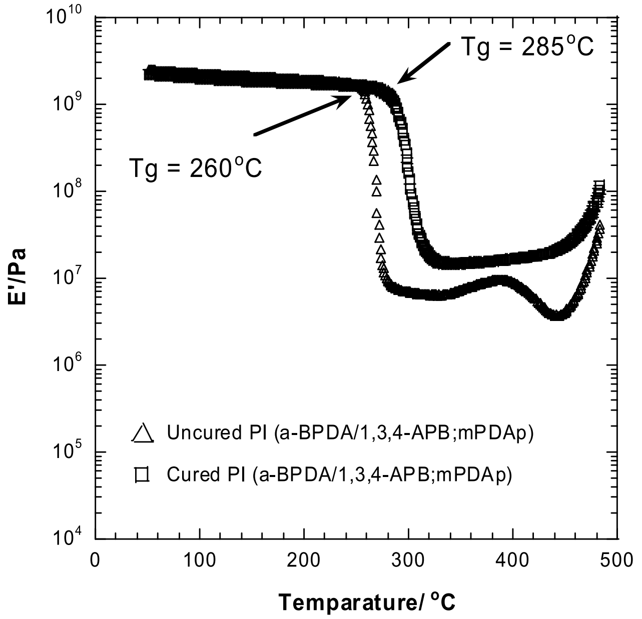


Fig. 8. DMA profiles of uncured and cured polyimide prepared from a-BPDA/1,3,4-APB; *m*PDAp (phenylethynyl concentration = 20%).

5% weight loss temperature of all polyimides showed more than 500 °C, indicating that the polyimides have high thermal stability (Table 2). TGA of the cured polyimides in Fig. 9 represented that almost no component volatilize until at around 500 °C.

In the DSC profiles in Figs. 1–4, it is observed that the thermograms of completely cured films represent exothermic shift in the range of over 450 °C, suggesting that the complex reaction occurred in the film. The storage moduli (E') of uncured (triangle) and cured (square) polyimides in Figs. 5–8 also increase at over 440 °C. These are ascribed that the thermal degradable crosslinking reaction proceeds at over 440 °C.

Changing the composition ratio of *m*PDAp and 3,4′-ODA, 1,3,4-APB, and 1,3,3-APB in the polyimide, that is, optimization of phenylethynyl concentration might be necessary to improve the toughness of cured film without sacrificing high T_g, which is in connection with the polyimide having wide process window.

4. Conclusion

In order to obtain thermoplastic (before curing) and thermosetting (after curing) polyimide films with high heat resistance, we prepared three kinds of polyimide having phenylethynyl group as the pendant in the polymer: a-BPDA/3,4′-ODA; *m*PDAp, a-BPDA/1,3,4-APB; *m*PDAp, and a-BPDA/1,3,3-APB; *m*PDAp (44% of concentration of curing group). All uncured films had

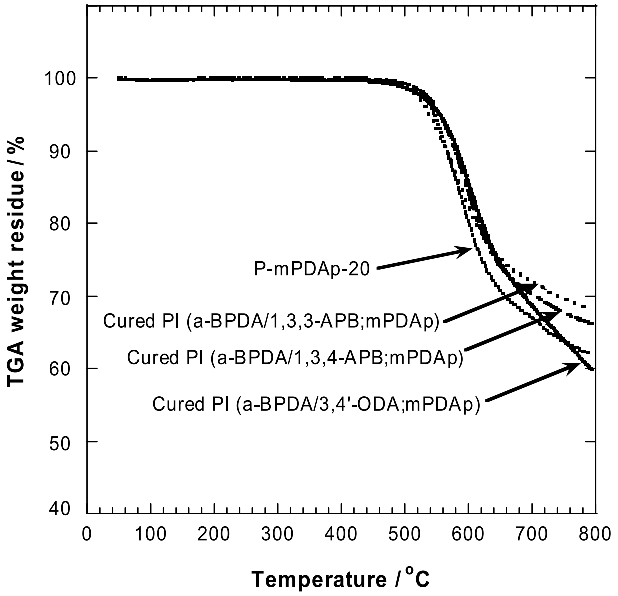


Fig. 9. TGA profiles of cured polyimides under nitrogen flow (heating rate = 5 °C/min).

Table 3
Tensile properties of cured a-BPDA/1,3,4-APB; *m*PDAp polyimide

Run	Concentration of phenylethynyl group (%)	Modulus (GPa)	Strength (MPa)	Elongation at break	
				Average (%)	Maximum (%)
1	44	3.3	38.3	1.2	2.2
2	20	2.8	109.3	11.3	14.0

appropriate T_gs (223–279 °C, DMA) and thermoplasticity (E' drop over $T_g = 10^3$, DMA). T_gs of cured films were found to increase dramatically to 290–379 °C (DMA) although the cured films were slightly brittle. The polyimide derived from 1,3,4-APB having less concentration of curing group (20%) was also prepared to improve further film flexibility and toughness, indicating that the elongation at break of the cured film was improved to 11.3%. Our first purpose has been achieved; the polyimide films showed thermoplasticity before curing and thermosetting with high T_g after curing. These properties indicated that the film derived from asymmetric dianhydride had promising potential for thermoplastic and thermosetting adhesive film.

Changing the composition ratio of monomers having pendent phenylethynyl group or introducing other monomers into the polyimide is necessary to improve the toughness of cured film without sacrificing high T_g.

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