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Effects of Dianhydrides on the Thermal Behavior of Linear and Crosslinked Polyimides

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ABSTRACT: To determine the thermal characteristics of linear and crosslinked polyimides (PIs), BTDA, ODPA, and 6FDA were used to synthesize polyimides. Thermal degradation temperature and glass transition temperature of the resulting PIs were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). To measure the change in modulus and coefficient of thermal expansion (CTE) depending on dianhydride structure, a dynamic mechanical analyzer (DMA) and thermo-mechanical analyzer (TMA) were used. The thermal degradation and glass transition temperature properties of linear PIs varied according to whether the linear chain adopted a bulky or flexible structure. Dynamic modulus and thermal expansion values of linear polyimides also showed good agreement with the TGA and DSC results. As we expected, linear polyimide with bulky 6FDA groups showed better thermal behavior than the flexible polyimides. Crosslinked polyimide nadic end-capped (norbornene) with a bulky dianhydride group had a lower thermal degradation temperature and higher CTE than flexible BTDA and ODPA polyimides. Our results indicate that the mobility of the dianhydride group affects the thermal behaviors of linear and crosslinked polyimides in different ways. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41412.

KEYWORDS: crosslinking; differential scanning calorimetry (DSC); polyimides; thermal properties; thermogravimetric analysis (TGA)

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INTRODUCTION

Polyimides (PIs) are polymers with high thermal stability, chemical resistance, mechanical properties, and a low dielectric constant.[1] Since the development of PIs for aerospace materials by NASA in the early 1970s, they have been used in various industries[2] and have been studied extensively. Long polyimide chains of high molecular weight have been used as organic materials in the electronics industry. Three-dimensional (3D) crosslinked polyimides have been developed for use in organic–inorganic hybrid materials.[3]

These 3D polyimides are crosslinked by an aromatic imide monomer that has a norbornene (NE) ring and that spontaneously reacts and makes a 3D polymer matrix after heat treatment.[4] Therefore, polyimides with NE can form a crosslinked structure that has desirable thermal properties.

When used as a component of organic-inorganic hybrid materials, a linear polyimide solution can cause bubbles, and high pressure is required to eliminate these bubbles because they increase viscosity.[5] However, polyimide crosslinked with NE results in a short chain structure that has low viscosity before crosslinking by heat treatment. Therefore, this polymer is preferable for use in combination with inorganic materials. Crosslinked polyimide with glass fibers has replaced metals in various industries, including the aerospace and automotive industries.[6]

In this study, we used three kinds of dianhydrides to synthesize linear and crosslinked polyimides. We measured thermal degradation, glass transition, modulus, and thermal expansion of these polyimides to determine the effect of dianhydrides on the thermal behaviors of linear and crosslinked polyimides.

EXPERIMENTAL

Materials

To synthesize crosslinked polyimides with various backbones, 3,3′4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic dianhydride (ODPA), 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,4′-oxydianiline (ODA), 5-norbornene-2,3-dicarboxylic, and monomethyl ester (NE) were purchased from Tokyo Chemical Industry. *N*-Methyl-2-pyrrolidone (NMP) was purchased from Duksan Chemical Co., Korea. All reagents in this study were used without further purification.

Preparation of Poly Amicacid(PAAs) for Linear PIs

PAAs for linear PI were synthesized in three steps. First, 3 mol of ODA was dissolved in NMP. Second, 3 mol of dianhydride

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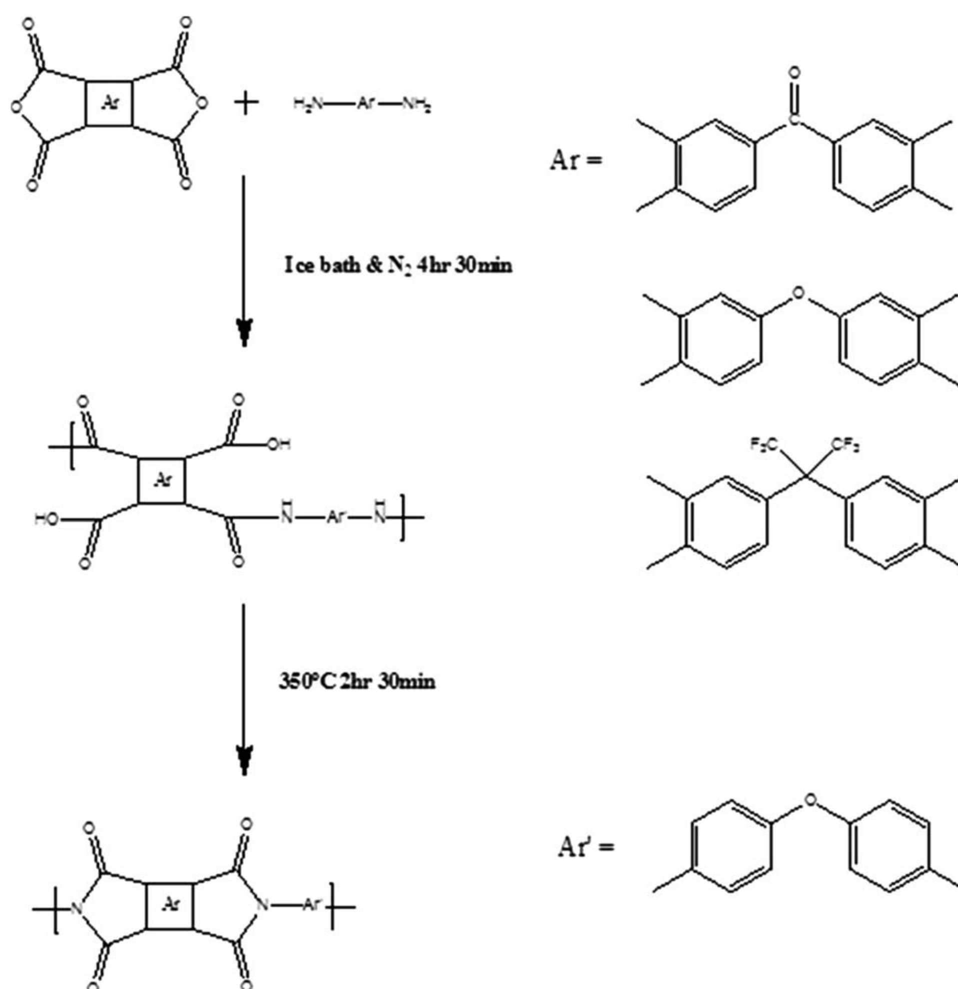

Scheme 1. Synthetic pathway for linear PI.

was added to the solution at 20°C. Third, the mixture was stirred at 0°C for 4.5 h in an ice bath, and then at 20°C for 12 h. The resulting solution contained 20 wt % PAAs in NMP.

The solution was spin-coated on a glass plate. Fully cured neat PI film was cured as follows: 100°C/1 h, 150°C/0.5 h, 200°C/0.5 h, 250°C/0.5 h, and 350°C/2.5 h, in air. The rate of temperature increase was 2°C/min. The synthetic pathway of PAA for linear PI films is described in Scheme 1.

Preparation of PAAs for NE-Crosslinked PIs

PAAs for crosslinked PI were synthesized by the following process. First, 3 mol of ODA was dissolved in NMP. Second, 2 mol of dianhydride was added to the solution at 20°C. Third, the mixture was stirred at 0°C for 4.5 h in an ice bath, and then 2 mol of NE was added to the solution and the solution was stirred at 20°C for 12 h. The resulting solution contained 20 wt % PAAs in NMP.

Then, the solution was spin-coated on a glass plate. PI films were cured as follows: 100°C/1 h, 150°C/0.5 h, 200°C/0.5 h, 250°C/0.5 h, and 350°C/2.5 h, in air. The rate of temperature increase was 2°C/min. Various molar ratios and synthetic pathways of PAA for crosslinked PI films are described in Scheme 2.

Characterization

Fourier transform infrared (FTIR) spectra of polyimides were measured with an Excalibur Series FT-IR (DIGILAB, USA) instrument.

Wide angle X-ray diffraction (WAXD) patterns were collected with a computer-controlled RINT 2000 Rigaku diffractometer using Ni-filtered Cu$K\alpha$ radiation ($\lambda = 1.5405$ Å). The X-ray diffractometer was operated at 40 kV/20 mA in continuous scan mode in the range of 2∼50° at a scanning speed of 5°/min.

Thermal degradation of the polyimides was assessed using a Q50 TGA (TA Instrument, USA) in the temperature range from 35 to 800°C at a heating rate of 20°C/min in a nitrogen atmosphere.

Glass transition temperatures (T_g) of the polyimides were investigated using a Q10 DSC (TA Instrument, USA) in a nitrogen atmosphere. Samples were heated at a rate of 10°C/min from 150 to 400°C.

Modulus behavior of the polyimides was measured using a DMA Q800 (TA Instrument Co., USA) in tension mode from 25 to 450°C at a heating rate of 10°C/min.

Scheme 2. Synthetic pathway of crosslinked PI.

Coefficient of thermal expansion (CTE) of the various polyimides was measured using a TMA-Q400 (TA Instrument, USA) from 25 to 400°C at a heating rate of 10°C/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

FTIR Spectra

FTIR measurements are widely used to identify the existence and disappearance of functional groups.[7] In this study, we used

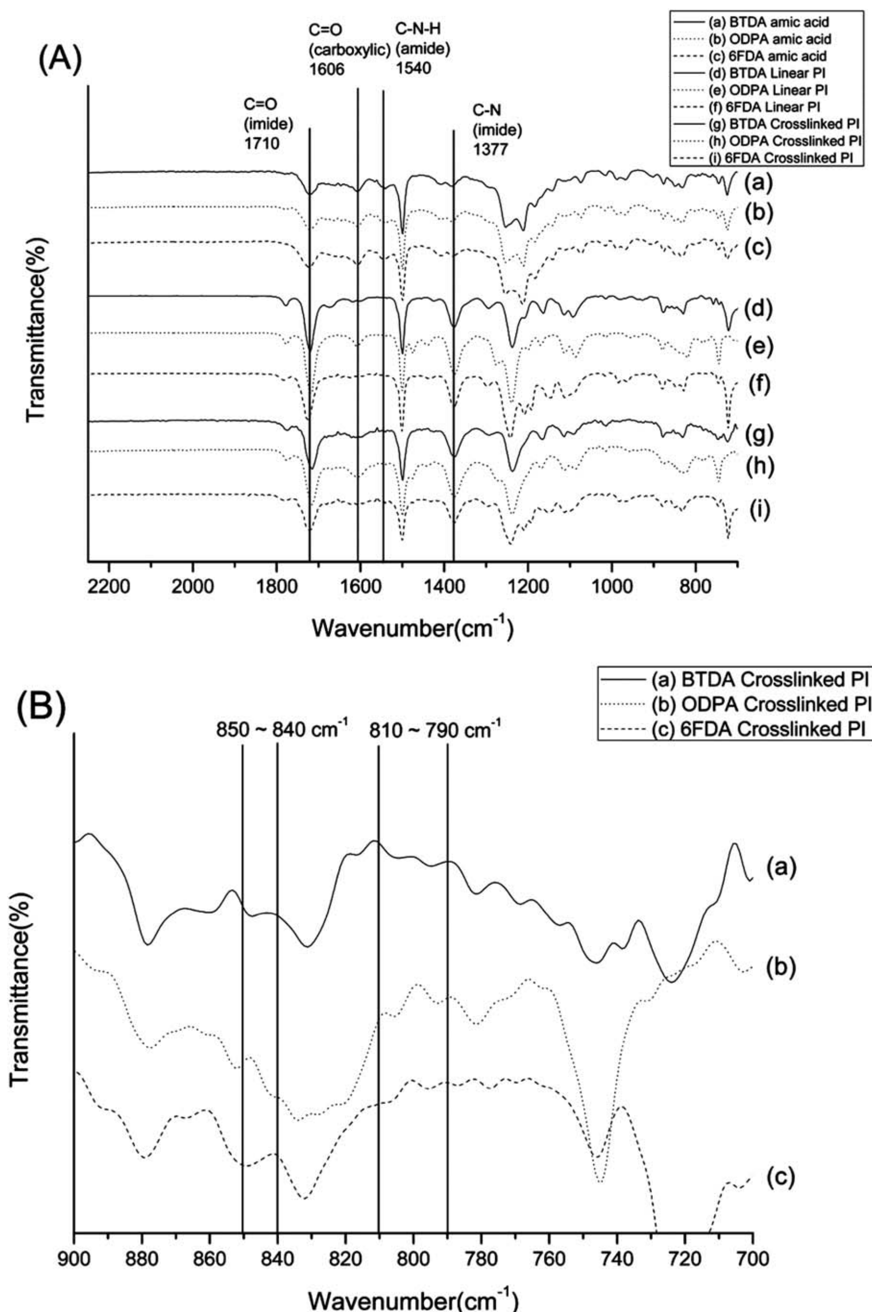

Figure 1. FTIR spectra polyimides (A) in long range, (B) in short range.

FTIR to confirm that imide rings were fully synthesized in the linear polyimides and that crosslinking occurred in the crosslinked polyimides, regardless of the type of dianhydride used. FTIR spectra are shown in Figure 1.

The FTIR spectra for 2250–700 cm^{-1} is shown in Figure 1(A). Two peaks corresponding to the amide C—N—H bond at 1540 cm^{-1} and the carboxylic C=O group at 1606 cm^{-1} were observed in the nonfully cured film.[8] After full curing, those peaks corresponding to amide and carboxylic were disappeared and absorption peaks of the imide group were present near the C=O bond at 1710 cm^{-1}, and a peak corresponding to the C—N bond was observed at 1377 cm^{-1} (Ref. [9]. These results indicated that imide rings were present in the linear and crosslinked polyimides were successfully synthesized [Figure 1(A)].

For the crosslinked polyimides, we confirmed peaks corresponding to crosslinking by examining the FTIR spectra at 900–700 cm^{-1}, as shown in Figure 1(B). After addition of NE to the end of the polyimide chain, crosslinking was initiated through heating.[10] Peaks of crosslinking corresponding to C=C bonds of the nadic ring at 843 cm^{-1} and C—H bonds at 810–790 cm^{-1} (Refs. 11 and 12) were weak and broad.[13]

These results indicated that linear and crosslinked polyimides were successfully synthesized.

Table I. Morphological Properties of Linear and Crosslinked Polyimides

Sample name	BTDA Linear PI	BTDA Crosslinked PI	ODPA Linear PI	ODPA Crosslinked PI	6FDA Linear PI	6FDA Crosslinked PI
2theta (θ)	18.16	17.64	20.22	16.12	17.56	16.18
Distance (Å)	4.88	5.02	4.38	5.49	5.05	5.47

Morphological Structure

The thermal behavior of a polymer is related to its morphology, which in turn is dependent on its chemical structure. We expected that crosslinking bonds in the polyimide matrix would change the morphology of the polyimide depending on its dianhydride structure. The morphological properties of linear and crosslinked polyimides were analyzed by XRD, and the results are shown in Table I and Figure 2.

The intermolecular distance of each polyimide increased by $0.15-1.11$ Å when the polyimide was crosslinked in the rank order of ODPA > 6FDA > BTDA. ODPA-crosslinked PI had high chain mobility due to the presence of a flexible ether linkage group (—C—O—C—), and there was a large increase in intermolecular distance. The increase in intermolecular distance of 6FDA-crosslinked PI was less than that of ODPA-crosslinked PI because of steric hindrance by the fluoromethyl group (—$C(CF_3)_2$—) and weak interactions between the molecules.[14] The intermolecular distance of BTDA-crosslinked PI increased slightly relative to the unlinked PI because of the dipole moment of the carboxyl group (—(C=O)—).[15]

The morphology of the polymer therefore changed upon crosslinking and trends were evident depending on the chain mobility and functional groups present. Physical and thermal properties of polymers are affected by morphology; therefore, we expected the crosslinked polyimides to show new thermal behaviors compared to those established for linear polyimides.[16]

Thermal Properties

We used TGA and DSC to study the effect of structure on the thermal stability of polyimides. Analyzed patterns are presented in Figures 3 and 4. The thermal properties of the polyimides differed between the crosslinked and linear polyimides, as we had predicted. The thermal stability results for the polyimides are summarized in Table II.

In this study, only 4,4'-ODA was used as a diamine so that we could determine the effect of dianhydrides on the thermal properties of the polymers. Linear structure-based films underwent 5% weight loss in the range of 550–560°C in nitrogen. Both BTDA and ODPA linear PIs, which contained oxygen bridges and carboxyl and ether groups in the dianhydride structure, showed high degradation temperatures of 554.34°C and 559.52°C, respectively. 6FDA linear PI had a higher thermal degradation temperature than the oxygen group-containing PIs because of the presence of fluoromethyl groups, which are highly thermally stable. Molecular packing and chain linearity of the dianhydride also affected the glass transition temperature; 6FDA linear PI had the highest glass transition temperature of

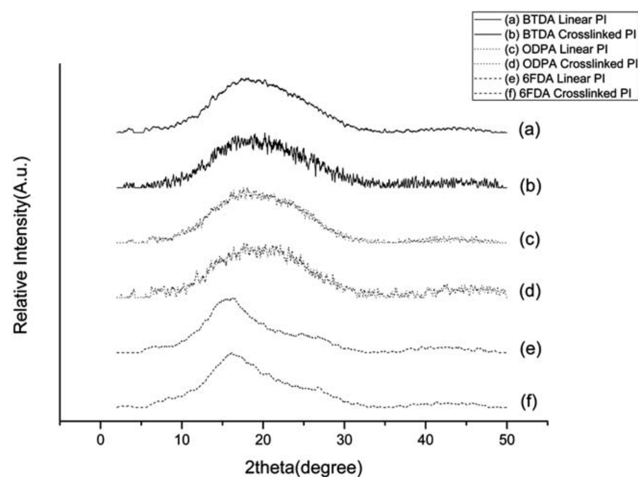

Figure 2. XRD patterns of polyimides.

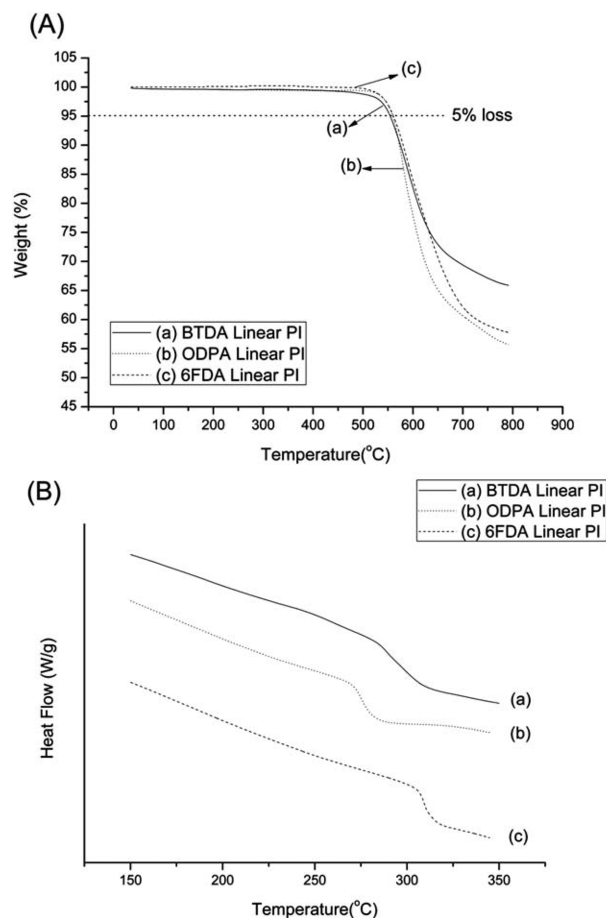

Figure 3. (A) TGA and (B) DSC curves of linear polyimide.

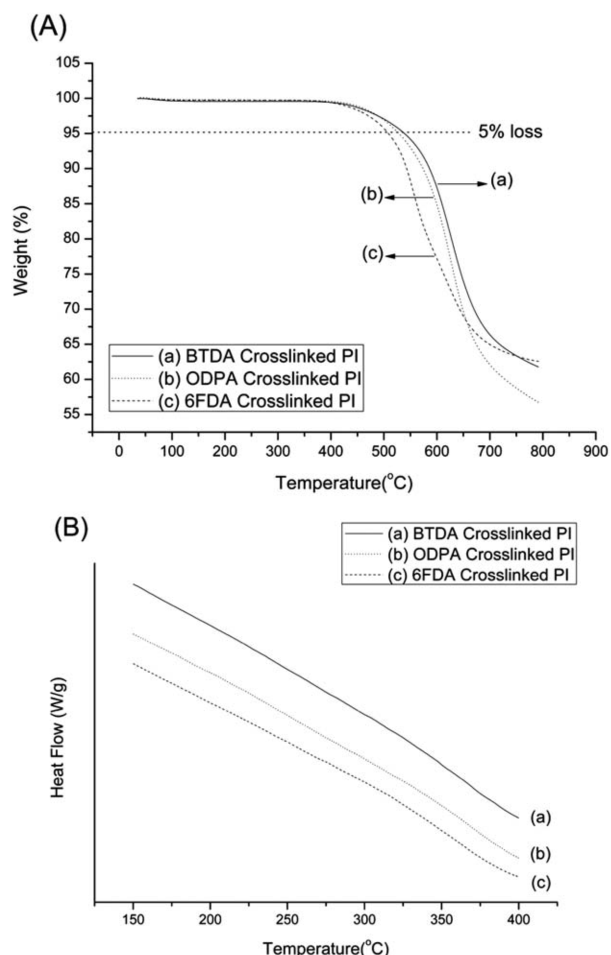

Figure 4. (A)TGA and (B)DSC curves of crosslinked polyimide.

309.40°C among the linear PIs because the bulky fluoromethyl groups of 6FDA limited chain motion.[17] In contrast, oxygen group-containing linear polyimides such as BTDA and ODPA had glass transition temperatures of 286.37°C and 274.64°C, respectively. Specifically, ODPA linear PI had the lowest glass transition temperature, because ether linkage groups have higher mobility than carboxyl groups.

The thermal degradation order was 6FDA > ODPA > BTDA, while the glass transition order was 6FDA > BTDA > ODPA. These results are consistent with previous findings[18] and confirm that fluoromethyl groups confer high thermal stability when incorporated in linear polyimides.

We observed a different relationship between thermal properties and dianhydride structure for the crosslinked polyimides.

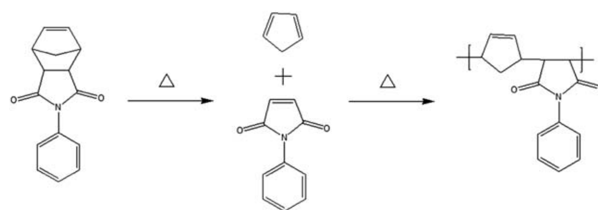

Figure 5. Proposed structure from the thermally induced reverse Diels-Alder recombination reaction.

Crosslinked polyimides had a lower thermal degradation temperature and increased glass transition temperature than the linear polyimides. The order of thermal properties was BTDA > ODPA > 6FDA.

The decrease in decomposition temperature and increase in glass transition temperature of the crosslinked polyimides can be explained by the presence of a crosslinking network bonds in the polymer matrix. Mechanism of crosslinking consists of degradation of the norbornene ring and the formation of a network between polyimide chains. This mechanism is known as a reverse Diels-Alder reaction and is shown in Figure 5.[19,20] Therefore, crosslinked parts or remained uncrosslinked single ends of polyimides can be decomposed at relatively lower temperatures than the main chains; the initial decomposition temperature was lower than that observed for the linear polyimide.[21] However, during the curing process, almost chains were connected to each other[13] and the motion of the chains was highly limited by crosslinking until decomposition.

The thermal stability order of crosslinked PIs was BTDA > ODPA > 6FDA. In the context of crosslinked polyimides, the fluoromethyl group did not improve thermal properties because the bulky group limited chain mobility. Low chain mobility decreased the likelihood of crosslinking, resulting in the presence of uncrosslinked chains. In contrast, polyimides with oxygen linkage dianhydride groups had high chain mobility, which facilitated crosslinking. These crosslinked PIs therefore had a higher thermal decomposition temperature than the fluoromethyl dianhydride-crosslinked PI. We also expected the BTDA dianhydride polyimide to have the highest glass transition temperature, but this was not the case, as shown in Figure 4(B). To accurately measure glass transition temperature and determine the effect of dianhydrides on the CTE of polyimide films, DMA and TMA instruments were used.

Dynamic Mechanical Analysis

The modulus of a polymer can be measured by DMA and expressed as the storage modulus and loss modulus according to temperature. The modulus of a polymer is related to stress

Table II. Thermal Properties of Linear and Crosslinked Polyimides

Sample name	BTDA Linear PI	BTDA Crosslinked PI	ODPA Linear PI	ODPA Crosslinked PI	6FDA Linear PI	6FDA Crosslinked PI
$T_{5\%}$ (°C)[a]	554.34	538.78	559.52	528.22	561.09	508.52
T_g (°C)	286.37	408.76[b]	274.64	394.34[b]	309.40	389.88[b]

[a] $T_{5\%}$, the temperature at 5% weight loss.
[b] It observed through DMA for the clear result.

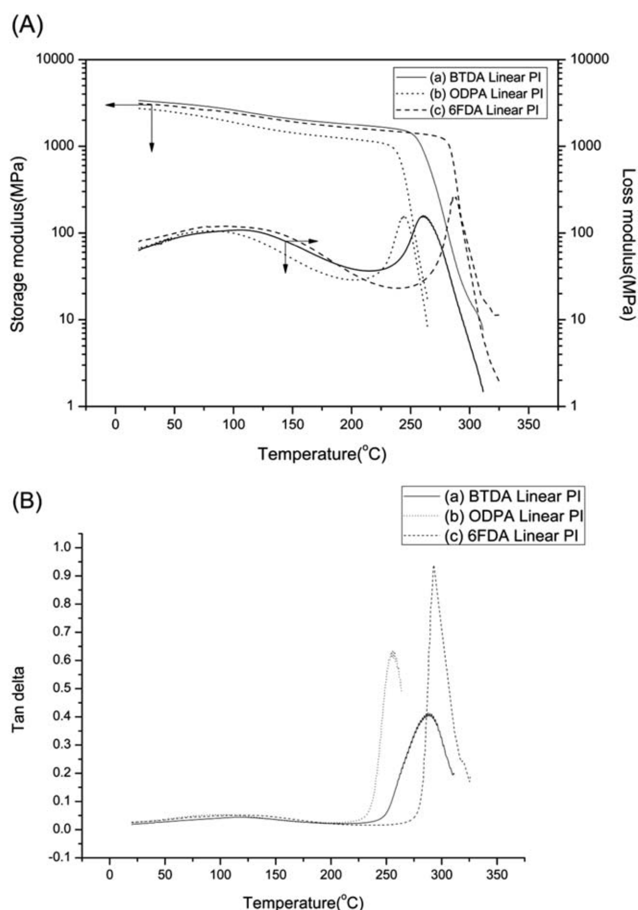

Figure 6. (A) modulus and (B) tan delta curves of linear polyimides.

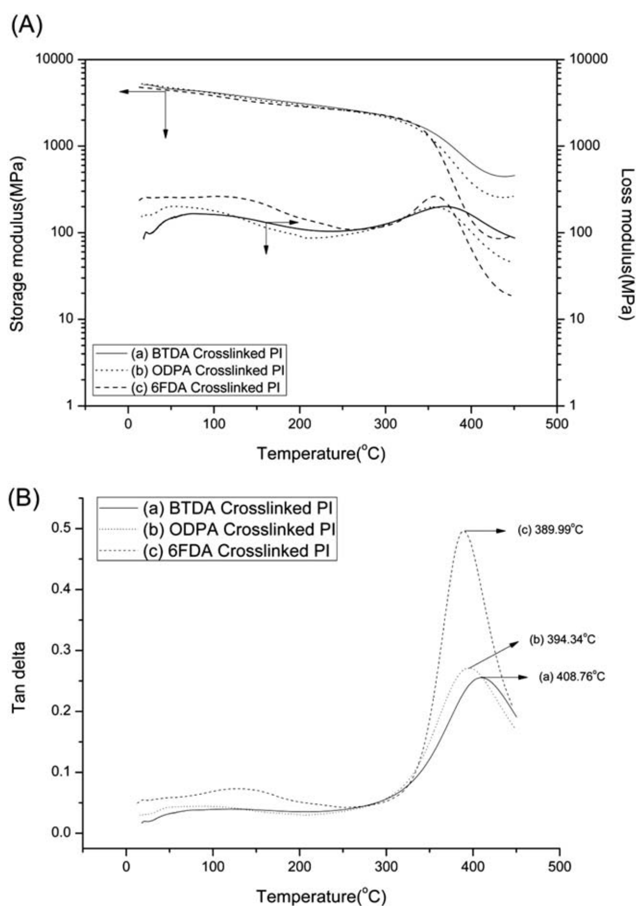

Figure 7. (A) modulus and (B) tan delta curves of crosslinked polyimides.

on polymer chains, and therefore the storage modulus decreases and the loss modulus increases with increasing temperature because polymer chains lose their rigidity at higher temperatures. When a polymer is heated up to its glass transition temperature, the storage modulus decreases dramatically and tan delta, the ratio of the storage modulus to the loss modulus, is maximized.

As shown in Figure 6, the storage modulus and loss modulus of high mobility polyimides were dramatically changed at lower temperatures than those of rigid polyimides, and the temperature at the maximum value of tan delta was almost the same as the glass transition temperature. Therefore, the starting temperature order of decreased modulus and increased tan delta was 6FDA > BTDA > ODPA for linear PIs, consistent with the TGA and DSC results. In the case of linear polyimides, we confirmed that the rigid fluoromethyl dianhydride PI with low mobility showed better thermal properties than the oxygen dianhydride PI with high mobility based on TGA, DSC, and DMA analyses.

The moduli of the crosslinked polyimides also changed dramatically near the glass transition temperature when the chain networks lost their rigidity, as shown in Figure 7. The glass transition temperature of crosslinked polyimides was near 400°C, as shown by the tan delta curves in Figure 7(B). With flexible dianhydrides, BTDA and ODPA, showed higher glass transition temperature as 408.76°C and 394.34°C than that of bulky dianhydride which is 6FDA, as 389.88°C. As we expected, DMA results showed good agreement that the starting temperatures of decreasing modulus order to be BTDA > ODPA > 6FDA, because crosslinked polyimide films with high mobility dianhydride had the best thermal properties based on TGA.

Thermomechanical Properties

We also investigated the effect of dianhydrides on thermal expansion. Thermal expansion of the polyimide films with temperature according to dianhydride structure is shown in Figure 8.

In the case of the linear polyimides, thermal expansion of polyimides occurred dramatically near the glass transition temperature and was higher for those PIs with higher chain mobility. Both BTDA and ODPA linear PIs had a larger coefficient of thermal expansion (CTE) than 6FDA linear PI, which indicates greater segmental motion or lower starting temperature of critical thermal expansion. The low CTE of the bulky fluoromethyl dianhydride PI means that this PI has lower segmental motion in the polymer matrix than that of oxygen-bridged linear PIs.[22]

In contrast, the crosslinked polyimides showed no critical thermal expansion under 380°C. This result indicates that the mobility of the polymer chains and thermal expansion decreased, because crosslinking increased the thermal stability of

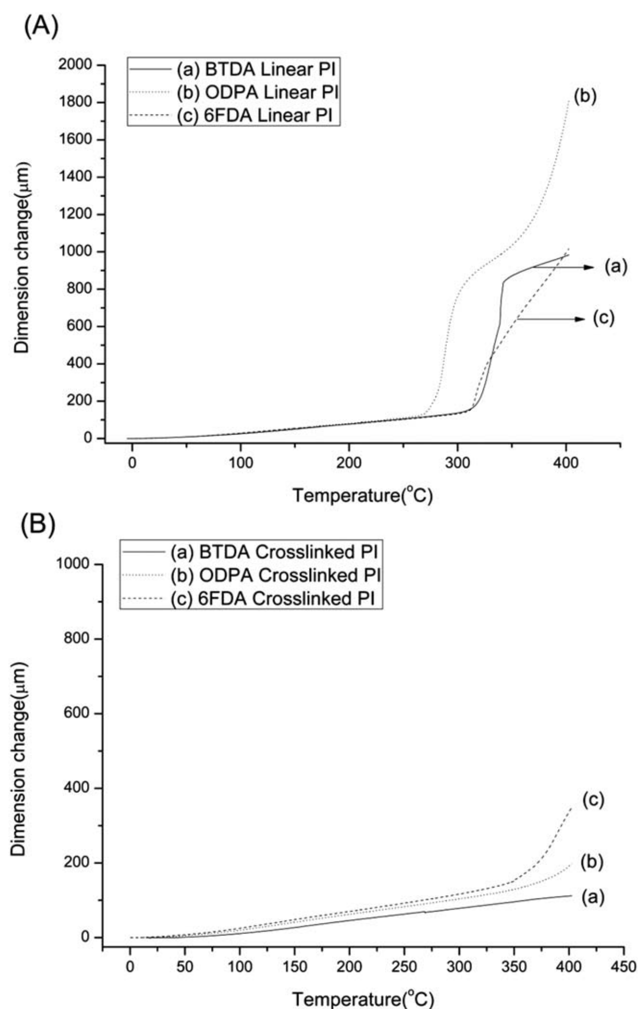

Figure 8. TMA curves of (A) linear and (B) crosslinked polyimides.

the polyimide film.[23] As we confirmed through TGA, DSC, and DMA, the thermal stability of crosslinked polyimides was close to 400°C without thermal degradation. As shown in Figure 8(B), only 6FDA crosslinked PI showed thermal expansion near the 380°C region; this means that the crosslinked network of 6FDA had less thermal stability and higher chain mobility than BTDA- and ODPA-crosslinked PI. This data is consistent with the TGA data. The bulky 6FDA dianhydride decreased the thermal stability of the crosslinked structure as shown by the TGA and TMA data. We confirmed that the thermal behaviors of linear and crosslinked polyimide films were critically affected by chain mobility, which was determined by the architecture of dianhydrides in different ways, as shown by TGA, DSC, DMA, and TMA. Lower chain mobility in linear films and higher chain mobility in crosslinked films were associated with superior thermal behavior.

CONCLUSIONS

Thermal behaviors of linear polyimides could be predicted from the mobility of the monomers. However, crosslinked polyimides showed different behaviors than linear structures. Thermal degradation temperature of the crosslinked PIs was lower than that of the linear PIs, but the glass transition temperature and thermal expansion of the crosslinked PIs were superior to those of the linear PIs. The bulky 6FDA crosslinked polyimide degraded at the lowest temperature and had the largest thermal expansion value. In contrast, the crosslinked networks of flexible BTDA and ODPA polyimide showed better thermal stability and had a lower coefficient of thermal expansion at high temperatures.

The effects of dianhydride on thermal behaviors differed between linear and crosslinked structures. Incorporation of bulky 6FDA in linear polyimides conferred good thermal properties to the resulting structure. However, in the case of crosslinked polyimides, dianhydrides that contained flexible linkages (BTDA and ODPA) were more heat stable materials.

Polyimides are widely used for high temperature processes and there is an increase in chain mobility and thermal expansion during these high temperature processes because linear polyimides have a low glass transition temperature near 300°C. However, crosslinked polyimides with flexible dianhydrides showed improved thermal stability, indicating that there were no large steric hindrance from network bonds and that thermal expansion was minimal. The results of this study confirmed that crosslinked polyimides are suitable materials for organic−inorganic hybrid composites and thin films for the electronic industry as they are resistant to thermal degradation, expansion, and stable at temperatures higher than 380°C.

ACKNOWLEDGMENTS

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