

Synthesis and Characterization of Aromatic Polyamide–amide–imide and Polyamide–imide copolymers

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Abstract : The polyamide–amide–imide (PAAI) was synthesized by reacting 4,4'-diaminobenzanilide (DBA) with trimellitic anhydride chloride using a two-stage heating. The precursor of polyamide–acids was formed at first stage and followed by the formation of imide of PAAI. Two polyamide–imides (PAIs) were prepared from benzidine (BZ) or 4,4'-diaminodiphenylether (DPE) with trimellitic anhydride chloride. These three polymers had glass transition temperature in the temperature range of 240–250 °C. X-ray data were obtained on thin film specimens cured at 250 °C. There was a minimal kind of short-range order consisting of the most probable distances between neighboring chains. The average segmental spacing of short-range order decreased in the order of polymers obtained from 4,4'-diaminobenzanilide (DBA), polyamide–imide, and 4,4'-diaminodiphenylether (DPE). The imidization of three polyamide–imides was confirmed by ¹⁵N MAS NMR and FT-IR spectroscopy. ¹⁵N NMR spectrum of cured polyamide–imide showed imide ¹⁵N peak, thereby providing an evidence for the imidization of three polyamide–imides.

Keywords: polyamide–imide, polyamide–amide–imide, ¹⁵N MAS NMR, imidization.

1. Introduction

There is much current commercial interest in polyimides because of their high thermal stability and good mechanical properties [1–6]. This is due to their aromatic and heterocyclic structures. The rigid structure in the polyimide chain imparts good properties, such as thermooxidative stability, but makes the material hard to process because of its poor solubility and high melting points. To

extend processability it has been studied the modifications of chemical structure via copolymerization of polyamide–imide (PAI) or introduction of acyclic moieties into main chain. The PAI copolymers have been extensively studied [6–13]. PAIs have shown great properties of both polyimide (PI) and polyamide (PA) bearing thermooxidative stability compared to PA and better processability than pure PI. Preparation of PAIs from aromatic diamines and trimellitic anhydride chloride is the most common method. Mixing the diamine and trimellitic anhydride chloride in polar aprotic solvent at ambient temperatures produces a solution of

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polyamic acid. Polyamic acid on subsequent heating at elevated temperatures loses water to form the PAIs by cyclodehydration [6–13]. We proposed to synthesize the new type of copolymers containing amide–amide groups in polyimide backbone. Polyamide–amide–imide (PAAI) has not been studied.

The purpose of this work was to study the effect of amide bridging group in diamine on the properties of polyamide–amide–imide (PAAI) and polyamide–imides (PAIs). The PAAI (hereafter expressed by DBA–PAAI) was synthesized by reacting 4,4'–diaminobenzanilide (DBA) and trimellitic anhydride chloride. The PAIs (BZ–PAI and DPE–PAI) were synthesized from benzidine (BZ) or 4,4'–diaminodiphenylether (DPE) with trimellitic anhydride chloride. These polymers were extensively characterized as films and powders to determine the thermal stability, viscosity, and crystallinity by TGA, DSC, XRD, ^{15}N NMR spectra, and XPS.

2. Materials and methods

2.1. Materials

4,4'–diaminodiphenylether (DPE) and 4,4'–diaminobenzanilide (DBA) were supplied from Wakayama Seika Kogyo Co. and purified by sublimation. Benzidine (BZ), trimellitic anhydride chloride (TAC), N,N–dimethylacetamide (DMAc), and triethylamine (TEA) were purchased from Aldrich Co. and used as received. DMAc was dried over calcium hydride (CaH_2) for 24 hours prior to distillation.

2.2. Measurements

Glass Transition temperatures were determined at $10\text{ }^\circ\text{C}/\text{min}$ on a DuPont Model 990 Thermal Analyzer. Thermogravimetric analyses of films were obtained at $10\text{ }^\circ\text{C}/\text{min}$ on a DuPont Model 990 Thermal Analyzer. Inherent viscosity measurements

were made with an Ubbelohde viscometer at $35\text{ }^\circ\text{C}$ on polyamide–acid solution at 0.5 % solids in DMAc. Wide angle X–ray scattering data was obtained on thin film specimens of the polymers. The X–ray diffractometer (MAC Science, Model: MXP18) was operated at 60 kV and 80 mA, using rotating anode (Cu target) with a flat sample holder and graphite monochromator. The ^{15}N CP MAS NMR spectra were recorded on a Bruker DSX 400 spectrometer operating at a ^{15}N frequency of 40.553 MHz and a spinning rate of 6.0 kHz. The spectra were obtained with an acquisition of 13 000–44 000 pulse transitions, which was repeated with a pulse length of 4.1 s, a contact time of 2000 s, and a recycle delay of 4 s. The ^{15}N chemical shifts are reported relatively to solid glycine. XPS valence spectra of the sample surfaces were obtained using PHI ESCA 5700 system with a hemispherical electron energy analyzer. Monochromatic Al $\text{K}\alpha$ (1486.6 eV) radiation was used as the excitation source. The pass energy was 23.5 eV. To cancel charging effect due to the ejection of electrons by x–ray source, neutralizer (PHI model 04–090) was used.

2.3. Polymer Synthesis

The polyamide–acids were prepared according to the general procedure. All glassware was flame–dried prior to use. To a 100 mL round bottom flask fitted with a condenser, magnetic stirrer, and a thermometer were placed DBA (10 mmol), TEA (10 mmol), and DMAc (36 mL). The reaction mixture was cooled in an ice–water bath and TAC (10 mmol) was added all at once. The temperature of the solution was maintained at room temperature and stirred rapidly for 6 hours under nitrogen. The viscous solution was poured into 10 volume times of ethanol, filtered, and refined finally by Soxhlet extraction. The DBA–PAAI was dried at $100\text{ }^\circ\text{C}$ under vacuum for 1 hour. The PAIs (BZ–PAI and DPE–PAI) were

synthesized from BZ or DPE with TAC similarly. The PAAI and PAIs were obtained from the thermal imidization of the polyamide-acid precursors in DMAc with concentration of 10 % solids by weight at 250 °C for 5 hours.

3. Results and Discussion

PAAI and PAIs were synthesized in two steps as shown in Fig. 1. The first stage of the synthesis was conducted at low temperature and resulted in polyamide-acid precursors. The obtained polyamide-acid powders were dissolved in DMAc at a concentration of 0.5 %(w/w), and inherent viscosities determined at 35 °C. The viscosities of three polymers (DBA-PAAI, BZ-PAI, and DPE-PAI) show 0.212, 0.302, and 0.214 dL/g respectively (Table 1). The DBA-PAAI polymer shows higher viscosity

than BZ-PAI and DPE-PAI because of better solubility in aprotic polar solvents due to amide bridge in diamine. The thermal imidization of the polyamide-acids was carried out on solvent-cast films.

Table 1. Inherent viscosities for polyamide-imide

Polymer	Inherent Viscosity (dL/g)*
DPE-Polyamideimide	0.212
DBA-Polyamideimide	0.302
BZ-Polyamideimide	0.214

The thermal behavior of the PAAI and PAIs was investigated by differential scanning calorimetry (DSC). The PAAI and PAIs showed glass transition temperatures (T_g) as shown in Fig. 2 and Table 2. The DBA-PAAI had a lower glass transition

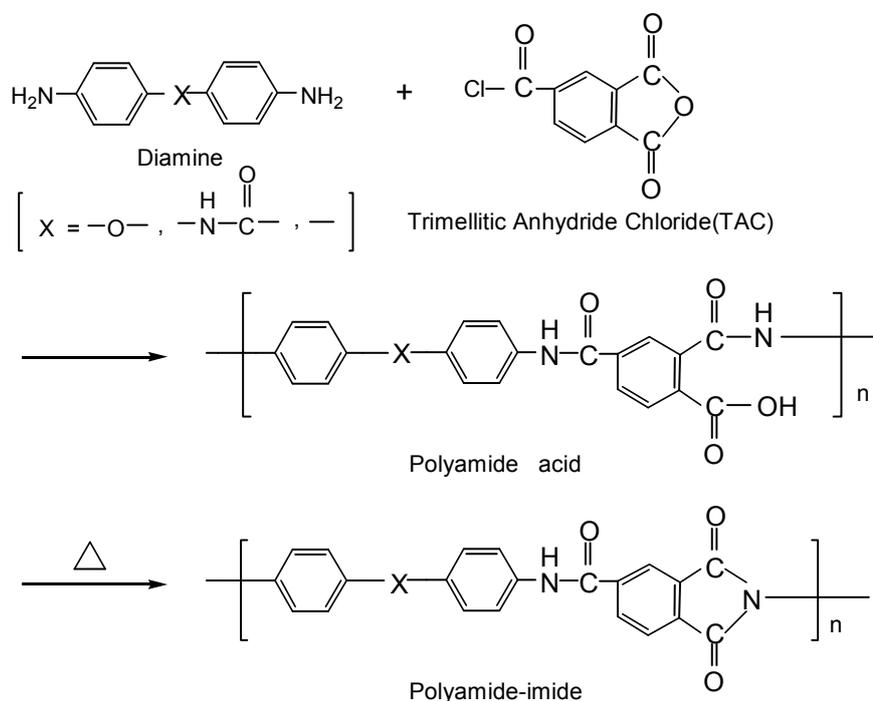


Fig. 1. Polymerization Scheme

Table 2. Glass transition temperatures for polyamide-imides

Polymer	Glass transition temperature (°C)
DPE-Polyamideimide	239
DBA-Polyamideimide	243
BZ-Polyamideimide	249

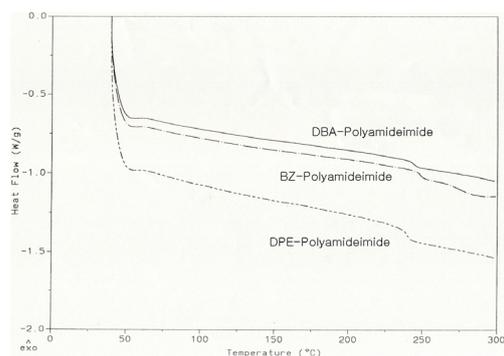


Fig. 2. DSC thermograms for polyamide-imides

temperature than those of other PAI polymers because the amide bond provides additional flexibility. Thermooxidative stability of the polymers was studied using thermogravimetric analysis (TGA) with results shown in Fig. 3. Most of the polymers showed excellent thermal stability at high temperature in nitrogen atmospheres. The DPE-PAI had low thermooxidative stability with 5 % weight loss at 472 °C compared to the DBA-PAAI, perhaps because the resonance structure of amide group of

DBA gave more stable structure than the ether group of DPE. The BZ-PAI without additional bridge showed relatively high thermooxidative stability (Table 3).

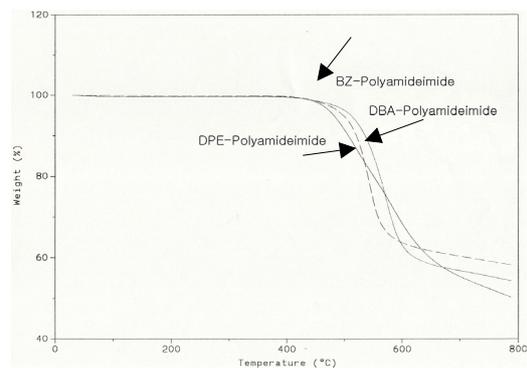


Fig. 3. TGA thermograms for polyamide-imides

In order to verify crystallinity X-ray data was obtained on thin film specimens cured at 250 °C for 2.5 hours. The information obtained from diffraction patterns of amorphous polymers is informative; however, it is far less definitive and precise than that for crystalline structure. As shown in Fig. 4, three polymers are belonging to amorphous polymer. In amorphous polymer there is no long-range order, but there is a minimal kind of short-range order consisting of the most probable distances between neighboring chains. The center of the broad peak of a diffraction pattern is attributed to average intersegmental spacing [14]. The d spacing can be calculated using Bragg's equation. 2

Table 3. TGA thermograms for polyamideimides

Polymer	Initial Decomposition Temperatures (°C)	Residue at 780 °C
DPE-Polyamide-imide	472	50.7
DBA-Polyamide-imide	509	58.4
BZ-Polyamide-imide	527	54.6

Θ and d spacing are shown in Table 4. Although three polyamide-imides did not show the crystallinity, there was a minimal kind of short-range order consisting of the most probable distances between neighboring chains. The average segmental spacing of three polymers was obtained: 4.23 Å for DBA-PAAI, 4.44 Å for BZ-PAI, 4.62 Å for DPE-PAI. The average segmental spacing of short-range decreased in the order of DBA-PAAI, BZ-PAI, and DPE-PAI. It has been reported that the polymer having a shorter intersegmental spacing d increases the initial thermal decomposition temperature due to its closer chain packing. In the thermogravimetric analysis DPE-PAI copolymer showed lower thermooxidative stability than the others because it is explained that, presumably, DPE-PAI copolymer has the relative large intersegmental spacing d .

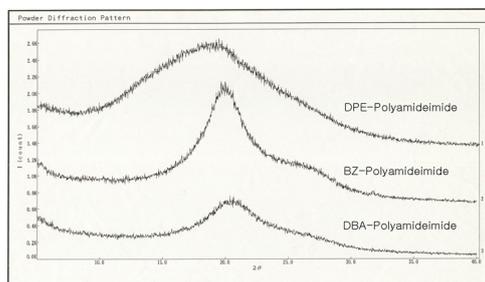


Fig. 4. X-ray diffraction curves for polyamide-imides

Table 4. XRD data for polyamideimides

Polymer	$2\Theta(^{\circ})$	d (Å)
DPE-Polyamide-imide	19	4.62
BZ-Polyamide-imide	20	4.44
DBA-Polyamide-imide	21	4.23

The ^{15}N CP MAS NMR spectroscopy was employed to confirm the imidization for polyamide-acids. Fig. 5 showed the ^{15}N CP

MAS NMR spectra for polyamide-acids cured at 100 °C for 1 hour where there is one peak (94 ppm) corresponding to amide N. After curing the polyamide-acids at 250 °C for 3 hours, ^{15}N CP MAS NMR spectra showed two peaks at 94 and 140 ppm in Fig. 6. A peak at 140 ppm corresponds to imide N in the imide ring. This results polyamide-acid could provide strong evidence for the imidization of polyamide-acid with increasing the temperature.

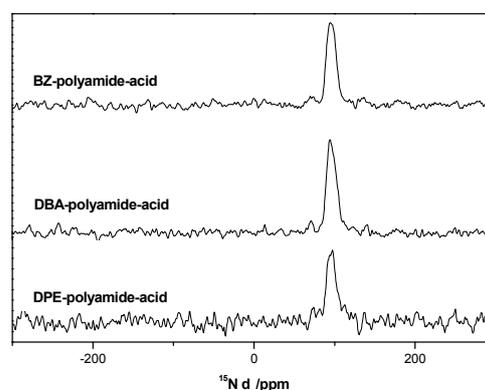


Fig. 5. NMR data for polyamide-imides after curing at 150 °C for 1 hour

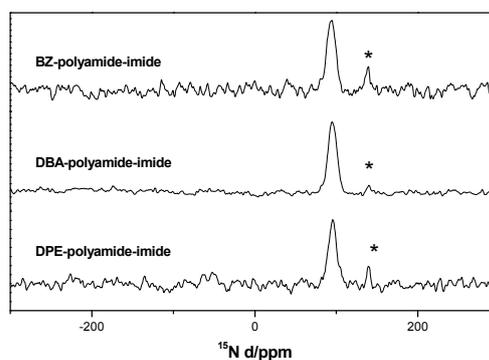


Fig. 6. NMR data for polyamide-imides after curing at 250 °C for 3 hours.

The valence band (VB) spectra of BZ-PAI film after curing at 150 °C for 1 hour and BZ-PAI film after curing at 250 °C for 3 hours are presented in Fig. 7. The VB

spectrum exhibits the modified density of states for occupied orbital. As shown in Fig. 7, the VB spectra of these samples are quite different. After curing BZ-PAI at 150 °C for 1 hour the valence spectrum is very broad, looks like a graphite-like structure which is

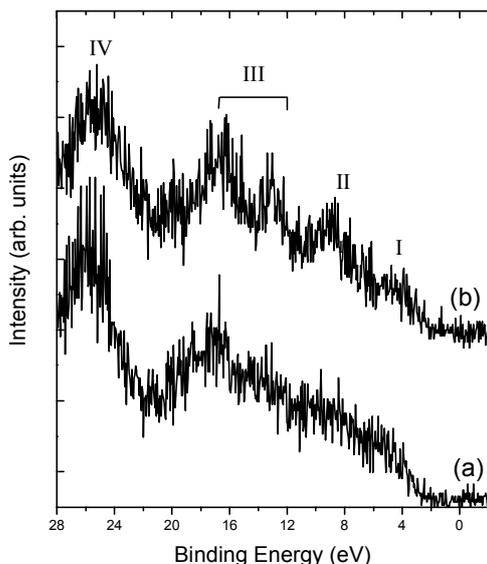


Fig. 7. The valence band (VB) spectra of (a) BZ-polyamide-acid film after curing at 150 °C for 1 hour and (b) BZ-polyamide-imide film after curing at 250 °C for 3 hours.

related to the amorphous carbon [15]. On the other hand, after curing BZ-PAI at 250 °C for 3 hours, the IV peak intensity decrease and the I-III peaks sharpen evidently. In the VB spectra for a polyimide, the ~5 eV peak (I) consists of carbon orbitals associated with benzene rings: the C(2p) orbital lying perpendicular to the molecule, the N(2p) and O(2p) lone pair orbitals lying perpendicular to the molecule. The peak (II) near 10 eV is made up of the imide characteristic bonds, i.e., C-C σ bonds, C-O orbitals perpendicular to the molecular plane, and C-H π bonds. The peak (III) structure between 14-17 eV is C (2s). The sharpening peak (IV) at ~25 eV

are due to N(2s) and O(2s) orbitals [15-18]. The change of the spectra, as the polyamide-acid cures, is probably caused by the oxygen derived 2s and 2p orbitals due to the H₂O products. Generally, a complete conversion of the polyamic acid to polyimide was known to produce water as a by-product [16-18]. In addition, we showed the imidization of polyamide-acid by appearance of I-III peaks which are the characteristic structure for polyimide. This result for imidization agrees well with the results of NMR spectra.

4. Conclusions

The initial thermal decomposition temperatures were obtained for 3 PAIs; 527 °C for BZ-PAI, 509 °C for DBA-PAAI, 472 °C for DPE-PAI. There was a minimal kind of short-range order consisting of the most probable distances between neighboring chains. The average segmental spacings were obtained for 3 polyamide-imides; 4.23 Å for DBA-PAAI, 4.44 Å for PAI from BZ, 4.62 Å for PAI from DPE. Because DPE-PAI has larger intersegmental spacing d , it shows decreased initial thermal decomposition temperature. In case of DBA-PAAI, and BZ-PAI they showed increased initial thermal decomposition temperature due to their closer chain packing. ¹⁵N NMR of cured polyamide-imide showed imide ¹⁵N peak at 140 ppm, thereby providing an evidence for the imidization of 3 PAIs.

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