

Synthesis and Characterization of Some Aromatic Polyimides

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ABSTRACT: The diamine 2-methyl-1,3-bis(4-aminophenoxy)benzene was prepared via a nucleophilic substitution reaction and was characterized with Fourier transform infrared, elemental analysis, and ¹H- and ¹³C-NMR spectroscopy. The prepared diamine was also characterized with single-crystal analysis. The geometric parameters of C₁₉H₁₈N₂O₂ were in the usual ranges. The dihedral angles between the central phenyl ring and the two terminal aromatic rings were 88.9 and 91.6°. The crystal structure was stabilized by N—H···N hydrogen bonds. The diamine was then polymerized with 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 3,4,9,10-perylene-tetracarboxylic acid dianhydride, and pyromellitic dianhydride by either a one-step solution polymerization reaction or a two-step procedure. These polymers had inherent viscosities ranging from 0.61 to 0.85 dL/gm. Some

of the polymers were soluble in most common organic solvents even at room temperature, and some were soluble on heating. The degradation temperatures of the resultant polymers fell in the range of 260–500°C in nitrogen (with only 10% weight loss). The specific heat capacity at 200°C ranged from 1.0 to 2.21 J g⁻¹ K⁻¹. The temperatures at which the maximum degradation of the polymer occurred ranged from 510 to 610°C. The glass-transition temperatures of the polyimides ranged from 182 to 191°C. The activation energy and enthalpy of the polyimides ranged from 44.44 to 73.91 kJ/mol and from 42.58 to 72.08 kJ/mol K, respectively. The moisture absorption was found in the range of 0.23–0.71%. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2101–2108, 2009

Key words: glass transition; polyimides; thermal properties

INTRODUCTION

Polyimides are high-performance polymers because of their heat and chemical resistance. A large number of polyimides with unique properties have been introduced for various industrial and consumer product applications.¹ One of the directions in the development of new polyimides is the synthesis and study of extended rodlike or rigid aromatic polyimides because such polyimides have potential as materials for thermally stable, high-modulus, high-strength fibers, as materials with a low thermal expansion coefficient for packing in microelectronic applications,² and as materials for gas-separation membranes. One of the problems with such rigid, rodlike polyimides is their poor solubility or processability, and they do not react below their decom-

position temperature; this restricts their applications as engineering materials.³ Many efforts have been made to improve their processability while maintaining their excellent thermal and mechanical properties.^{4,5} For example, bulky lateral substituents,^{6–11} flexible alkyl side chains,^{12–14} noncoplanar biphenyl moieties, and flexible alkyl or aryl ether spacers^{15–17} have been used to enhance the solubility and thus processability. One of the successful approaches to increasing the solubility is the introduction of flexible segments [e.g., —O—, —SO₂—, —CH₂—, and —C(CF₃—)₂] and bulky pendent groups (e.g., *t*-butyl and adamantyl) into the polymer backbone.^{18,19} Unfortunately, noncoplanar structures and pendent aliphatic segments that enhance the solubility also generally degrade the thermal properties. Fluorine-containing polyimides have received a great deal of attention because fluorine lowers the thermal expansion coefficient. Recently, Hsio et al.²⁰ reported some soluble thermoplastic polyimides derived from spiro-linked diamine structures in an effort to overcome this problem. These polymers had glass-transition temperatures (*T*_g's) between 236 and 256°C and were stable up to

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450°C (in N₂). However, except for those incorporating 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and diphenylsulfone tetracarboxylic anhydride, these polyimides were not soluble.²¹

Other work has shown the incorporation of 1,1-bis(4-aminophenyl)cyclohexane and various methyl-substituted cyclohexane derivatives to form soluble polyimides with T_g values in the range of 290–370°C.²² New aromatic dianhydrides have also been reported to yield soluble polyimides with acceptable T_g values and oxidative stability.²³ Recent studies have demonstrated that polyimides derived from diamines with ether bridge and CF₃ substituents are soluble in most organic solvents and have good thermal stability and low moisture uptake. A recent approach is the introduction of an amine functionality or dianhydride into the heterocyclic ring by the formation of ether linkages with a nucleophilic aromatic substitution reaction to increase the solubility. Benzimidazoles, quinoxaline, and benzothiazole were incorporated in these studies.^{23–26} On the other hand, the incorporation of pendant groups can impart significant mobility while providing good solubility because of the decreased chain packing leading to crystallization. In this connection, we became interested in the ability of 2-methyl-1,3-bis(4-aminophenyl)benzene (MAPB) to influence the chain flexibility of aromatic polyimides. Through the incorporation of MAPB into the polyimide, enhanced solubility would be expected. With this aim in mind, in this article, we describe the synthesis and characterization of this diamine and its polyimides.

EXPERIMENTAL

Materials

2-Methyl resorcinol, *p*-chloronitrobenzene, anhydrous potassium carbonate, dimethylacetamide (DMAc), 5% palladium charcoal, hydrazine monohydrate, ethanol, 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA), 6FDA, 3,4,9,10-perylenetetracarboxylic acid dianhydride (PD), and pyromellitic dianhydride (PMDA; analytical-reagent grade) from Aldrich (Milwaukee, WI) were used as received. All the other reagents and solvents were analytical-grade and were used without further purification.

Measurements

¹H- and ¹³C-NMR spectra were obtained with a JEOL 270 spectrophotometer (Peabody, Boston) in dimethyl sulfoxide (DMSO) with tetramethylsilane as an internal reference. IR measurements (KBr pellets) were recorded in the range of 400–4000 cm⁻¹ on a Bio-Rad Excalibur model FTS 3000 MX (Hercules, CA) Fourier transform infrared (FTIR) apparatus. Melting points were recorded on an Electrothermal IA 9000 series digital

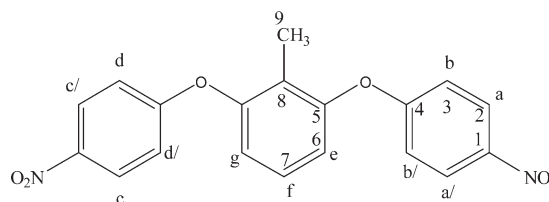
melting point apparatus (Chula Vista, CA). Inherent viscosities were obtained with a Gilmount falling ball viscometer (Vernon Hills, Illinois). Thermal and differential scanning calorimetry (DSC) analyses were carried out with a PerkinElmer TGA-7 (Waltman, Massachusetts) and a Netzsch DSC-404C (Selb, Germany). Elemental analysis was carried out with a PerkinElmer CHNS/O 2400 (Waltman, Massachusetts). Wide-angle diffractograms were obtained with a X'Pert PRO 3040/60 diffractometer (Eindhoven, Netherland). Moisture absorption was determined through the weighing of the changes in dried pellets before and after immersion in distilled water at 25°C for 24 h. The activation energy, entropy, and enthalpy were calculated with the Horowitz and Metzger method.

Monomer synthesis

2-Methyl-1,3-bis(4-nitrophenoxy)benzene (MNPB)

A mixture of 5.0 g (0.040 mol) of 2-methyl resorcinol, 11.04 g (0.08 mol) of potassium carbonate, and 12.68 g (0.08 mol) of *p*-chloronitrobenzene in a two-necked, round-bottom flask with 90 mL of DMAc was heated at 100°C for 18 h under a nitrogen atmosphere. The color of the solution changed from yellow to dark brown as the reaction proceeded. After cooling to room temperature, the reaction mixture was poured into 500 mL of water to form a solid, which was washed thoroughly with water and then separated by filtration. The crude product was recrystallized from ethanol.

Yield: 87%. mp: 212°C. ANAL. calcd for C₁₉H₁₄O₆N₂ (molecular weight = 366): C, 62.29 wt %; H, 3.82 wt %; N, 7.65 wt %. Found: C, 62.11 wt %; H, 3.65 wt %; N, 7.80 wt %. IR (KBr pellet, cm⁻¹): 1578 (aromatic C=C), 1512 and 1330 (NO₂), 1239 (C—O—C). ¹H-NMR (DMSO-*d*₆, δ, ppm): 6.539 (d, 4H, $J_{ba} = J_{b'a'} = J_{dc} = J_{d'c'} = 8.1$ Hz, bb' and dd'), 8.561 (d, 4H, $J_{ab} = J_{a'b'} = J_{cd} = J_{c'd'} = 8.7$ Hz, aa' and cc'), 6.735–6.864 (m, 3H, efg), 2.30 (s, 3H, Me). ¹³C-NMR (DMSO-*d*₆, ppm): 10.1 (1C, C9), 117.36 (2C, C6,6'), 119.16 (1C, C8), 126.11 (4C, C3,3'), 127.14 (1C, C7), 140 (4C, C2,2'), 143.10 (2C, C1,1'), 163.17 (2C, C4,4'), 154.16 (2C, C5,5').



MAPB

A 250-mL, two-necked flask was charged with 2 g (2.73 mmol) of MNPB, 20 mL of hydrazine

TABLE I
Crystal Data and Structure Refinement for MAPB

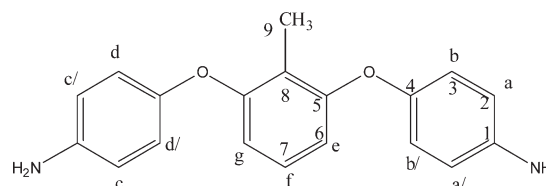
| | |
|---|--|
| Identification code | MAPB |
| Empirical formula | C ₁₉ H ₁₈ N ₂ O ₂ |
| Formula weight | 306.35 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | <i>Pc</i> |
| Unit cell dimensions | $a = 11.4230(18)$ Å, $\alpha = 90^\circ$, $b = 7.3013(10)$ Å, $\beta = 104.586(12)^\circ$, $c = 10.0638(16)$ Å, $\gamma = 90^\circ$ |
| Volume | $812.3(2)$ Å ³ |
| Z | 2 |
| Density (calculated) | 1.253 mg/m ³ |
| Absorption coefficient | 0.082 mm ⁻¹ |
| <i>F</i> (000) | 324 |
| Crystal size | 0.29 × 0.12 × 0.12 mm ³ |
| θ range for data collection | 3.69–25.59° |
| Index ranges | $-12 \leq h \leq 13$, $-8 \leq k \leq 8$, $-12 \leq l \leq 12$ |
| Reflections collected | 4203 |
| Independent reflections | 1508 [<i>R</i> (int) = 0.0580] |
| Completeness to $\theta = 25.00^\circ$ | 99.0% |
| Absorption correction | None |
| Maximum and minimum transmission | 0.9902 and 0.9765 |
| Refinement method | Full-matrix least squares on <i>F</i> ² |
| Data/restraints/parameters | 1508/2/226 |
| Goodness of fit on <i>F</i> ² | 1.064 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0546, <i>wR</i> ₂ = 0.1435 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0605, <i>wR</i> ₂ = 0.1479 |
| Absolute structure parameter | 0(2) |
| Extinction coefficient | 0.043(11) |
| Largest different peak and hole | 0.379 and −0.224 e/Å ³ |

monohydrate, 100 mL of ethanol, and 0.12 g of 5% palladium on carbon (Pd-C). The mixture was refluxed for 16 h and then filtered to remove the Pd-C. The solvent was evaporated, and the crude solid was recrystallized from ethanol to yield 85% of the theoretically calculated yield.

mp: 184°C. ANAL. calcd for C₁₉H₁₈O₂N₂ (molecular weight = 306): C, 74.50 wt %; H, 5.88 wt %; N, 9.15 wt %. Found: C, 74.12 wt %; H, 5.66 wt %; N, 9.45 wt %. mp: 184°C. IR (KBr pellet, cm⁻¹): 3453 and 3376 (NH₂), 1630 (N-H bending), 1260 (C-O-C), 1459 (NH deformation), 2922 (CH₂ Stretching). ¹H-NMR (DMSO-*d*₆, δ, ppm): 4.945 (s, 4H, NH₂), 6.739 (d, 4H, *J*_{ba} = *J*_{b'a'} = *J*_{dc} = *J*_{d'c'} = 8.4 Hz, bb' and dd'), 6.598 (d, 4H, *J*_{ab} = *J*_{a'b'} = *J*_{cd} = *J*_{c'd'} = 8.7 Hz, aa' and cc'), 6.945–7.020 (m, 3H, efg), 2.02 (s, 3H, Me). ¹³C-NMR (DMSO-*d*₆, ppm): 9.43 (1C, C9), 110.5 (2C, C6,6'), 117.54 (1C, C8), 120.62 (4C, C3,3'), 126.94 (1C,

C7), 140 (4C, C2,2')145.5 (2C, C1,1'), 146.83 (2C, C4,4'), 158.09 (2C, C5,5').

The single crystal for the diamine was grown during slow crystallization in an ethanol solution. A crystal size of 0.38 mm × 0.11 mm × 0.10 mm was used for X-ray structure determination. Crystal data were obtained for compound MAPB crystallized in a monoclinic system with space group *Pc* [*M* = 306.35, *a* = 11.4230(18) Å, *b* = 7.3013(10) Å, *c* = 10.0638(16) Å, $\alpha = 90^\circ$, $\beta = 104.586(12)^\circ$, and $\gamma = 90^\circ$, where *Dc* = 1.253 mg/m³ for *Z* = 2 and *V* = 812.3(2) Å³]. Least-squares refinement based on 4203 independent reflections converged to final values of *R*₁ = 0.0546, *wR*₂ = 0.1435, and *S* (goodness of fit) = 1.064. Crystallographic experimental data are provided in Tables I and II, and an Oak Ridge thermal ellipsoid plot drawing of MAPB is shown in Figure 1.



Polymer synthesis

To a stirred solution of MAPB (0.38 g, 1.238 mmol) in 8 mL of DMAc was added BTDA (0.4 g, 1.238 mmol). The mixture was stirred at room temperature for 24 h under a nitrogen atmosphere to form a poly(amic acid) (precursor). The film was cast onto a glass plate through the heating of this solution of poly(amic acid) for 18 h at 80°C, for 2 h at 150°C, for 2 h at 200°C, for 2 h at 250°C, and for 2 h at 280°C;

TABLE II
Important Bond Lengths [Å] and Angles [°] for MAPB

| Bond lengths [Å] | Angles [°] |
|------------------|------------|
| O(1)–C(11) | 1.400 (5) |
| O(2)–C(3) | 1.402 (5) |
| N(1)–C(14) | 1.413 (5) |
| N(2)–C(24) | 1.404 (5) |
| N(2)–H(2A) | 0.97 (6) |
| C(4)–H(4) | 0.9500 |
| C(5)–H(5) | 0.9500 |
| C(6)–H(6) | 0.9500 |
| C(13)–H(13) | 0.9500 |
| C(14)–C(15) | 1.398 (6) |
| C(15)–H(15) | 0.9500 |
| C(16)–H(16) | 0.9500 |
| C(21)–C(22) | 1.379 (6) |
| C(22)–H(22) | 0.9500 |
| C(23)–H(23) | 0.9500 |
| C(24)–C(25) | 1.405 (6) |
| C(25)–C(26) | 1.380 (6) |

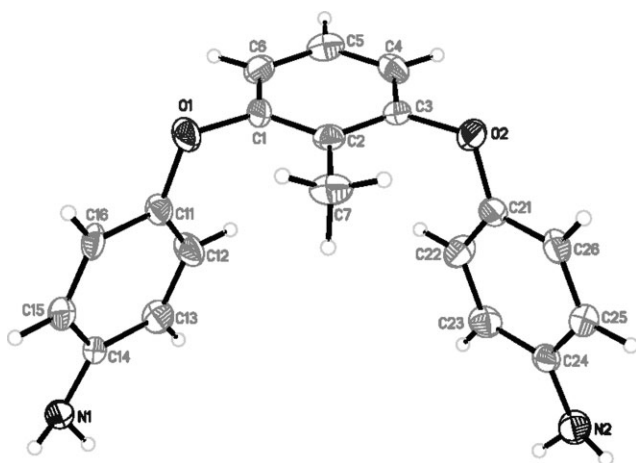


Figure 1 Oak Ridge thermal ellipsoid plot drawing of $C_{19}H_{18}O_2N_2$ (MAPB).

this converted the polymeric acid into polyimide films. The same procedure was adopted for the polymerization of MAPB with 6FDA and PMDA; however, the polymerization with PD was carried out with the following procedure. In a 250-mL, two-necked, round-bottom flask fitted with a nitrogen inlet and outlet, diamine (0.39 g, 1.27 mmol), dianhydride (0.5 g, 1.27 mmol), *m*-cresol (20 mL), and isoquinoline (1 mL) were added. The mixture was heated to 180–200°C under nitrogen for 6 h and then cooled to room temperature. The resulting dark red solution was poured into 300 mL of acetone, and the resulting solid was washed with 1N sodium hydroxide followed by water. After drying at 150°C overnight, the polyimide was obtained as a dark red solid. The inherent viscosities of the polymers were subsequently determined at a concentration of 0.2 g/dL at 25°C.

RESULTS AND DISCUSSION

Monomer synthesis

The diamine MAPB was prepared in two steps according to the well-developed method shown in Figure 2. The first step was the Williamson etherification reaction of 2-methyl resorcinol and *p*-chloronitrobenzene in the presence of potassium carbonate in DMAc, and this was followed by stirring of the mixture at 100°C for 18 h. The diamine MAPB was readily obtained in a good yield by the catalytic reduction of the intermediate dinitro compound with hydrazine hydrate and Pd–C as a catalyst in refluxing ethanol. Elemental, FTIR, and NMR analyses were carried out to confirm the structures of the intermediate and diamine. The nitro group of the intermediate compound gave two absorption bands at 1512 and 1330 cm^{-1} (NO_2 asymmetric and symmet-

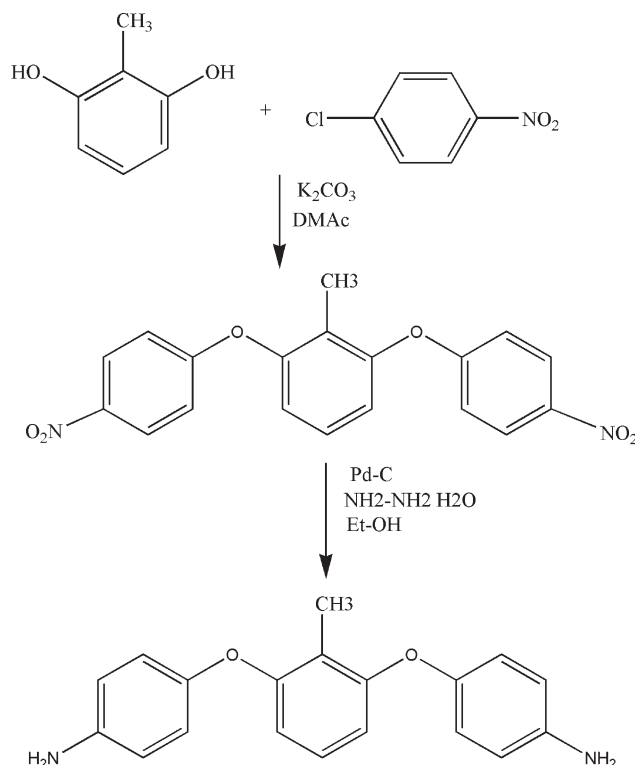


Figure 2 Scheme for the synthesis of the diamine.

ric stretching). After reduction, the characteristic absorption of the nitro compound disappeared, and the amino group showed a pair of N–H stretching bands in the region of 3300–3400 cm^{-1} . All the spectroscopic data were in good agreement with the expected structure. The molecular structure of the diamine was also confirmed by X-ray crystal analysis. Geometric parameters were in the usual ranges. The dihedral angles between the central phenyl ring and the two terminal aromatic rings were 88.9 and 91.6°. The crystal structure was stabilized by N–H···N hydrogen bonds.

Polymer synthesis

The diamine monomer was polymerized with four different aromatic dianhydrides: BTDA, 6FDA, PMDA, and PD (Fig. 3). The polyimides of BTDA, 6FDA, and PMDA were prepared with a conventional two-step procedure that involved ring-opening polyaddition at room temperature to poly(amic acid) followed by sequential heating to 280°C to obtain the corresponding polyimides. The polyimide of PD was prepared by a different method. The poly(amic acid) precursors were prepared by the gradual addition of dianhydride to the diamine solution. The mixture was stirred at room temperature overnight to get a highly viscous poly(amic acid) solution. The thermal conversion to polyimides was carried out

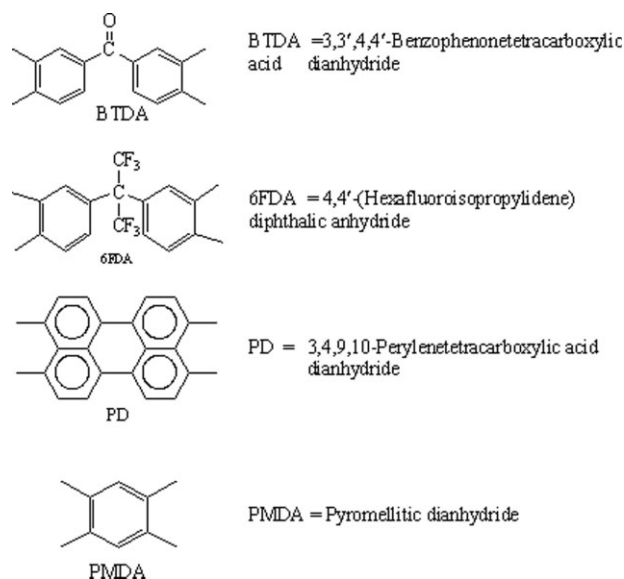


Figure 3 Four different acid dianhydrides used for polymerization.

through the heating of the poly(amic acid) solution at 80°C for 18 h, at 150°C for 2 h, at 200°C for 2 h, and at 280°C for 2 h.²⁰ A rapid temperature elevation resulted in cracked or brittle films. The inherent viscosities determined for some polymer films yielded values in the range of 0.61–0.85 dL/g at a concentration of 0.2 g/dL at 25°C, and this indicated the high molecular weights of the polymers, as shown in Table I. The obtained polyimides were subjected to solubility and thermal studies. The formation of the polyimides was confirmed by IR and elemental analyses. All the polyimides exhibited the characteristic imide group absorptions around 1775 and 1716 (typical of imide carbonyl symmetric and asymmetric stretching), 1386 (C–N stretch), and 1100 and 711 cm⁻¹ (imide ring deformation). The disappearance of the amide and carboxyl bands indicated virtually complete conversion of the poly(amic acid) precursor into polyimides. The results of the elemental analysis of all the polyimides were in good agreement with the calculated values. The inherent viscosities determined for polymer films, except for MAPB–BTDA, were in the range of 0.61–

0.85 dL/g, reflecting the high molecular weights of the polymers.

Organosolubility

Some of the thermally cured polyimides exhibited good solubility in solvents such as DMSO, dimethylformamide (DMF), DMAc, *m*-cresol, tetrahydrofuran (THF), and H₂SO₄; therefore, the inherent viscosity of the polyimides was characterized and found to be in the range of 0.61–0.85 dL/g. Some polymers were soluble on heating, whereas some were slightly soluble, and some were insoluble. The organosolubility behavior of the polymers generally depended on their chain packing ability and intermolecular interactions, which were affected by the rigidity, symmetry, and regularity of the backbone. From Table III, it was observed that the introduction of a fluorinated dianhydride component (6FDA) was especially effective for high solubility, regardless of the diamine component. This increase in solubility might be attributed to the molecular asymmetry and the presence of bulky trifluoromethyl groups, which increased the disorder in the chains and hindered the dense chain stacking, thereby reducing the inter-chain interactions and thus enhancing solubility. The poor solubility of the thermally cured polyimides might be attributed to crosslinking within the polymer chain or the tight chain packing and aggregation during imidization at an elevated temperature. Besides, the solubility behavior of the polyimides obtained with 6FDA was also attributed to the capability of hydrogen bonding.²⁷

X-ray diffraction data

All the polyimides were characterized in wide-angle X-ray diffraction studies. From the diffraction patterns shown in Figure 4, it was observed that all the polyimides except MAPB–6FDA displayed a semi-crystalline pattern, whereas MAPB–6FDA displayed a nearly completely amorphous pattern and failed to show crystallinity, apparently because bulky CF₃ groups disrupted the symmetry or dense chain packing, leading to highly ordered regions.²⁷

TABLE III
Inherent Viscosity and Solubility of the Polymers

| Polymer | DMSO | DMF | DMAc | <i>m</i> -Cresol | THF | H ₂ SO ₄ | Inherent viscosity (dL/g) |
|-----------|------|-----|------|------------------|-----|--------------------------------|---------------------------|
| MAPB–BTDA | – | – | – | – | – | + | – |
| MAPB–6FDA | ++ | ++ | ++ | ++ | – | +++ | 0.85 ^a |
| MAPB–PD | + | + | + | + | – | ++ | 0.61 ^b |
| MAPB–PMDA | – | – | – | – | – | ++ | 0.74 ^b |

+++ = soluble at room temperature; ++ = soluble on heating; + = slightly soluble on heating; – = insoluble.

^a Measured from 0.2 g/dL at 25°C in DMSO.

^b Measured from 0.2 g/dL at 25°C in H₂SO₄.

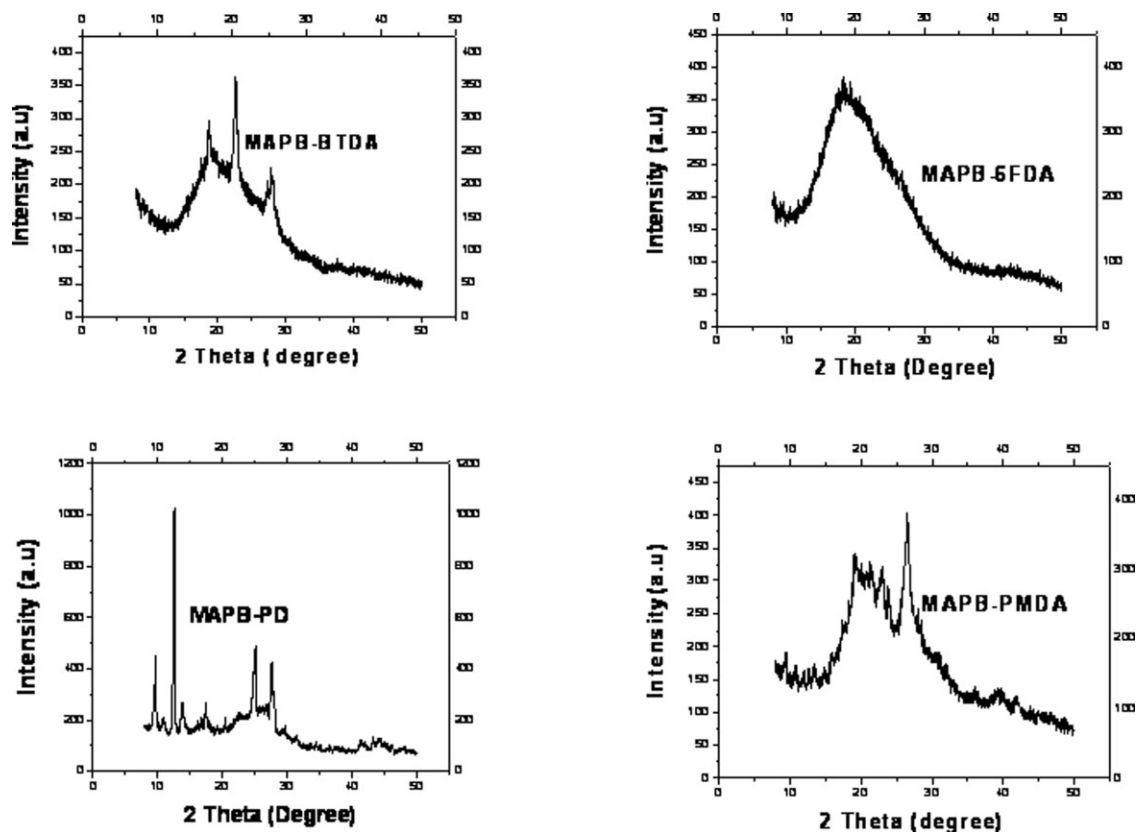


Figure 4 Wide-angle X-ray diffractograms of the polymers.

Moisture absorption studies of the polyimides

The moisture absorption of the polyimides was measured through the weighing of the dried polymer before and after immersion in distilled water at 25°C for 24 h. The moisture absorption of the polyimides ranged from 0.23 to 0.71%. The polyimide MAPB-6FDA exhibited lower moisture absorption (hydrophobicity) than the other polyimides because of the higher fluorine content in the repeat unit.²⁷

Thermal properties

The thermal properties of the polyimides were investigated by thermogravimetric analysis (TGA)

and DSC. For TGA, samples were held for 1 min at 50°C and were run up to 730°C at a heating rate of 20°C/min under an N₂ atmosphere. Similarly, for DSC, samples were held for 1 min at 50°C and were run up to 400°C at a heating rate of 20°C/min. The thermal properties of the polyimides are shown in Table IV.

The thermal stability of the polymers was also evaluated in terms of the temperature at 10% weight loss, maximum degradation temperature, and residual weight at 600°C, as listed in Table IV. The typical TGA and DSC curves are shown in Figure 5. By comparing the maximum degradation temperature and residual weight at 600°C of the synthesized

TABLE IV
Thermal Behavior of the Polymers in a Nitrogen Flow

| Polymer | Specific heat capacity at 200°C (J g ⁻¹ K ⁻¹) ^a | Thermal stability ^b | | Residual weight at 600°C | T _g (°C) | Activation energy (kJ/mol) | Entropy (kJ/mol k) | Enthalpy (kJ/mol) |
|-----------|---|-----------------------------------|------------------------------------|--------------------------|---------------------|----------------------------|--------------------|-------------------|
| | | T ₁₀ (°C) ^c | T _{max} (°C) ^d | | | | | |
| MAPB-BTDA | 2.2149 | 500 | 530 | 60 | — | 44.44 | 0.177 | 42.58 |
| MAPB-6FDA | 1.6985 | 300 | 510 | 54 | 182 | 73.91 | 0.473 | 72.08 |
| MAPB-PD | 1.000 | 550 | 550 | 32 | — | 46.89 | 0.194 | 45.06 |
| MAPB-PMDA | 1.8414 | 270 | 610 | 65 | 191 | 51.04 | 0.245 | 49.21 |

^a Measured by DSC under nitrogen at a heating rate of 10°C/min.

^b Measured by TGA under nitrogen at a heating rate of 10°C/min.

^c Temperature of 10% weight loss.

^d Maximum degradation temperature obtained from differential curves.

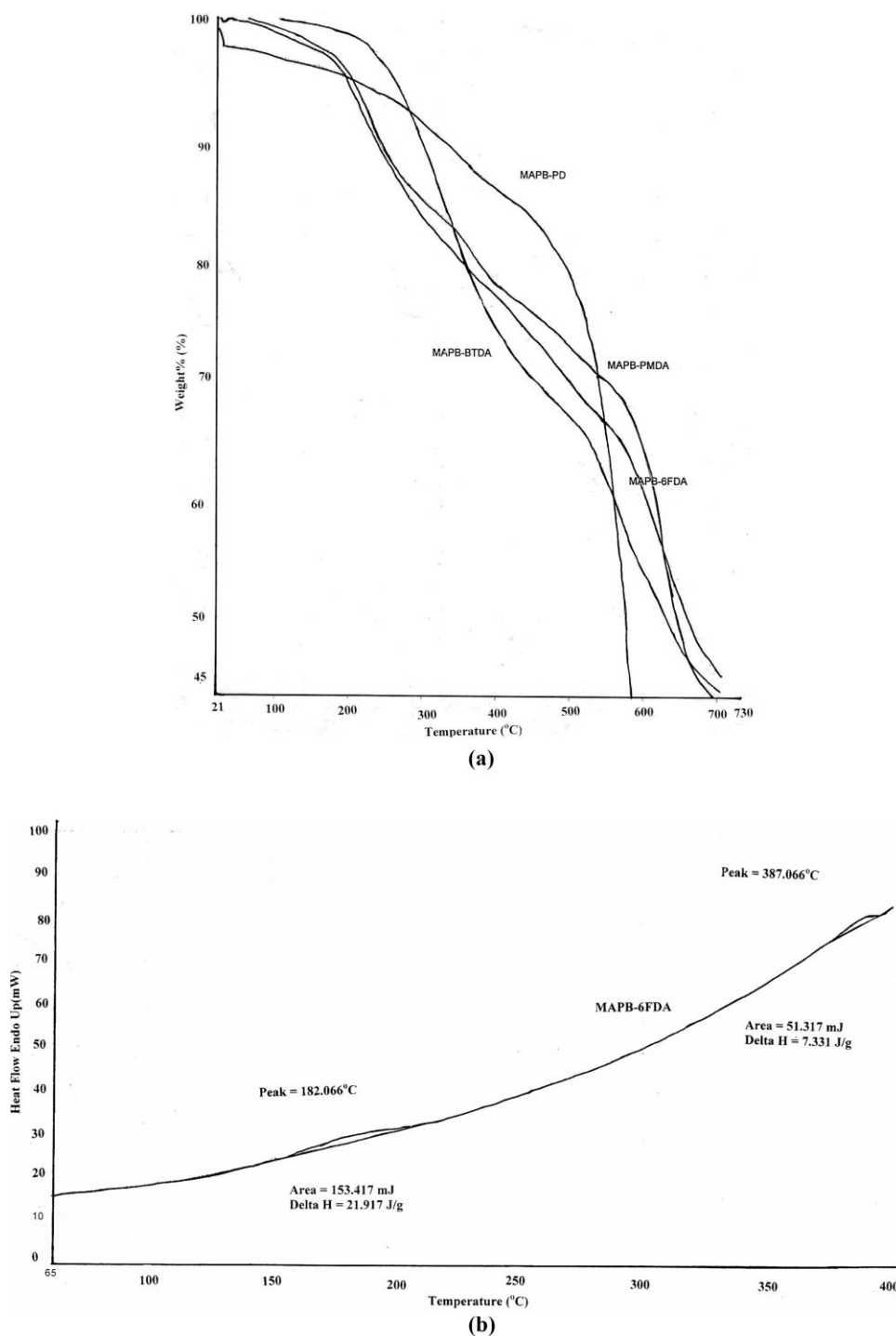


Figure 5 (a) TGA spectra of the synthesized polyimides and (b) DSC scan of the polyimide derived from 6FDA.

polyimides, we observed that the polyimide derived from PMDA had a high maximum degradation temperature and residual weight at 600°C in comparison with the other polyimides because of the very rigid dianhydride monomer and compact aggregation of the polymer chain. The polyimides derived from the PMDA unit also had a higher T_g value than the polyimide from 6FDA because the presence of bulky CF_3 groups reduced the chain interaction, caused the

poor packing of the polymer chains, and lowered the T_g value. The decrease in the T_g value was due to the increased free volume caused by bulky CF_3 groups. By comparing the temperatures at 10% weight loss for the polymers, we can see that the introduction of the diacid PD was especially effective for improving the thermal stability of the polyimides, regardless of the diamine component. This increase in thermal stability can be attributed to the

rigid and bulky PD unit, which inhibited the rotation of bonds, resulting in an increase in chain stiffness,²⁸ whereas the polyimides containing the HF unit were thermally less stable than those with the PD unit; this was probably due to the different packing density of the polymer aggregation and the interaction of the polymer chain.²⁸ The presence of bulky CF₃ groups reduced the chain interactions, caused the poor packing of the polymer chain, and lowered the thermal stability. The temperature at which maximum degradation of the polymers occurred lay between 300 and 550°C. The specific heat capacity ranged from 1.0 to 2.21 J g⁻¹ K⁻¹ at 200°C. *T_g* values of the polyimides ranged from 182 to 191°C. The thermal degradation kinetics for the polymers were calculated from TGA curves, and the activation energy of the pyrolysis was obtained with the Horowitz and Metzger method, which is an integral method used for the determination of kinetic parameters. In this method, the double logarithm of the reciprocal of the weight fraction of the reactant was plotted against the temperature difference, and the kinetic parameters were calculated by some mathematical calculations using a battery program based on the Horowitz and Metzger method. The thermal degradation of the polyimides in the absence of oxygen was believed to involve the direct cleavage of the C–N bond. The activation energy and enthalpy of the polyimides calculated here fell in the range of 44.44–73.91 kJ/mol and 42.58–72.08 kJ/mol K.²⁹ The activation energy of the polyimides can be correlated to the aromatic character in the polymer structure; therefore, the higher value of the activation energy in MAPB–PD can be attributed to the higher aromatic character.

CONCLUSIONS

A new diamine, MAPB, was prepared through the nucleophilic substitution reaction of *p*-chloronitrobenzene and 2-methyl resorcinol followed by the catalytic reduction of the dinitro intermediate by hydrazine monohydrate. A series of polyimides were synthesized from the diamine and various aromatic dianhydrides by thermal imidization. The resulting polyimides had excellent thermal stability and moderate-to-high *T_g* values of 182–191°C. All the polyimides showed semicrystalline patterns, except for MAPB–6FDA, which showed a completely amorphous pattern. Thus, this series of polyimides exhibited a good combination of properties required

for high-performance materials and demonstrated promising potential for future applications.

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