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SHORT COMMUNICATION

Synthesis and characterization of some Schiff-base-containing polyimides

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Abstract The diamine, 4-aminophenyloxy-*N*-4-[(4-amiophenyloxy)benzylidene]aniline, was prepared via the nucleophilic substitution reaction and was polymerized with different dianhydrides either by one-step solution polymerization reaction or two-step procedure. The latter includes ring-opening polyaddition to give poly(amic acid), followed by cyclodehydration to polyimides. The inherent viscosity ranges from 0.61–0.79 dl/g. Some of the polymers were soluble in most of the organic solvents such as DMSO, DMF, DMAc, NMP, and *m*-cresol even at room temperature. The degradation temperature of the resultant polymers falls in the ranges from 240–500 °C in nitrogen with only 10% weight loss. Specific heat capacity at 200 °C ranges from 1.0929–2.6275 J g^{-1} k^{-1}. The temperature at which the maximum degradation of the polymer occurs ranges from 600–630 °C. The glass transition temperature (Tg) values of the polyimides ranged from 185 to 272 °C. The activation energy and enthalpy of the polyimides ranged from 47.5–55.0 kJ/mole and 45.7–53.0 kJ/mole and the moisture absorption in the range of 0.23–0.72%.

Keywords Schiff base · Polyimides · Thermal stability

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Introduction

Aromatic polyimides are considered as a class of high-performance polymers that have found a wide range of applications in advanced technologies [1, 2]. They can be synthesized from the conventional polycondensation of A–A and B–B monomers, namely, an aromatic dianhydride and an aromatic diamine. Many rod-like polyimides, however, are insoluble in common organic solvents due to their rigid backbones, thus, limiting their applications. Therefore, much work has been done to improve the processability of aromatic polyimides while maintaining their excellent level of thermal and mechanical properties [3, 4]. There are a few ways to modify the polymer structure such as introduction of pendent groups (aromatic or alkyl groups) on to the polymer chain [5–9] and incorporation of non-coplanar structural units in the main chain [10]. To achieve such a goal, of course, it is necessary to design and synthesize new monomers, either diamine or dianhydride or both, which can fulfill this requirement. Much effort has been put into designing and synthesizing new dianhydrides [11, 12] and/or diamines [13–17], thus, producing a great variety of soluble and processable polyimides for various purposes.

One of these is poly(azomethine)s, known as polyimines or Schiff-base polymers. The interest for this class of polymers renewed in the last years because aromatic poly(azomethine)s are isoelectronic with poly(*p*-phenylene vinylene)s, which are the most-known electroluminescent polymers [18]. Conjugated poly (azomethines), polyimines or poly-(Schiff bases) are another interesting class of conjugated polymers containing nitrogen atoms in a polymer backbone. The first poly(azomethines) were prepared by Adams et al. from terephthalaldehyde and benzidine and dianisidine in 1923 [19]. The basic aromatic conjugated poly(azomethine) is poly(1,4-phenylene-methylidynenitrilo–1, 4-phenylenenitrilomethylidine; PPV) [20], which is isoelectronic with poly(*p*-phenylene-vinylene; PPV). Unlike PPV, the imine nitrogen of the PPI backbone introduces additional useful features and chemical flexibility including high solubility in concentrated sulfuric acid and the complexation with Lewis acids [20, 21].

A major obstacle to characterizing and developing most conjugated aromatic poly(azomethines) has been their intractability and insolubility in common organic solvents. Several methods have been reported to improve the processability of conjugated poly(azomethines) by modification and selection of polymer structure; for example, unsymmetrical [22] or symmetrical [23] substitutions in the main chain aromatic benzene rings with flexible alkyl or alkoxy side chains. A recent approach based on the reversible Lewis acid–base complexation has also been successfully applied to the processing of non-substituted and substituted poly(azomethines) [21]. Keeping in view the interesting properties of the poly(azomethines), here, we have introduced 4-aminophenyloxy-*N*-4-[(4-aminophenyloxy)benzylidene]aniline (AABA) in the polymer backbone. The preparation and physicochemical characterization including XRD, FTIR, TGA, DSC, and elemental analysis of the polymers are described herein.

Experiment

Materials

p-Fluoronitrobenzene, potassium carbonate, *p*-aminophenol, *p*-hydroxybenzaldehyde, 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (purity≥97%), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (purity≥99%), 3,4,9,10-perylenetetracarboxylic acid dianhydride (purity≥97%), and pyromellitic dianhydrides (purity≥97%) of analytical grade from Aldrich were used as received. All the other reagents and solvents were of analytical grade and used without further purification.

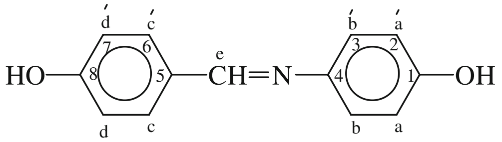
Measurements

^{13}C, ^{1}H NMR spectra were obtained on instrument Jeol 270 spectrophotometer in DMSO-d_6 using tetramethylsilane as an internal reference. Infrared measurements were recorded in the range of 400–4,000 cm^{-1} on Bio-Rad Excalibur FTIR Model FTS 3000 MX. Melting points were recorded on Electrothermal IA 9000 series digital melting point apparatus. Inherent viscosities were obtained using Gilmount falling ball viscometer. Thermal and DSC analysis were carried out using Perkin Elmer TGA-7 and DSC 404C Netzch. Elemental analysis was carried out using Perkin Elmer CHNS/O 2400.Wide-angle diffractograms were obtained in transmission mode with Ni-filtered Cu Kα radiation on a Rigaku Geiger Flex D-3C X-ray diffractometer (Rigaku, Japan). Moisture absorption was determined by weighing the changes of the dried films before and after immersion in deionized water at 25 °C for 24 h. Activation energy, entropy, and enthalpy were calculated using the Horowitz and Metzger method [24].

Monomer synthesis

N-[4-hydroxybenzylidene]-4-aminophenol (**a**)

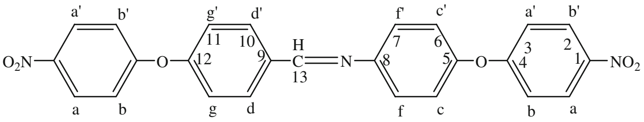
In a two-neck flask equipped with condenser and magnetic stirrer (prebaked on vacuum to exclude any moisture), 2.70 g of *p*-aminophenol (0.025 mol in 15–20 ml of absolute ethanol was treated with 3.05 g of *p*-hydroxybenzaldehyde (0.025 mol) and five to seven drops of glacial acetic acid was added as a catalyst. The reaction mixture was heated at reflux for 6 h and was monitored by TLC. The precipitates were collected by evaporating the solvent on rotary evaporator. The crude product was recrystallized from methanol; yield 82%, m.p. 218 °C. The recrystallized compound was stored in air-tight glass bottles for further studies. Anal. calcd. for $C_{13}H_{11}NO_2$ (213): C=73.23%, H=5.16%, N=6.57% and found C=72.95%, H=5.25%, N=6.75%. IR (KBr pellet) in cm^{-1}: 3,408 (OH stretching), 1,600 (C=C stretching), 1,655 (C=N stretching). ^{1}H NMR (DMSO-d_6) in δ (ppm) and J (Hz): 6.75 (2H, d, $J_{ba}=J_{b'a'}$=7.25), 7.25 (2H, d, $J_{cd}=J_{c'd'}$=8.27), 7.80 (2H, d, $J_{dc}=J_{d'c'}$=8.28), 8.55 (2H, d, $J_{ab}=J_{a'b'}$=7.44), 9.50 (1H, s). ^{13}C NMR (DMSO-d_6) in δ (ppm):116 (2C, C2), 116.1 (2C, C7), 122.6 (2C, C3), 128.2 (C5), 130.7 (2C, C6), 143.5 (C4), 156.1 (C8), 157.4 (C1), 160.4 (C9).



4-Nitrophenyloxy-N-4[(4-nitrophenyloxy)benzylidene] aniline (NNBA) (**b**)

A mixture of 1 g of (**a**; 4.7 mmol), 1.30 g of potassium carbonate (9.4 mmol) and 1 ml of 4-fluoronitrobenzene (9.4 mmol) in a two-neck round-bottom flask having 60 ml of DMAc was treated at 100 °C for 20 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured in 700 ml of water to form dark brown solid which was thoroughly washed with water and separated by filtration. The crude product was recrystallized from ethanol. Yield 87%, m.p. 148°C. Anal. calcd. for

$C_{25}H_{17}N_3O_6$ (455): C=65.93%, H=3.73%, N=9.23% and found C=65.75%, H=3.45%, N=9.08%. IR (KBr pellet) in cm^{-1}: 1,664 (C=N stretching), 1,584 (aromatic C=C), 1,514 and 1,344 (NO$_2$), 1,253 (C−O−C). ^{1}H NMR (DMSO-d_6) in δ (ppm) and J (Hz): 6.21 (2H, d, $J_{cf}=J_{c'f'}=9.12$), 6.30 (4H, d, $J_{ba}=J_{b'a'}=7.02$), 6.31 (2H, d, $J_{fc}=J_{f'c'}=9.10$), 7.30 (2H, d, $J_{dg}=J_{d'g'}=9.79$), 7.43 (2H, d, $J_{gd}=J_{g'd'}=9.82$), 8.37 (4H, d, $J_{ab}=J_{a'b'}=6.98$), 8.39 (1H, s). ^{13}C NMR (DMSO-d_6) in δ (ppm): 102.3 (1C, C8), 109.5 (4C, C3,3′), 116.1 (2C, C10), 125.7 (1C, C12), 125.8 (1C, C9), 129.2 (2C, C11), 130.9 (2C, C1), 132.8 (2C, C6), 134.9 (4C, C2,2′), 135.5 (1C, C5), 157.4 (2C, C4), 158.7 (2C, C7), 159.5 (1C, C13)



4-Aminophenyloxy-N-4-[(4-aminophenyloxy)benzylidene] aniline (AABA) (**c**)

A 250-ml two-neck flask was charged with 1 g of (**b**; 2.20 mmol), 10 ml of hydrazine monohydrate, 80 ml of ethanol and 0.06 g of 5% palladium on carbon (Pd−C). The mixture was refluxed for 16 h and then filtered to remove Pd−C and the resulting solid was recrystallized from ethanol to give 87% yield and was stored in glass bottles for further studies; m.p 178 °C. Anal. calcd. for $C_{25}H_{21}N_3O_6$ (395): C=75.94%, H=5.31%, N=10.63% and found C=75.75%, H=5.08%, N=10.83%. IR (KBr pellet) in cm^{-1}: 3,400, 3,364 (NH$_2$), 1,624 (N−H bending), 1,216 (C−O−C). ^{1}H NMR (DMSO-d_6) in δ (ppm) and J (Hz): 3.6 (4H, s), 6.62 (4H, d, $J_{ab}=J_{a'b'}=8.61$), 6.75 (2H, d, $J_{cf}=J_{c'f'}=9.0$), 6.83 (4H, d, $J_{ba}=J_{b'a'}=8.63$), 6.89 (2H, d, $J_{fc}=J_{f'c'}=8.95$), 7.05 (2H, d,, $J_{gd} = J_{g'd'}=9.70$), 7.81(2H, d, $J_{dg} = J_{d'g'}=9.68$), 8.67(1H,s), ^{13}C NMR (DMSO-d_6) in δ (ppm): 115.4 (2C, C1), 115.9 (4C, C3,3′), 119.4 (4C, C2,2′), 121.8 (2C, C10), 127 (1C, C8), 130.6(2C,C11), 138.9 (2C, C6), 143.3(2C, C7), 145(1C,C9), 145.7(1C,C12), 146.3(1C, C5), 149.3 (2C, C4), 161 (1C, C13; Fig. 1).

Polymer synthesis

To a stirred solution of AABA (0.49 g, 1.238 mmol) in 8 ml of DMAc was added 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BP; 0.4 g, 1.238 mmol). The mixture was stirred at room temperature for 2 h under argon atmosphere to form a polyamic acid (precursor). The film was casted onto a glass plate by heating this solution of polyamic acid for 18 h at 80 °C, 2 h at 150 °C, 2 h at 200 °C, 2 h at 250 °C, and 2 h at 280 °C which converted polymeric acid into polyimide films. The same procedure was adopted for the polymerization of AABA with 4,4′-hexafluoroisopropylidene diphthalic anhydride (HF) and pyromellitic dianhydrides (PMDA), however, the polymerization with perylene dianhydride was carried out by the following procedure: in a 250-ml two-neck round-bottom flask fitted with nitrogen inlet and outlet [(0.50 g, 1.27 mmol), dianhydride (0.5 g, 1.27 mmol)], *m*-cresol diamine (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 (1 N) sodium hydroxide followed by water. After drying at 150 °C overnight, polyimide was obtained as dark red solid. The inherent viscosities of the polymers were subsequently determined at a concentration of 0.2 g/dl at 25 °C.

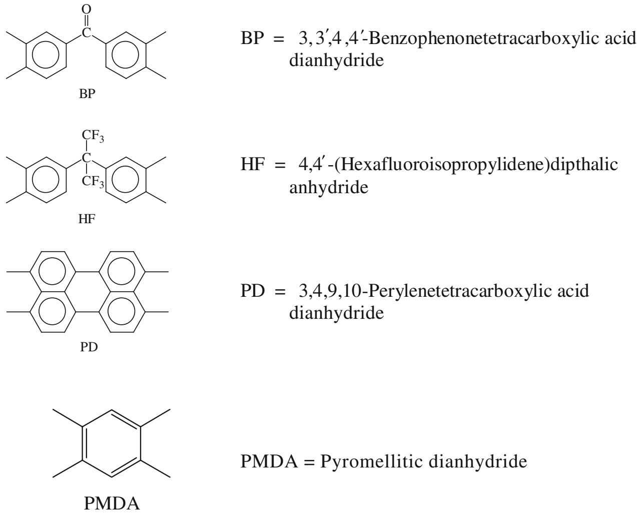
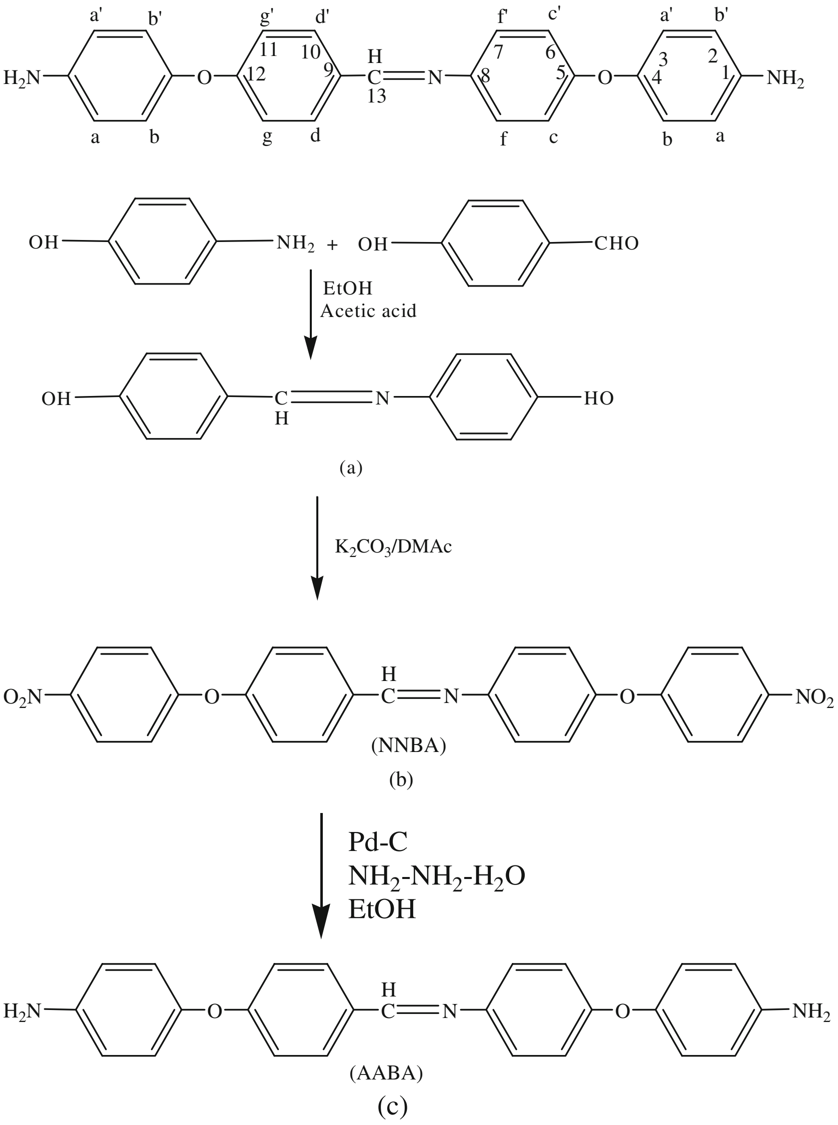


Fig. 1 Four different acid dianhydrides used for polymerization

Results and discussion

Monomer synthesis

The diamine AABA was synthesized in three steps (Scheme 1). Compound (**a**) was prepared by refluxing *p*-aminophenol and *p*-hydroxybenzaldehyde in the presence of catalytic amount of acid in dry ethanol for 6 h. The crude product was recrystallized in methanol. The second step involves the nucleophilic substitution reaction of the *N*-[4-hydroxybenzylidene]-4-aminophenol and *p*-fluoronitrobenzene in the presence of anhydrous potassium carbonate to obtain the dinitro compound (NNBA). In the third step, diamine AABA was prepared by the reduction of dinitro compound with hydrazine monohydrate/Pd−C. All the synthesized compounds were characterized by IR, NMR,



Scheme 1 Synthesized diamine AABA

and elemental analysis. The structures of the dinitro compound and diamine monomer were confirmed by elemental analysis as well as FTIR and NMR spectroscopic techniques. In IR spectrum, NNBA revealed absorption bands around 1,514 and 1,344 cm^{-1} due to symmetric and asymmetric stretching of the nitro group. After reduction, the characteristic absorption of nitro groups disappeared and the characteristic bands of amino groups at 3,400 and 3,364 cm^{-1} (N–H stretching), 1,624 cm^{-1} (N–H bending), and 1,621 cm^{-1} (C=N stretching) were observed. ^{1}H NMR and ^{13}C NMR of the dinitro and diamine in DMSO-d_6 were taken to confirm the structures. The ^{1}H NMR spectrum confirms that the nitro groups have been completely converted in to amine groups by the high-field shift of the aromatic protons and the signal at 3.6 ppm corresponds to the amino group. In the ^{13}C NMR spectrum of the diamine monomer, all the carbon atoms resonated in the region of 115–161 ppm and the data is consistent with the proposed structure.

Polymer synthesis

The diamine monomer was polymerized with four different aromatic dianhydrides namely 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BP), 4,4′-hexafluoroisopropylidene)diphthalic anhydride (HF), pyromellitic dianhydrides (PMDA) and 3,4,9,10-perylene tetracarboxylic acid dianhydride (PD). The polyimides of BP,HF, and PMDA were prepared by following a conventional two-step procedure before the ring-opening polyaddition at room temperature to poly(amic acid), followed by sequential heating to 280 °C to obtain the corresponding polyimides.

Table 1 Inherent viscosity and solubility of polymers

Polymer	DMSO	DMF	DMAc	*m*-cresol	THF	H_2SO_4	η_{inn} (dl/gm)
AABA-BP	−	−	−	−	−	+	−
AABA-HF	++	++	++	++	−	+++	0.79[a]
AABA-PD	+	+	+	+	−	++	0.61[b]
AABA-PMDA	−	−	−	−	−	++	0.63[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 H_2SO_4

The polyimide of perylene dianhydride was prepared by a different method. The polyamic acid precursors were prepared by the addition of dianhydride to the diamine solution gradually. The molecular weights were high enough to cast flexible, tough, and transparent poly(amic acid) films. The thermal conversion to polyimides was carried out by heating the poly(amic acid) films at 80 °C for 18 h, 150 °C for 2 h, 200 °C for 2 h, and 280 °C for 2 h. A rapid temperature elevation resulted in cracked or brittle films. The inherent viscosities determined for some polymer films give values in the range of 0.61–0.79 dl/g at a concentration of 0.2 g/dl at 25 °C which indicates high molecular weights of the polymers as shown in Table 1. The polyimides obtained were subjected to solubility and thermal studies. Some of the thermally cured exhibited excellent solubility in polar solvents such as DMSO, DMF, and DMAc. The formation of polyimides was confirmed by IR and elemental analysis. All the polyimides exhibited the characteristic imide group absorption around 1,780 and 1,725 cm^{-1} (typical of imide carbonyl a symmetric and asymmetric stretching), 1,380 cm^{-1} (C−N stretch) and 1,100 and 730 cm^{-1} (imide-ring deformation). The disappearance of the amide and carboxyl bands indicated a virtually complete conversion of the poly(amic acid) precursor into polyimides. The results of the elemental analysis of all the polyimides are found in good agreement with the calculated one. The inherent viscosities determined for polymer films except AABA-BP and gave values in the range of 0.61–0.79 dl/g, reflecting high molecular weight of the polymers [25]. The solubility of the polyimides was determined qualitatively and the results are listed in Table 1. The solvents like DMSO, DMF, DMAc, *m*-cresol, and THF were tested. Some polymers are soluble on heating while some are slightly soluble and some are insoluble.

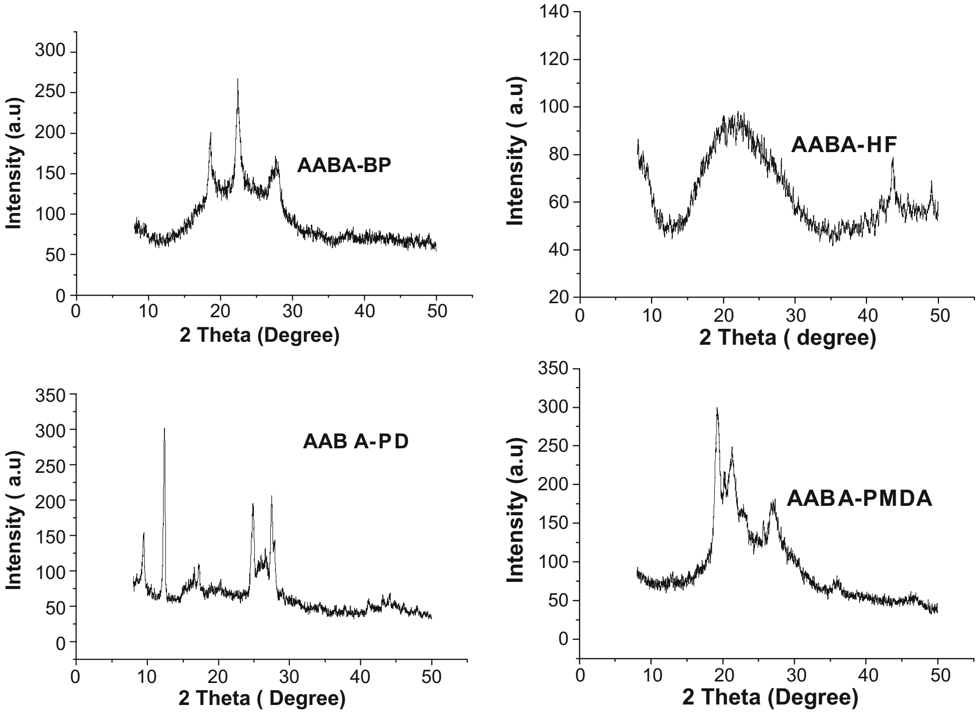


Fig. 2 Wide-angle X-ray diffractograms of polymers

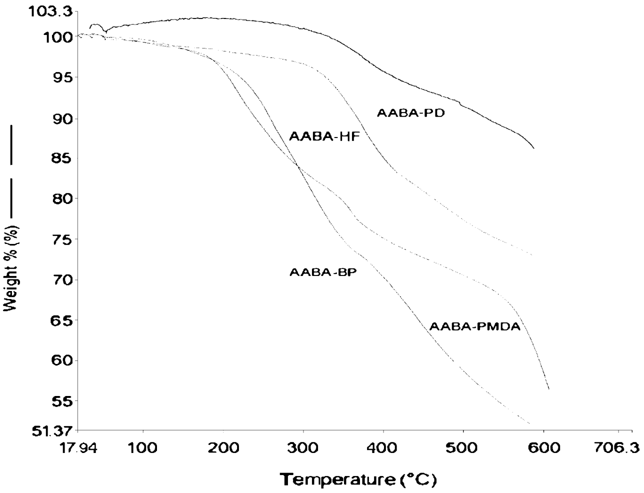


Fig. 3 TGA curves of the synthesized polyimides

Organo solubility

The organo solubility behavior of the polymers generally depended on their chain-packing ability and intermolecular interactions that was affected by the rigidity, symmetry, and the regularity of the backbone. From Table 1, it was noticed that the introduction of fluorinated dianhydride component (HF) is especially effective for the high solubility, irrespective of the diamine component. This increase in solubility might be attributed to the molecular asymmetry and the presence of bulky trifluoromethyl groups, which increase the disorder in the chains and hinders the dense chain stacking, thereby reducing the interchain interactions and so enhancing solubility. The poor solubility of the thermally cured polyimides might be attributed to cross-linking within polymer chain or the tight chain packing and aggregation during imidization at elevated temperature. Besides, the solubility behavior of the polyimides obtained with AABA was also attributed to the capability of the hydrogen bonding.

X-ray diffraction data

All the polyimides were characterized with WAXD studies. As can be seen from the diffraction pattern shown in Fig. 2, all the polyimides except AABA-HF displayed a semicrystalline pattern whereas AABA-HF displayed a nearly completely amorphous pattern because the bulky CF_3 groups disrupted the symmetry or dense chain packing led to highly ordered regions [25].

Moisture absorption of the polyimides

The moisture absorption of the polyimides ranges from 0.23–0.72%. The polyimide AABA-HF containing a fluorine unit exhibited the lowest moisture absorption than the other polyimides. AABA-HF exhibited the lowest moisture absorption (hydrophobicity) because of the higher fluorine content in the repeat unit (Fig. 3).

Thermal properties

Thermal properties of the polyimides were investigated by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. Table 2 presents the thermal properties of the polyimides. The results of the TGA analysis showed no significant weight loss below 300 °C in nitrogen. The maximum degradation temperature ($T_{\max}$) for most of the polymers lies between 600 and 630 °C. The thermal stability of the polymers was also evaluated in terms of 10% weight loss (T_{10}), maximum degradation temperature ($T_{\max}$), and residual weight at 600 °C as listed in Table 2. It has been

Table 2 Thermal behavior of polymers in nitrogen flow

Polymer	Sp. heat capacity[a] at 200°C (J g^{-1} k^{-1})	Thermal stability[b]		R_{600} (%)[e]	Tg (°C)[f]	Activation energy (kJ/mol)	Entropy (kJ/mol k)	Enthalpy (kJ/mol)
		T_{10} (°C)[c]	$T_{\max}$(°C)[d]					
AABA-BP	2.5473	300	620	70	190	54.5	0.261	52.6
AABA-HF	1.5186	360	630	71.1	272	53.0	0.252	51.0
AABA-PD	1.0929	500	600	72	–	55.0	0.273	53.0
AABA-PMDA	2.6275	240	600	60	185	47.5	0.203	45.7

[a] Measured from DSC under nitrogen at heating rate of 10 °C/min

[b] Measured from TGA under nitrogen at heating rate of 10 °C/min

[c] Temperature at 10% weight loss

[d] Maximum degradation temperature obtained from differential curves

[e] Residual weight at 600 °C

[f] Tg (glass transition temperature)

seen by comparing T_{10} of the polymers that the introduction of the diacid PD is especially effective to improve the thermal stability of the polyimides regardless of the diamine component. This increase in thermal stability is attributed to a rigid and bulky PD unit which inhibit the rotation of bonds, resulting in an increase in chain stiffness while the polyimides having an HF unit are less thermally stable than the PD unit which is probably due to the different packing density of the polymer aggregation and the interaction of the polymer chain. The presence of a bulky CF_3 group reduces the chain interactions and causes the poor packing of the polymer chain and lowers the thermal stability. The specific heat capacity ranges from 1.0929 to 2.6275 J g^{-1} k^{-1} at 200 °C. Tg values of the polyimides ranged from 185 to 272 °C. The thermal degradation kinetics for the polymers was calculated from TGA curves and the activation energy of the pyrolysis was obtained using the Horowitz and Metzger method which is an integral method for the determination of kinetic parameters. In this method, double logarithm of the reciprocal of the weight fraction of the reactant is 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 the oxygen is believed to involve the direct cleavage of the C–N bond. The activation energy and enthalpy of the polyimides calculated here fall in the range of 47.5–55.0 kJ/mole and 45.7–53.0 kJ/mole.

Conclusions

The diamine AABA was successfully prepared in high purity and high yield and was polymerized with four different aromatic dianhydrides to obtain moderate- to high-molecular-weight polyimides. Polyimides with 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride, 4,4′-(hexafluoroisopropylidene) diphthalic anhydride and pyromellitic dianhydrides could be thermally converted into tough and flexible polyimide films. Few polyimides synthesized were soluble in most of the organic solvents such as DMSO, DMF, DMAc, and *m*-cresol. The degradation for 10% weight loss ranges from 240–500 °C. The maximum degradation temperature ranges from 600–630 °C and specific heat capacity from 1.0929 to 2.6275 J g^{-1} k^{-1} at 200 °C. Tg values of the polyimides ranged from 185 to 272°C. All polyimides show a semicrystalline pattern except AABA-HF, which shows a completely amorphous pattern. The moisture absorption of the polyimides is in the range of 0.23–0.72%. Activation energy and enthalpy of the polyimides is in the range of 47.5–55.0 kJ/mole and 45.7–53.0 kJ/mole. These polyimides could be considered as new processable high-performance polymeric materials.

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