

Synthesis and Properties of Organosoluble Polyimides Based on Novel Flourene-ring Containing Diacetamido-Diamine

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ABSTRACT: A new diacetamido-diamine monomer, *N'*-[7-(acetyl-4-aminoanilino)-9,9-dioctylfluorene-2-yl]-*N'*-4-aminophenyl acetamide (ADOAc), with flourene-based structure was prepared from the reaction of 4-aminoacetanilide with 2,7-dibromo-9,9-dioctylfluorene in the presence of 10 mol % CuI, 20 mol % *N,N'*-dimethylethylene diamine as catalyst and K_2CO_3 as base. Two new flourene-ring containing polyimides were prepared from the reaction of ADOAc with aromatic dianhydrides such as pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) via chemical imidization of poly(amic acid). The new diamine and the related polyimides were characterized by using conventional methods

such as FT-IR, NMR, and elemental analysis. The polyimides obtained from the reaction of ADOAc with PMDA (PIa) and of ADOAc with BTDA (PIb) had inherent viscosity of 0.49 and 0.58 dL/g respectively, and showed excellent solubility in a variety of organic solvents. The polyimides of PIa and PIb showed excellent thermal stability with 10% weight loss in nitrogen atmosphere at temperatures of 418°C and 407°C and T_g of 172°C and 167°C, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 815–821, 2009

Key words: polyimide; soluble; thermal properties; synthesis

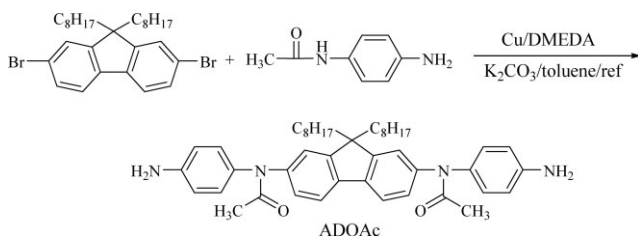
INTRODUCTION

Wholly aromatic polyimides are well accepted as high performance material for their excellent thermal stabilities, chemical resistance, mechanical and electrical properties.^{1–3} Polyimides are mainly used in the aerospace and electronic industries in the form of films and moldings. However, aromatic polyimides are usually difficult to process because of their poor solubility in organic solvents and high melting or softening temperature. Fully aromatic polyimides are mostly insoluble in conventional organic solvents and infusible materials.⁴ To develop easily process able high-performance polyimides, modifications that increase the solubility while maintaining the rigid-rod character and the thermal stability are of particular interest. Many attempts have been made to improve the solubility and process ability of polymers by introduction of: Flexible segments (such as $-O-$, $-S-$, $-CO-$, $-SO_2-$, $-CH_2-$, $-NHCO-$ and/or metasubstituted phenylene) which provide kinks between the rigid phenyl rings in the backbone and lead to enhanced solubility,^{5–10} bulky lateral substituents (such as *t*-butyl,

phenyl, and adamantly groups) which decrease close-packing in the polymer backbone and lead to enhanced solubility of the polymer,^{11–16} 2,2'-disubstituted biphenylene in a para-linked polymer chain which lower the crystallization tendency markedly and enhance the solubility significantly as a result of decreasing the intermolecular forces between the polymer chains,^{17–21} unsymmetrical moieties in the backbone of polyimide such as phthalazinone heterocyclic units,^{22–25} alicyclic moieties into the polymer backbone,^{26–28} and flexible alkyl side chain groups which decrease close-packing and produces amorphous soluble polymers.^{29,30} Another approach to overcome this problem has been development of poly(amide-imides)s (PAI) as an alternative material offering a compromise between thermal stability and process ability. A number of PAIs containing different extent of amide to imide ratios have been reported by following different synthetic pathways.^{31–35}

In this study, we report a successful synthesis of a novel diacetamido-diamine monomer by using a new amidation method based on Cu(I) as catalyst.³⁶ The monomer contains diacetamido-diamine groups and flourene ring with flexible aliphatic side chains. The characterization of monomer was carried out by FT-IR, ¹HNMR, and elemental analysis. The diacetamido-diamine was used in polycondensation reaction

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Scheme 1 Synthesis procedure for preparation of *N'*-[7-(acetyl-4-aminoanilino)-9,9-dioctylfluorene-2-yl]-*N'*-4-aminophenyl acetamide (ADOAc).

with two aromatic dianhydrides to prepare new polyimides. The polyimides were characterized by FT-IR and NMR spectroscopies, and also their inherent viscosity, solubility, and thermal properties were studied.

EXPERIMENTAL

Materials

All chemicals were purchased either from Merck or Fluka Co. (Germany). 2,7-dibromo-9,9-dioctylfluorene was synthesized according to the procedure given in the literature.^{37,38} Toluene was purified by distillation over sodium. *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were purified by distillation over calcium hydride under reduced pressure. Dianhydrides [Pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)] were dried in a vacuum oven at 110°C for 5 h. All other reagents and solvents were used without further purification.

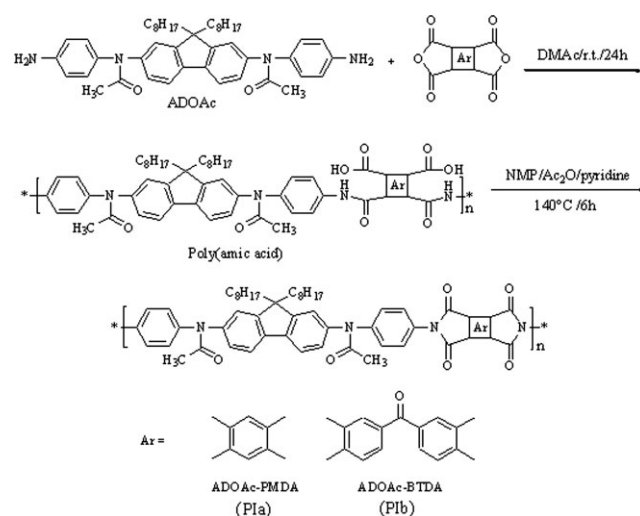
Instruments

IR spectra were recorded on KBr pellets by using Bruker FTIR Vector 22 spectrophotometer (USA) over the range of 400–4000 cm^{-1} . $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded by using Bruker DRX 500 MHz Advance instrument (Germany), with CDCl_3 and DMSO-d_6 as solvent. Elemental analysis was carried out by using a CHN-600 Leco elemental analyzer. Melting point (uncorrected) was measured by using a Barnstead Electro thermal engineering LTD 9200 apparatus (Germany). Inherent viscosity (at a concentration of 0.5 g/dL) was measured by using Ubbelohde suspended-level viscometer at 25°C in NMP as solvent. Thermo gravimetric analysis (TGA) was carried out in the temperature range of 30–700°C by using TGA 951 analyzer of Du Pont Instruments (USA) well equipped with a PC at a heating rate of 10°C/min under nitrogen atmosphere (20 cm^3/min). Differential scanning calorimeter (DSC) was recorded by using Pyris 6 DSC of Perkin-Elmer (USA) under nitrogen atmosphere (20 cm^3/min) and at a heating rate of 10°C/min.

Synthesis of *N'*-[7-(acetyl-4-aminoanilino)-9,9-dioctylfluorene-2-yl]-*N'*-4-aminophenyl acetamide (ADOAc)

A 100 mL two-necked flask equipped with a magnetic stirrer, a condenser, and an argon inlet/outlet tube was charged with CuI (0.192 g, 1 mmol, 10 mol %), 9,9-dioctyl-2,7-dibromofluorene (2.74 g, 5 mmol), 4-aminoacetanilide (1.88 g, 12.5 mmol), and K_2CO_3 (2.8 g, 20.3 mmol), briefly evacuated, and backfilled with argon. *N,N'*-dimethylethylene diamine (DMEDA) (0.2152 mL, 2 mmol) and toluene (20 mL) were added under argon. The reaction mixture was stirred at 110–115°C for 36 h. During this time, progress of the reaction was monitored by thin-layer chromatography. The resulting pale-brown suspension was allowed to reach room temperature and then filtered through a 0.5 × 1 cm pad of silica gel eluting with a mixture of 1:1 ethyl acetate-dichloromethane (100 mL). The filtrate was evaporated, and then purified with column chromatography (SiO_2 , ethyl acetate-dichloromethane 1:4). Pale-brown crystalline product was obtained with the overall yield of 89.6% (3.8 g) and melting point of 119–121°C. Elemental analysis of the diamine ($\text{C}_{45}\text{H}_{58}\text{N}_4\text{O}_2$) was calculated: C, 78.71%; H, 8.45%; N, 8.16%, and found: C, 78.58%; H, 8.56%; N, —. The procedure for the preparation of diacetamidodiamine is shown in Scheme 1. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ (ppm): 7.63(b,2H), 7.26–7.20(m,4H), 7.09(d,4H), 6.70(b,4H), 3.78(s,4H), 2.11(s,6H), 1.91(b,4H), 1.26–.04(m,20H), 0.88(t,6H), 0.66(b, 4H).

$^{13}\text{C-NMR}$ (500 MHz, CDCl_3) δ (ppm): 171.39, 145.06, 143.13, 129.77, 127.73, 127.30, 124.97, 123.30, 121.11, 119.98, 116.01, 55.71, 40.38, 32.20, 30.31, 30.13, 29.64, 29.50, 24.30, 23.04, 14.55.



Scheme 2 Synthesis procedure for preparation of polyimides.

TABLE I
Yield, Spectroscopic Data, and Elemental Analysis of Polyimides

Polyimide code	Yield (%)	¹ H NMR δ(ppm)	FT-IR ν(cm ⁻¹)	Elemental analysis					
				Calculated (%)			Found (%)		
				C	H	N	C	H	N
PIa C ₅₄ H ₅₆ N ₄ O ₆	91	8.36(2H), 7.86–7.36(14H), 2.03–1.94(10H), 0.96(20H), 0.78(6H), 0.50(4H).	3051, 2927 and 2857, 1777, 1729, 1671, 1608, 1509, 1466, 1368, 1297, 1113, 1092, 1015, 817, 725.	75.68	6.58	6.54	76.11	6.41	–
PIb C ₆₁ H ₆₀ N ₄ O ₇	92	8.25(2H), 8.18–8.14(4H), 7.89(2H), 7.47(12H), 2.01(10H), 0.97(20H), 0.72(6H), 0.53(4H).	3050, 2926 and 2860, 1783, 1729, 1678, 1605, 1510, 1470, 1371, 1298, 1210, 1090, 830, 725.	76.23	6.29	5.83	76.50	6.27	–

Polyimide synthesis

General procedure for the preparation of polyimides is illustrated in Scheme 2. A 100-mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 2 mmol (1.37 g) of the diamine (ADOAc) and 15 mL of dry NMP. The mixture was stirred at 0°C for 0.5 h. Then 2 mmol of dianhydride was added and the mixture was stirred at 0°C for 1 h. The temperature was raised to room temperature and the solution was stirred for 24 h. Poly(amic acid) was precipitated by pouring the flask content into 200 mL of a 3:1 volume mixture of water and methanol. Then it was filtered, washed with hot water and dried overnight in vacuum at 40°C, (the overall yields of poly(amic acid) was > 90%). Chemical cyclization was applied for conversion of poly(amic acid) to polyimide: Into a 100-mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and a reflux condenser was placed 1.0 g of poly(amic acid) and 5 mL of dry DMAc. The mixture was stirred and then 5 mL of acetic anhydride and 2.5 mL of pyridine were

added. The mixture was stirred for 0.5 h and then slowly heated to 140°C and held for 6 h at the same temperature. After that the mixture was cooled and poured into water, it then was filtered, washed with hot water and methanol, and dried overnight in vacuum at 120°C. The overall yields of polyimide were over 90%.

RESULTS AND DISCUSSION

Monomer synthesis and characterization

The diacetamido-diamine monomer (ADOAc) was synthesized in one step by the C(aryl)-N coupling reaction (amidation) of 2,7-dibromo-9,9-dioctylfluorene with 4-aminoacetanilide in the presence of CuI/DMEDA as catalyst and K₂CO₃ as base. The synthesis conditions are also shown in Scheme 1. FT-IR, ¹H-NMR, ¹³C-NMR, and elemental analysis were used to confirm the structure of the prepared monomer. FT-IR spectra of ADOAc showed characteristic bands at 3459–3357 cm⁻¹ (N–H stretching), 3033 (aromatic C–H stretching), 2926–2860 (C–H stretching of CH₃ groups), 1656 (C=O), and 1583 (C=C). The

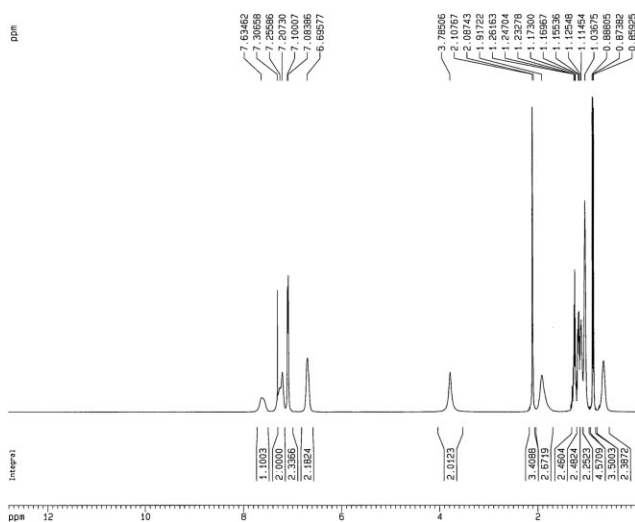


Figure 1 ¹H NMR, spectra of diamine (ADOAc).

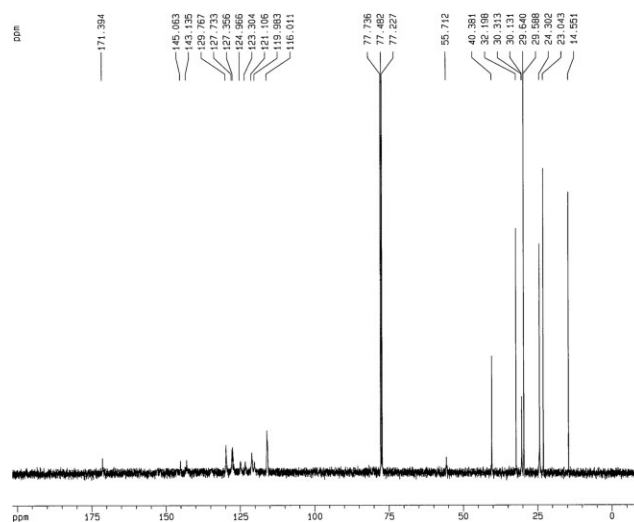


Figure 2 ¹³C NMR spectra of diamine (ADOAc).

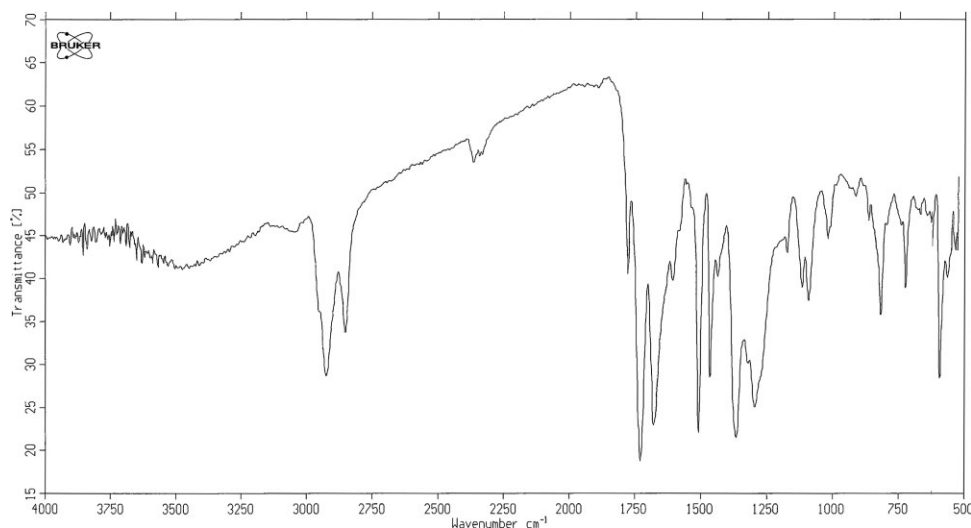


Figure 3 FTIR spectra of PIa.

$^1\text{H-NMR}$ spectra showed the characteristic signals at 3.78 ppm, related to NH_2 protons. The $^{13}\text{C-NMR}$ spectra also showed the characteristic signals at 171.39 ppm related to the carbon of carbonyl group. The general characterization data are shown in Table I. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra are shown in Figures 1 and 2, respectively.

Polyimides preparation and characterization

Polyimides were prepared by the conventional two-step polymerization method, as outlined in Scheme 2, involving ring-opening polyaddition of diamine (ADOAc) with aromatic dianhydrides (PMDA and BTDA) forming poly(amic acid) and subsequent chemical imidization. Reaction of dianhydrides with diamine at ambient temperature gave viscous poly(amic acid) solutions. The chemical imidization of poly(amic acid) proceeded with a dehydrating agent such as a mixture of acetic anhydride and pyridine. The dehydration was effective and afforded polyimides.

The chemical structure of the polyimides was characterized by FT-IR, $^1\text{H-NMR}$, and elemental analysis. The elemental analysis data (Table I) of the polyimides were in good agreement with their calculated values. Figure 3 shows the FTIR spectrum of a representative polyimide. FT-IR spectrum shows the characteristic bands at 3050 cm^{-1} (aromatic C—H stretching), 2927 and 2860 cm^{-1} (C—H stretching of CH_3 groups), 1780 and 1729 cm^{-1} (asymmetric and symmetric stretches of imide carbonyl groups C=O), 1675 (amide C=O group), 1605 and 1510 (aromatic C=C stretching), 1298 (C—O stretching), a band at 1364 from C—N—C stretching of the imide ring, and at 1100 and 725 from imide ring deformation which all confirmed the formation of imide structure. The

$^1\text{H-NMR}$ spectrum of the representative polyimide (PI1a) is shown in Figure 4. $^1\text{H-NMR}$ spectrum shows two group characteristic signals at the aromatic region of 7.36–8.36 ppm and aliphatic region of 0.50–2.16 ppm. The integral signals were analyzed to compare the real amount of aliphatic and aromatic protons with the theoretical ones:

- For real results of PIa: aliphatic/aromatic = 2.55 and of PIb: aliphatic/aromatic = 1.98
- For theoretical assumption of PIa: aliphatic/aromatic = 2.50 and of PIb: aliphatic/aromatic = 2.00

Comparison of the ratios of real amounts of aromatic and aliphatic with the theoretical assumptions confirmed the chemical structure of new polyimides (Figs. 3 and 4). The spectroscopic data of the

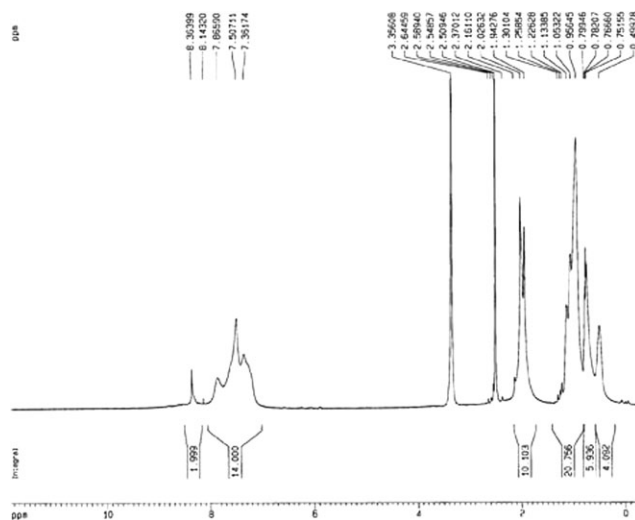


Figure 4 $^1\text{H-NMR}$ spectra of PIa.

TABLE II
Inherent Viscosity and Solubility of Polyimides

Polyimide code	η_{inh} (dl/g)	DMAC	DMF	NMP	DMSO	HMPA	DO	PY	THF	CCl ₄
PIa	0.49	++	++	++	+h	+h	++	++	++	+h
PIb	0.58	++	++	++	+h	+h	++	++	++	+h

++, Soluble at room temperature; +h, Soluble after heating (60°C); DMAC, *N,N*-dimethyl acetamide; DMF, *N,N'*-dimethyl formamide; NMP, *N*-methyl pyrrolidone; DMSO, dimethyl sulfoxide; HMPA, hexamethyl phosphor amide; DO, dioxane; Py, pyridin; THF, tetrahydro furan.

polyimides agreed well with the proposed structure shown in Scheme 2. The yield, spectroscopic data and elemental analysis of polyimides are collected in Table I.

Polyimides properties

One of the major objectives of this study was to produce modified polyimides with improved solubility. The polyimides were readily soluble in common polar aprotic solvents at room temperature, Table II. These polymers exhibited a good solubility in a variety of solvents such as DMAC, *N,N'*-dimethyl formamide (DMF), *N*-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), hexamethyl phosphor amide (HMPA), dioxane, pyridine, and tetrahydro furan (THF). The excellent solubility of polyimides may be as a result of structural modification through the incorporation of two octyl groups at the 9-position of the fluorene ring and acetamide (-N(CO(CH₃))-) moieties in the repeating unit of the polymer chain. These groups disturb the planarity of aromatic units, render chain close packing and crystallinity, increase fractional free volume that increases chain rotational and flexural mobility, and thus leading to the increase in solubility.

The inherent viscosity of the polyamides, as a suitable criterion for the evaluation of molecular weight, was measured at a concentration of 0.5 g/dL in DMF at 25°C (Table II). According to the type of bridging between the phthalimide groups in the dianhydride part of the polyimide and the mobility of polymer chain, the inherent viscosity of the polyimide containing PMDA was higher than that of the BTDA. The inherent viscosity of the polyimides, PIa

and PIb, varied from 0.49 to 0.58 dL/g, respectively. The molecular weights of polyimides were sufficient for casting tough and flexible films.

The thermal properties of the polyimides were evaluated by DSC and TGA and the data are summarized in Table III. DSC curves of the representative polyimides were shown in Figure 5. The glass transition temperatures (T_g) of the polyimides were found to be 172°C and 167°C for PIa and PIb, respectively. The PMDA-based polyimide (PIa) exhibited higher T_g values than the BTDA-based polyimide because of the presence of a rigid pyromellitic unit which enhanced the rigidity of the polymer chain and hence the T_g . In general, the polyimides prepared in the present study exhibited lower T_g values than those reported for other polyamides (>288°C and > 218°C)^{20,25} and also for the commercial polyimide, namely, Ultem 1000 (T_g 215°C). This property can make these polyimides attractive from the point of processability as long as the thermal stability does not reduce significantly which is discussed below.

TGA curves of the representative polyimides were shown in Figure 6. The relative thermal stability of the polyimides was determined by noting the initial decomposition temperature, the temperature of maximum rate of weight loss (T_{max}) and the percent of char yield at 700°C. The results are summarized in Table III. The weight loss of polyimides started at temperature of above 240°C and a significant weight loss occurred only beyond this temperature. A 10% weight loss temperature (T_{10}) of the polyimides in the atmosphere of nitrogen at a heating rate of 10°C min⁻¹ was observed in the temperature range of 407–418°C indicating high thermal stability of the

TABLE III
Thermal Characteristic Data of Polyimides

Polyimide code	T_g (°C)	IDT	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield % at 700°C	LOI
PIa	172	240	374	418	467	58.42	40.86
PIb	167	238	356	407	446	53.57	38.9

T_g , glass transition temperature; IDT, initial decomposition temperature; T_5 , temperature for 5% weight loss; T_{10} , temperature for 10% weight loss; T_{max} : maximum decomposition temperature; Char yield, weight of polymer remained at 700°C; LOI, limiting oxygen index.

polymers. A major mass loss from 85 to 65% was observed in the temperature range of 450–550°C. The char yield of the polyimides PIa and PIb, which correlates to the ability to sustain combustion, was high (58.4% and 53.5%) at 700°C. The char yield tends to depend on the structure of diimide and it was highest for PMDA-based polyimide which can be due to the stiffness of the polymer chain because of the presence of rigid pyromellitic unit. To compare the thermal behavior of the polyamides, BTDA-based polyimide with carbonyl group which provides kinks between the rigid phenyl rings in the backbone of polymer increase the flexibility of polyimide chains and thus reduce thermal properties to some extent. The Char yield can also be used as criteria for evaluating limiting oxygen index (LOI) of the polyimides in accordance with Van Krevelen and Hoftyzer equation.³⁹

$$\text{LOI} = 17.5 + 0.4 \text{ CR}$$

where CR = char yield

Both polyimides PIa and PIb had LOI values, calculated based on their char yield, higher than 28. On the basis of LOI values, such materials can be classified as self-extinguishing and flame resistant polymer.

CONCLUSIONS

A novel aromatic diacetamido-diamine monomer was prepared containing fluorene ring with long aliphatic side chains and characterized by conventional methods. The synthesized aromatic diacetamido-diamine monomer was used for the preparation of

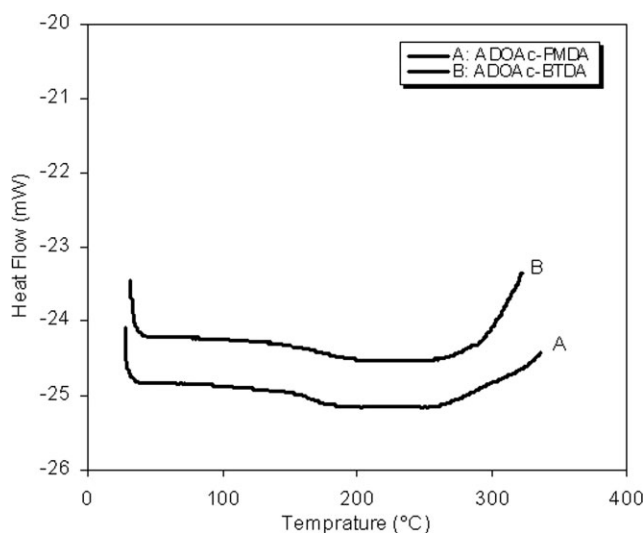


Figure 5 The DSC curves of PIa and PIb.

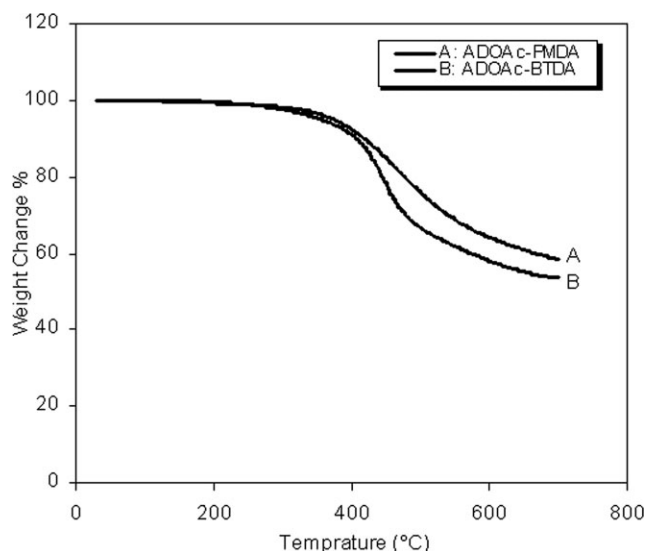


Figure 6 The TGA curves of PIa and PIb.

polyimides in reaction with two aromatic tetracarboxylic acid dianhydrides. The introduction of substituted fluorene ring with acetamide groups along the polymer backbone resulted in polyimides with nicely balanced solubility and thermal stability. These polymers exhibited the characteristic of thermal stability by the fluorene group with reduced glass transition temperature of the rigid-rod-like structure which could improve the processing characteristics. These properties can make these polyimides attractive for practical applications such as processable high-temperature engineering plastics.

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