

New Fluorene-Based Thermally Stable Five- and Six-Membered Rings Polyimides with Enhanced Solubility

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ABSTRACT: A novel ester diamine, 9-(3,5-diaminobenzoyloxy) fluorene, as a new monomer for preparation of polyimides was synthesized via two successive reactions. In the first step, reaction of 3,5-dinitrobenzoylchloride with 9-hydroxy fluorene in the presence of sodium hydroxide led to preparation of 9-(3,5-dinitrobenzoyloxy) fluorene. Second reaction was reduction of the nitro groups by tin (II) chloride and fuming hydrochloric acid to produce 9-(3,5-diaminobenzoyloxy) fluorene. The new diamine containing bulky fluorene group was characterized and polycondensed with different dianhydrides via two methods to produce polyimides. The new five-membered and six-

membered ring polyimides were characterized and their properties including solubility behavior, inherent viscosity, thermal behavior and stability, and crystallinity were studied. They exhibited favorable balance of physical and thermal properties and their solubility were improved without sacrificing their thermal stability. Six-membered rings polyimides showed higher thermal stability and lower solubility in comparison to related five-membered ring polyimides. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2891–2901, 2012

Key words: polyimide; thermal properties; high performance polymers; fluorene; diamine

INTRODUCTION

High performance polyimides are heat resistant polymers that generally show excellent mechanical strength and stability. They exhibit favorable balance of physical and chemical properties and they are widely used in microelectronic and aerospace engineering.¹ However, because of processing difficulties due to their high glass transition or melting temperature and poor solubility in most organic solvents, the technological and industrial application of rigid polyimides are limited. Wide-ranging investigations on the structure–property relationship of polyimides have specified that the difficulties in processing of conventional aromatic polyimides are outcome from the inherent molecular features of aromatic polyimides such as the molecular chain stiffness, high polarity, and high intermolecular association force.^{2,3}

To improve their processability and solubility through the design and synthesis of new monomers and therefore producing a great variety of soluble and processable polyimides for various purposes and applications; different methods have been used for modification of polymer structure. The main concept behind all these approaches is the reduction of

the packing force and the increase of the free volume of the polymers.^{4–6}

Solubilization of the polyimides has been targeted by several methods, such as introduction of flexible linkage, bulky units in the polymer backbone, bulky pendant substituents, or noncoplanar moieties.^{7–12} Among these approaches, introduction of bulky pendant substituents and hetroaromatic rings into polyimide chains has been considered to be efficient, which can provide not only enhanced solubility but also good thermostability and processability. Introduction of bulky pendant groups into the main chain of polymers led to improving the solubility and processability by lowering the interchains interactions and inhibition of the packing of the chains.^{13–21}

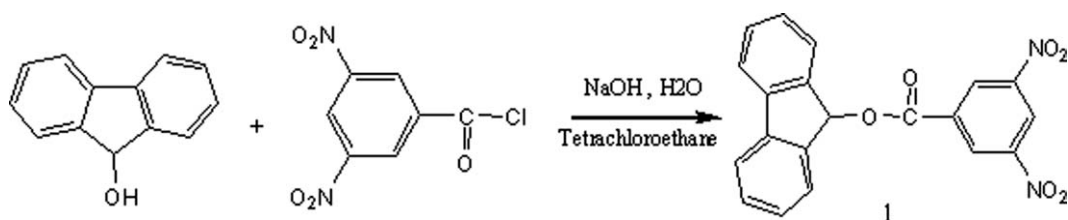
In our study, new five- and six-membered ring polyimides were synthesized from a novel diamine containing fluorene ring and flexible ester group (as a bulky pendant group) via one-step and two-step methods of imidization. The physical properties of the obtained polymers were studied and the structure–property relation was investigated.

EXPERIMENTAL

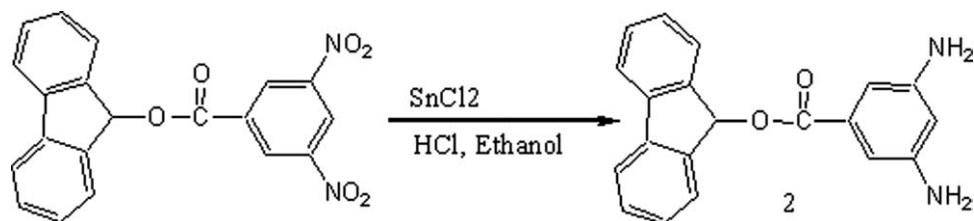
Materials

All chemicals were purchased either from Merck or Aldrich Chemical. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and toluene were purified by

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Scheme 1 Synthesis of dinitro compound.



Scheme 2 Synthesis of diamino compound.

distillation over calcium hydride under reduced pressure. *m*-Cresol was dried over P₂O₅ and distilled under reduced pressure. Dianhydrides were dried in a vacuum oven at 120°C for 5 h.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrophotometer from KBr pressed samples. The ¹H-NMR spectra were recorded in dimethyl sulfoxide (DMSO-*d*₆) solution using a Bruker Avance DPX 400-MHz instrument. A CHN-O-Rapid Heraeus elemental analyzer performed elemental analyses. Differential scanning calorimetric (DSC) studies were performed on a

Stanton Redcraft STA-780 instrument and thermogravimetric analysis (TGA) was done in a Polymer Lab TGA-1500 in air at a heating rate of 10°C/min. The dynamic mechanical measurements were carried out in a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) at heating rate of 5°C/min⁻¹ from room temperature to 350°C at 1 Hz. The value of tan δ and the storage modulus versus temperature were recorded for each sample. Inherent viscosities were measured with an Ubbelohde viscometer. Wide angle X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (Siemens model D 5000) using Ni-filtered Cu Kα radiation (40 kV, 25 mA) with scanning rate of 3°/min.

TABLE I
Monomer Characterization Data

Substrate	IR (KBr) cm ⁻¹	NMR (DMSO- <i>d</i> ₆)δ	Elemental analysis					
			Calc.			Found		
			C	H	N	C	H	N
Dinitro	3091 (Aromatic C-H, Str.) 1727 (C=O, Str.) 1538 (NO ₂ , Asymm. Str.) 1346 (NO ₂ , Symm. Str.) 1274 (C-O, Str.)	7.04s(1H), 7.34t(2H) 7.48t(2H), 7.69d(2H) 7.88d(2H), 8.86s(2H) 9.01s(1H)	63.83	3.19	7.45	64.01	3.24	7.38
Diamine	3420 (N-H str.) 3103 (Aromatic C-H, Str.) 1708 (C=O, Str.) 1227 (C-O, Str.)	4.97s(4H), 5.99s(1H) 6.41s(2H), 6.89s(1H) 7.31t(2H), 7.44t(2H) 7.58d(2H), 7.85d(2H)	75.95	5.06	8.86	76.02	4.99	8.81

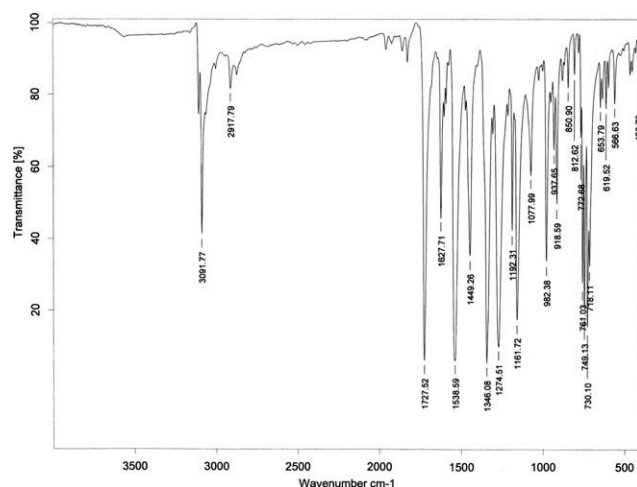


Figure 1 FTIR spectrum of dinitro compound.

Monomer synthesis

Synthesis of 9-(3,5-dinitrobenzoyloxy) fluorene

9-Hydroxy fluorene (3.189 g, 0.0168 mol) was placed into a two-necked round-bottomed flask with 1.8 g (0.045 mol) of sodium hydroxide and 45 mL of water. The mixture was stirred at room temperature for 30 min. Then a solution of 3.745 g (0.0159 mol) 3,5-dinitrobenzoyl chloride in 24 mL of tetrachloroethane was added to the flask in dropwise manner over 5 min at 0–5°C using ice-water bath. The mixture was stirred for 6 h at room temperature. The product was filtered and washed with hot water. It

was dried in vacuum oven at 90°C for 7 h. Yield was about 85%. m.p. = 117–120°C.

Synthesis of 9-(3,5-diaminobenzoyloxy) fluorene

9-(3,5-Dinitrobenzoyloxy) fluorene (1.505 g, 0.004 mol) and SnCl₂ (12 g) were placed into a round-bottomed flask. Then a solution of 13.2 mL of fuming hydrochloric acid in 35 mL of ethanol was added to the flask at room temperature. The mixture was stirred for 6 h, after that the mixture was neutralized with sodium hydroxide 25%. Then the product was extracted repeatedly using chloroform and the organic layer was concentrated under reduced pressure. Finally, the obtained solid was dried overnight under vacuum at 40°C. Yield was about 70%. m.p. = 199–201°C.

Polyimide synthesis

Two-step method

Diamine (1.5 mmol) and 12 mL of dry NMP were placed into a 100 mL, two-necked, round bottomed flask that equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube. The mixture was stirred at 0°C for 0.5 h. Then 1.5 mmol of dianhydride was added and the mixture was stirred at 0°C for 1 h. The mixture was raised to room temperature and the solution was stirred for 24 h. After that the content of the flask was precipitated using 200 mL of water and methanol (3 : 1 v/v) mixture. The poly(amic acid) was filtered and

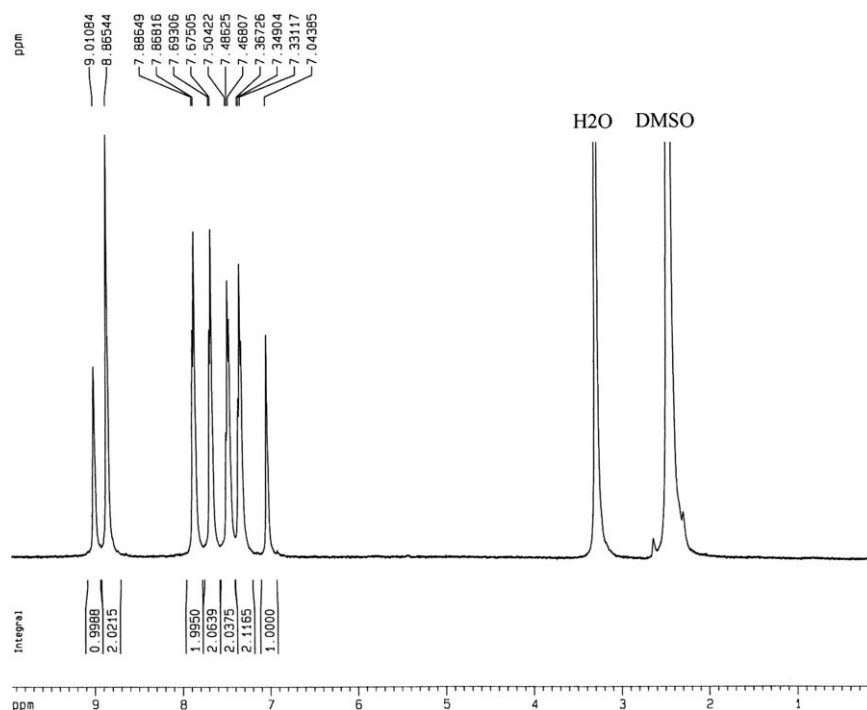


Figure 2 ¹H-NMR spectrum of dinitro compound.

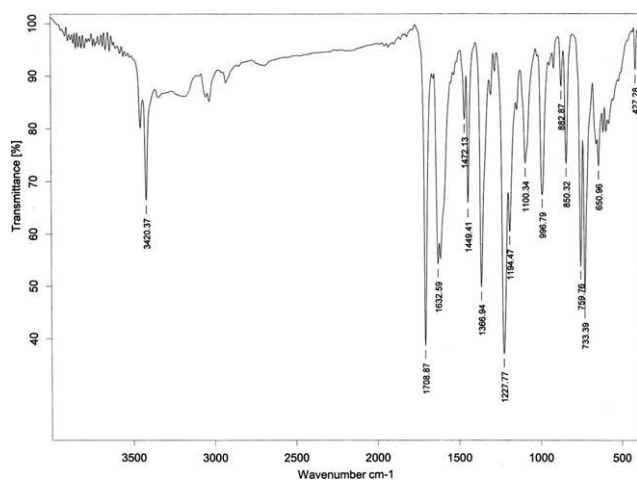


Figure 3 FTIR spectrum of diamino compound.

washed with water and dried overnight under vacuum at 40°C. Yields were over 89%.

Chemical cyclization was used for conversion of poly(amic acid) to polyimide:

About 1 g of poly(amic acid) and 5 mL of dry DMAc was placed into a 100 mL, two-necked, round-bottomed flask equipped with magnetic stirrer, nitrogen gas inlet tube, and reflux condenser. The mixture was stirred and then 5 mL of acetic anhydride and 2.5 mL of dry pyridine were added. The mixture was stirred for 0.5 h and then was slowly heated to 140°C and held for 6 h at the same

temperature. Afterward, the mixture was cooled and poured in to water; it was filtered, washed with hot water, and dried over night in vacuum at 120°C. Yields were greater than 92%.

One-step method

Dianhydride (3 mmol), 3 mmol of diamine, and 0.732 g of benzoic acid were added to a 250-mL, three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, a condenser, and a nitrogen inlet/outlet. About 18.5 mL of *m*-cresol was added and then the reaction mixture was heated at 80°C for 4 h and then at 180°C for 9 h. Next, 0.78 g isoquinoline was added to the reaction mixture, and it was heated at 180°C for another 9 h. The reaction mixture was cooled to room temperature and precipitated into an excess of isopropyl alcohol. The precipitated polyimide was collected by filtration and was dried in a vacuum oven at 120°C for 6 h and then at 150°C for 24 h. Yields greater than 93% were obtained.

RESULTS AND DISCUSSION

The main goal of this study was the preparation of new polyimides containing fluorene bulky group to improve solubility without substantial reduction of thermal stability. Accordingly, a new aromatic

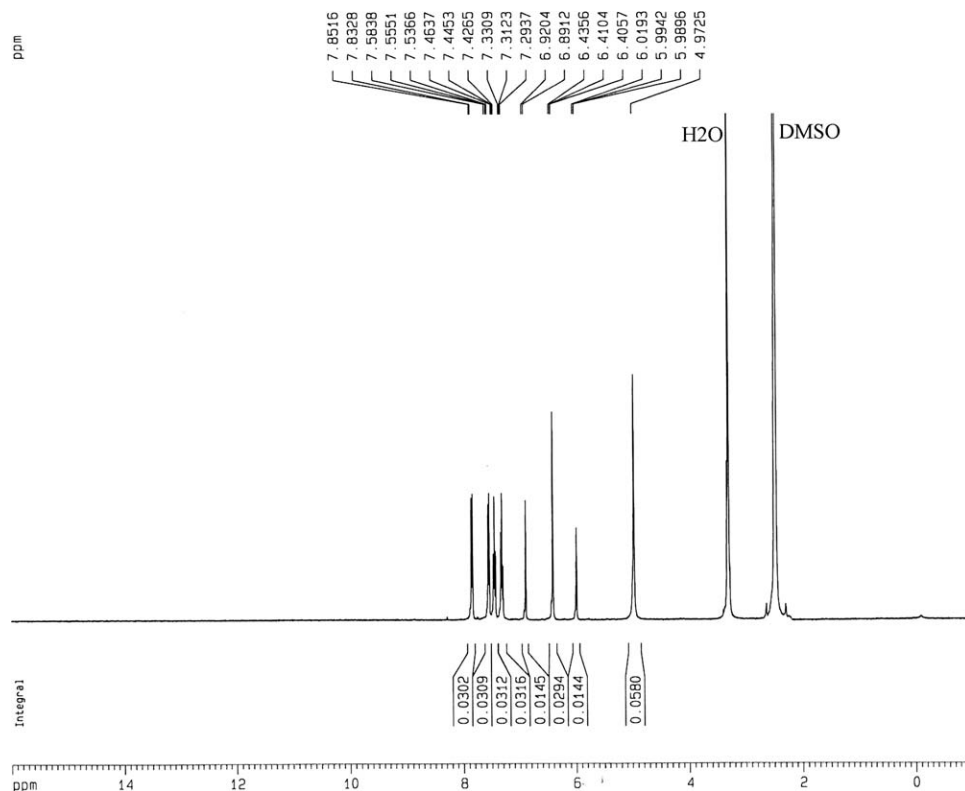
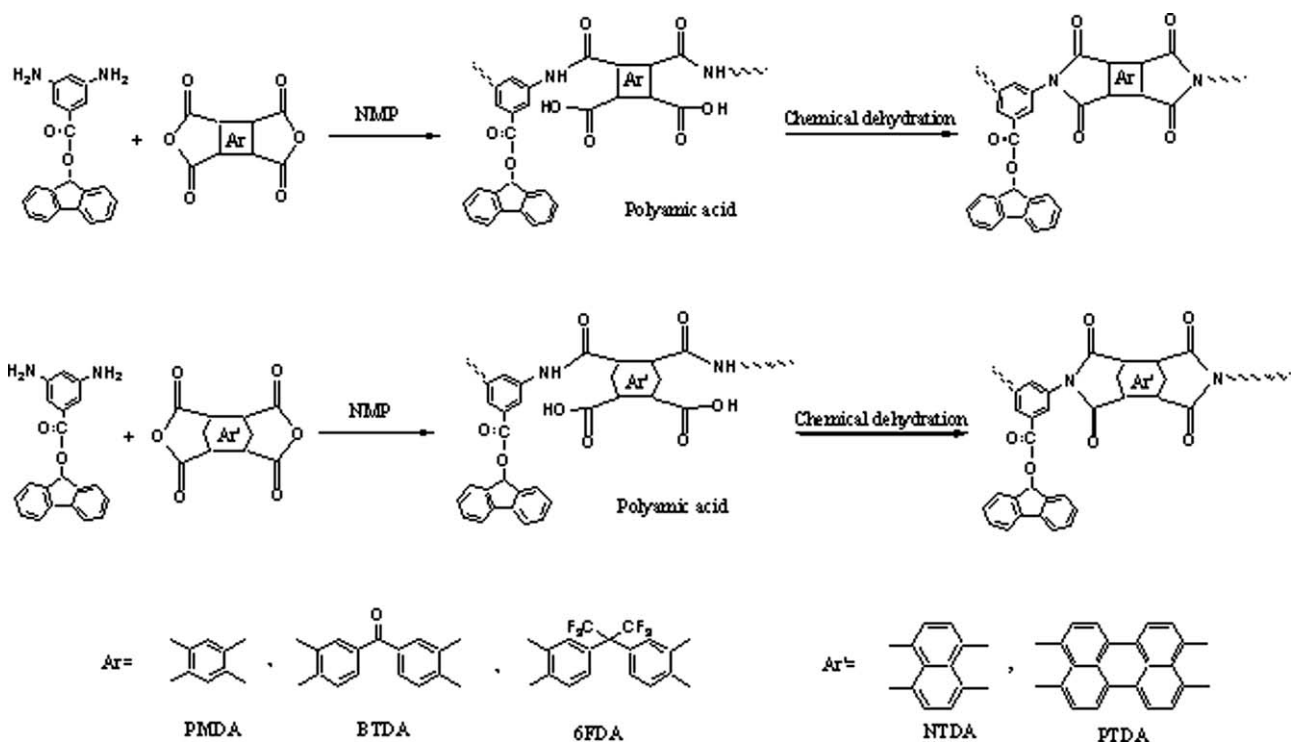
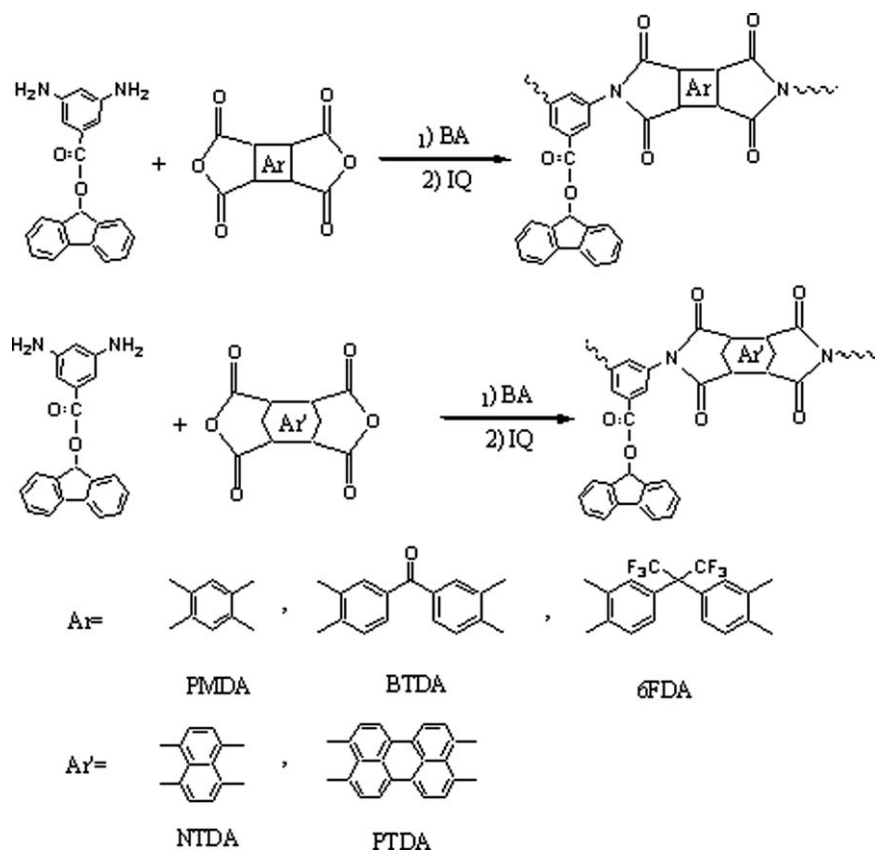


Figure 4 $^1\text{H-NMR}$ spectrum of diamino compound.



Scheme 3 Two-step method of polyimide synthesis.



Scheme 4 One-step method of polyimide synthesis.

TABLE II
Characterization of Polyimides

Polyimide	NMR (DMSO-d ₆) ppm	IR (KBr) cm ⁻¹	Elemental analysis					
			Calc.			Found		
			C	H	N	C	H	N
Diamine-NTDA	7.04 (s, 1H)	1724 (Ester C=O, Str.)	74.45	2.92	5.11	74.15	3.12	4.99
	7.33 (t, 2H)	1713 (Imide C=O, Asymm. Str.)						
	7.48 (t, 2H)	1679 (Imide C=O, Symm. Str.)						
	7.65 (d, 2H)	1335 (C–N, Symm. Str.)						
	7.80 (s, 1H)	1247 (C–O, Str.)						
	7.88 (d, 2H)	768 (C–O, Bend.)						
	8.21 (s, 2H)							
	8.63 (d, 4H)							
	7.05 (s, 1H)	1722 (Ester C=O, Str.)						
Diamine-PTDA	7.34 (t, 2H)	1715 (Imide C=O, Asymm. Str.)	78.57	2.98	4.17	78.22	3.15	4.02
	7.49 (t, 2H)	1677 (Imide C=O, Symm. Str.)						
	7.65 (d, 2H)	1338 (C–N, Symm. Str.)						
	7.79 (s, 1H)	1249 (C–O, Str.)						
	7.82 (d, 4H)	759 (C–O, Bend.)						
	7.89 (d, 2H)							
	8.00 (d, 4H)							
	8.23 (s, 2H)							
	7.02 (s, 1H)	1778 (Imide C=O, Asymm. Str.)						
Diamine-PMDA	7.32 (t, 2H)	1726 (Imide C=O, Symm. Str.; Ester C=O, Str.)	72.29	2.81	5.62	72.08	3.00	5.80
	7.46 (t, 2H)	1371 (C–N, Symm. Str.)						
	7.63 (d, 2H)	1246 (C–O, Str.)						
	7.78 (s, 1H)	723 (C–O, Bend.)						
	7.86 (d, 2H)							
	8.19 (s, 2H)							
	8.26 (s, 2H)							
	7.00 (s, 1H)	1780 (Imide C=O, Asymm. Str.)						
	Diamine-BTDA	7.30 (t, 2H)						
7.43 (t, 2H)		1356 (C–N, Symm. Str.)						
7.60 (d, 2H)		1243 (C–O, Str.)						
7.75 (s, 1H)		715 (C–O, Bend.)						
7.83 (d, 2H)								
7.88 (d, 2H)								
7.90 (s, 2H)								
8.15 (s, 2H)								
8.21 (d, 2H)								
6.99 (s, 1H)	1786 (Imide C=O, Asymm. Str.)							
Diamine-6FDA	7.28 (t, 2H)	1731 (Imide C=O, Symm. Str.; Ester C=O, Str.)	64.64	2.49	3.87	64.42	2.23	4.00
	7.41 (t, 2H)	1352 (C–N, Symm. Str.)						
	7.59 (d, 2H)	1255 (C–O, Str.)						
	7.65 (s, 2H)	720 (C–O, Bend.)						
	7.72 (s, 1H)							
	7.81 (d, 2H)							
	7.84 (d, 2H)							
	8.01 (d, 2H)							
	8.12 (s, 2H)							

diamine bearing ester group and fluorene ring was synthesized. In the first step, 3,5-dinitrobenzoylchloride was reacted with 9-hydroxy fluorene in the presence of sodium hydroxide for the preparation of 9-(3,5-dinitrobenzoyloxy) fluorene (Scheme 1). Next step was reduction of the nitro groups with SnCl₂ in the presence of fuming hydrochloric acid and etha-

nol (Scheme 2). Structures of these products were confirmed with conventional analyses including FTIR and ¹H-NMR spectra and elemental analysis. Results of these characterization methods were presented in Table I. In the FTIR spectrum of dinitro compound (Fig. 1), in addition to disappearance of OH group band of 9-hydroxy fluorene at 3297 cm⁻¹

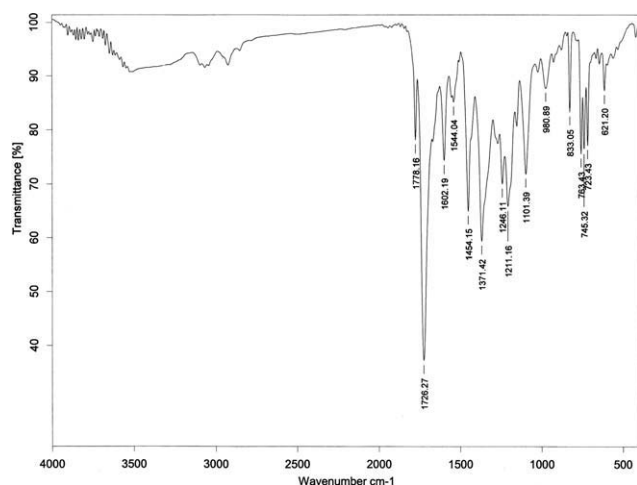


Figure 5 FTIR spectrum of PMDA-based polyimide (two-step method).

and also carbonyl group band of 3,5-dinitrobenzoyl chloride at 1706 cm^{-1} , a carbonyl group band of newly formed ester was appeared at 1727 cm^{-1} . Also in $^1\text{H-NMR}$ spectrum of dinitro compound (Fig. 2), OH group of 9-hydroxy fluorene at 2.43 ppm was disappeared and in addition to appearance of aromatic hydrogens from 3,5-dinitrobenzoylchloride moiety, the fluorene hydrogens were appeared at 8.87 and 9.01 ppm.

In the FTIR spectrum of diamino compound (Fig. 3) conversion of nitro groups to amino groups

was confirmed by presence of NH group band at 3420 cm^{-1} and absence of NO_2 groups bands at 1538 and 1346 cm^{-1} . In $^1\text{H-NMR}$ spectrum of diamine (Fig. 4), the NH group was observed at 4.97 ppm and aromatic peaks shifted to higher fields due to electron-donating character of NH_2 group. Therefore, a new fully aromatic diamine containing ester group and bulky fluorene ring was prepared.

Various commercially available aromatic tetracarboxylic acid dianhydrides including pyromellitic dianhydride (PMDA), benzophenonetetracarboxylic dianhydride (BTDA), hexafluoroisopropylidene diphthalic anhydride (6FDA), 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), and perylene-tetracarboxylic dianhydride (PTDA) were used for polycondensation with the diamine via two-step and one-step synthetic methods for preparation of polyimides as shown in Schemes 3 and 4. One-step method is useful for polymerization of unreactive dianhydrides such as aromatic and six-membered dianhydrides. In one-step method related polyimides were synthesized by high temperature polycondensation reaction in a high boiling solvent (*m*-cresol) at $180\text{--}190^\circ\text{C}$ in the presence of an acidic and a basic catalyst. The acidic catalyst (benzoic acid) was used to promote the formation of the *trans*-isoimide. The basic catalyst (isoquinoline) was needed to convert the *trans*-isoimide into polyimide. Generally, in one-step method chain growth and imidization take place spontaneously.^{22,23}

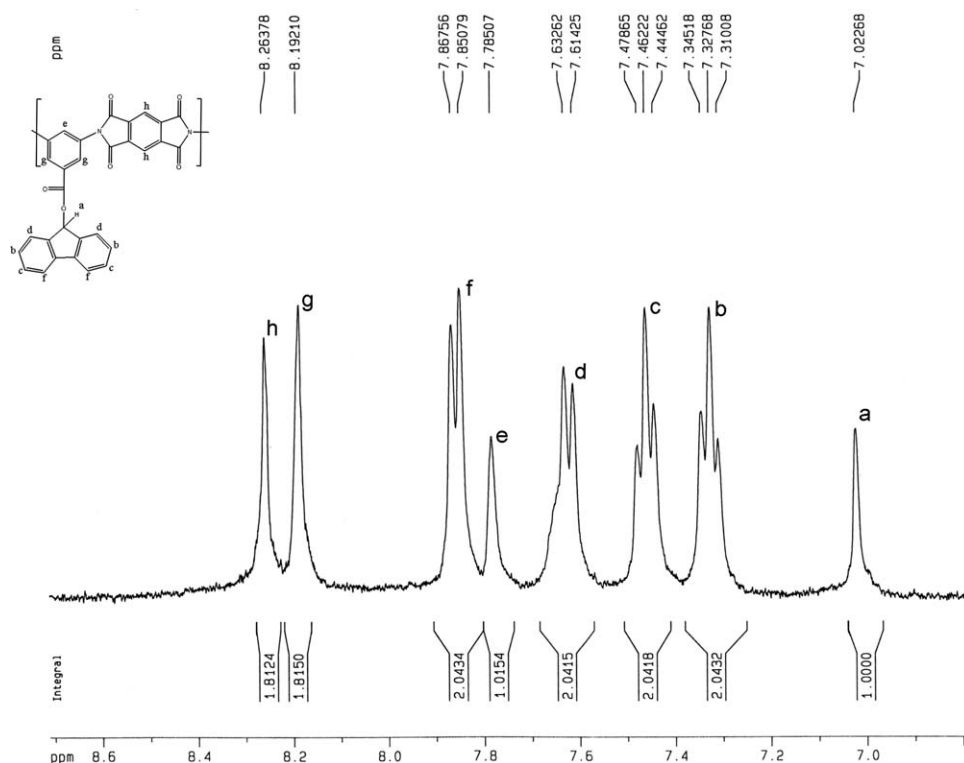


Figure 6 $^1\text{H-NMR}$ spectrum of PMDA-based polyimide (two-step method).

TABLE III
Yields and Viscosities of the Polyimides

Polyimide	Yield (%)		η_{inh} (dL/g) ^a	
	One-step method	Two-step method	One-step method	Two-step method
Diamine-NTDA	94	90	0.60	0.45
Diamine-PTDA	92	88	0.56	0.40
Diamine-PMDA	96	91	0.61	0.46
Diamine-BTDA	97	92	0.61	0.44
Diamine-6-FDA	95	90	0.59	0.43

^a Measured at a concentration of 0.5 g/dL in NMP at 30°C.

In two-step method, the diamine reacted with a dianhydride at low temperatures to produce polyamic acid. Then the polyamic acid was converted to related polyimide by chemical dehydration using pyridine and acetic anhydride. Structures of the obtained polyimides were confirmed by instrumental techniques and the results were collected in Table II. The FTIR and ¹H-NMR spectra of PMDA-based polyimide prepared via two-step method were brought in Figures 5 and 6, respectively.

In this study, polyimides were prepared in both one-step and two-step methods to investigate the effect of reaction conditions in improving the molecular weight of final polyimides containing five- and six-membered rings.

The yields of polymers from one-step method were slightly higher than two-step method. The inherent viscosity of polymers, as a criterion for estimation of molecular weight was measured at a concentration of 0.5 g.dL⁻¹ in NMP at 30°C (Table III). The obtained viscosity of these polyimides revealed reasonable molecular weights. The prepared polyimides via one-step method showed higher viscosities and therefore better growth of molecular weights of polymers than two-step method (Table III).

As it was mentioned, one of the main drawbacks of polyimides is their low solubility. For instance, it has been reported that most of polyimides derived

from 4,4'-diamino-4''-hydroxytriphenylamine monomer were not soluble in organic solvents.²⁴ The reported solubility of polyimides derived from 2,6-bis(3-aminobenzoyl) pyridine was about 1 g/dL.²⁵

The prepared polyimides in this study showed improved solubility in dipolar aprotic solvents including DMF, DMAc, NMP, DMSO, and *m*-cresol. The improved solubility (about 2.1–2.7 g/dL⁻¹) was attributed to the introduction of bulky pendant fluorene unit and ester group in side branch of polyimides. Incorporating bulky pendant groups along the polymer backbone is a general approach that has proven to be effective because it enhances free volume and reduces the packing force.^{26–29} The bulky fluorene pendant group reduced chain–chain interactions and decreased the close packing of the chains, so the solubility of polymer increased.

Also *meta*-catenation of diamine increased the solubility due to penetration of solvent into the backbone of unsymmetrical polyimides with reduction of the packing force and the increasing of the free volume of the polymers. On the other hands, the solubility of polyimides derived from BTDA and 6FDA was higher than PMDA, NTDA, and PTDA-derived polyimides. Presence of some flexible groups was the main reason for this behavior because of the fact that carbonyl and hexafluoroisopropylidene groups in BTDA and 6FDA respectively, have low rotational bond energy in comparison to the other polyimides, which reduced the polymer chains interaction and rigidity.^{15,24,30}

DSC, DMTA, and TGA techniques were used to study the thermal behavior and thermal stability of the obtained polyimides. Changes in the slope of base line of DSC were considered as glass transition temperature (T_g) of the polymers (Fig. 7). They were in the range of 182–228°C (Table IV). According to the obtained results, PTDA-based polyimide showed highest glass transition temperature among the prepared polymers. It might be related to the rigid structure of PTDA and also its bulkiness that led to entanglement of chains and therefore restriction of

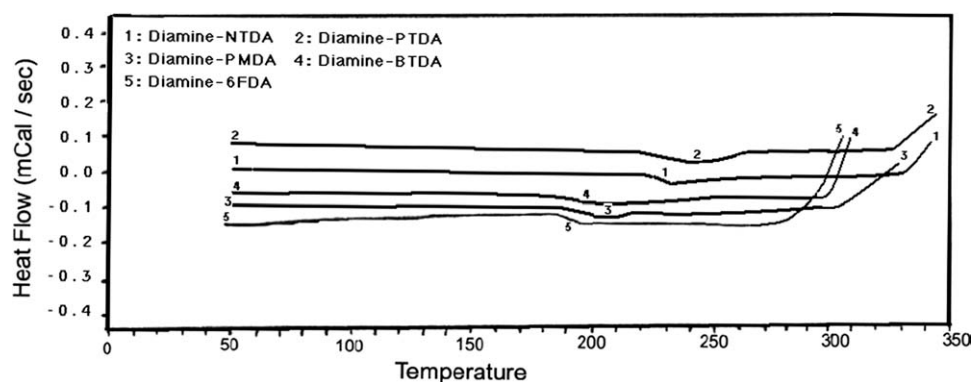


Figure 7 DSC curves of polyimides (one-step method).

TABLE IV
Thermal Characterization Data of the Polyimides

Polyimide	T_g (°C)		T_0 (°C)		T_{10} (°C)		Char yield at 600°C (%)	
	One-step method	Two-step method	One-step method	Two-step method	One-step method	Two-step method	One-step method	Two-step method
Diamine-NTDA	228	220	328	320	442	433	61	57
Diamine-PTDA	240	231	324	318	437	428	60	55
Diamine-PMDA	208	199	303	296	424	412	57	52
Diamine-BTDA	198	192	295	283	410	403	54	50
Diamine-6-FDA	191	182	290	282	401	395	52	47

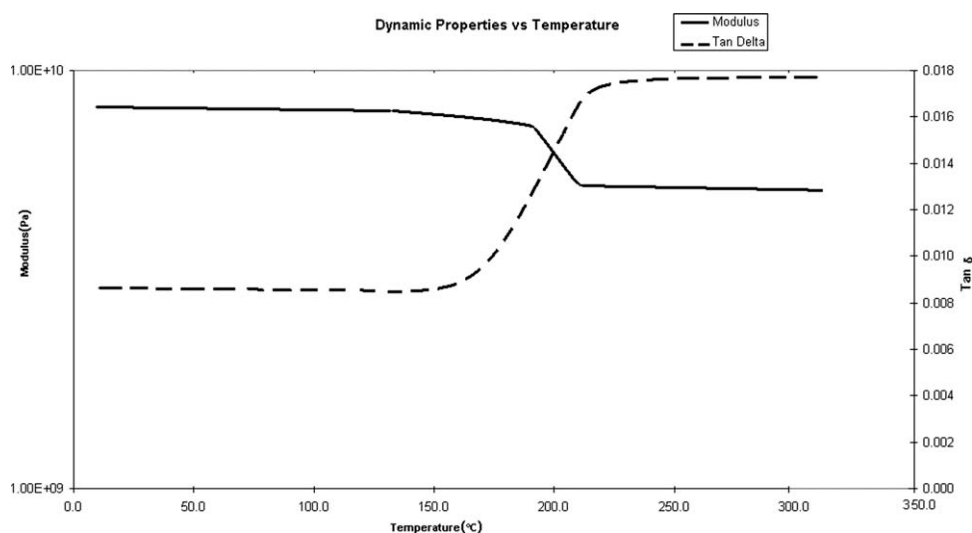


Figure 8 DMTA curve of BTDA-based polyimide (one-step method).

rotation. Similar situation but some what weaker was observed for NTDA-based polyimide. For five-membered ring polyimides, BTDA- and 6FDA-based polyimides revealed lower T_g than PMDA-based polymers. Presence of flexible carbonyl group and hexafluoroisopropylidene unit reduced their T_g in respect to rigid PMDA moieties. In DMTA analysis, T_g was considered as decreasing in storage modulus with increasing of $\tan \delta$, which confirmed the obtained data from DSC technique. A representative DMTA curve was shown in Figure 8. TGA analysis in air at a heating rate of 10°C/min was used for evaluation of thermal stability of prepared polyimides. The results of TGA analysis were collected in Table IV and a representative TGA curve was shown in Figure 9. Accordingly, the polyimides obtained from both methods showed high thermal stability that could be related to the fully aromatic structure of the polymers without any weak linkages. The initial decomposition temperature (T_0), the temperature for 10% gravimetric loss (T_{10}), and char yield that are important criteria for evaluation of thermal stability were studied. Polyimides prepared from one-step method showed higher thermal stability in

comparison to the same polyimides prepared via two-step method. This was related to increasing of molecular weights and therefore higher chain interactions in one-step method in respect to two-step method.

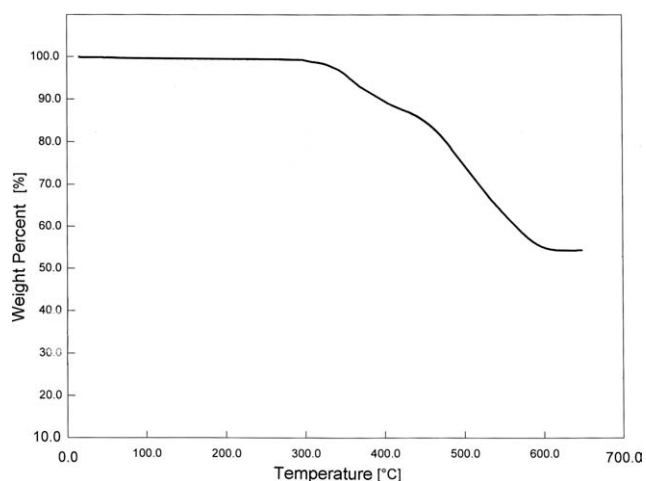


Figure 9 TGA curve of BTDA-based polyimide (one-step method).

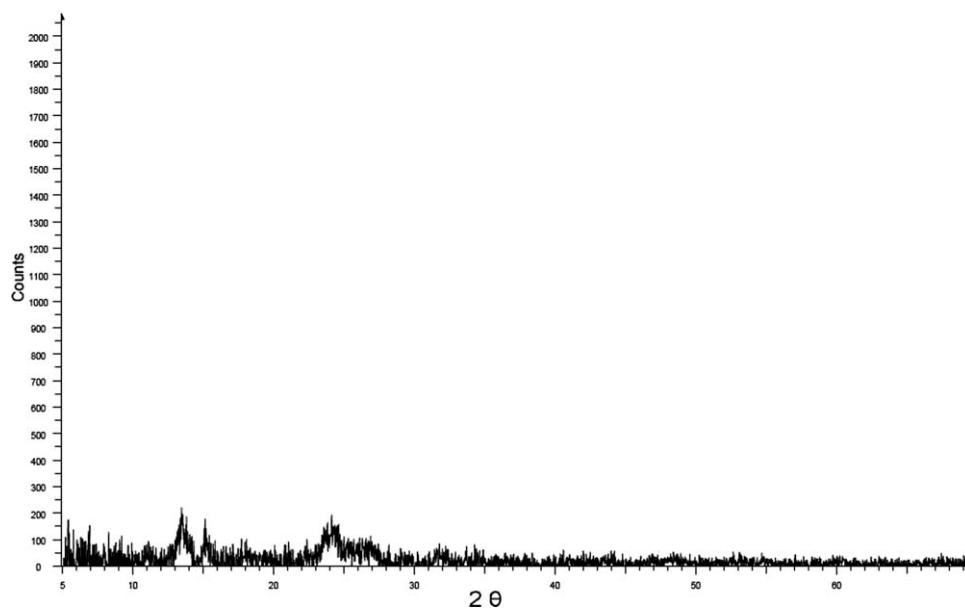


Figure 10 Wide-angle X-ray diffraction pattern of BTDA-based polyimide (one-step method).

Another observation was that six-membered ring polyimides (PTDA and NTDA-based polyimides) had higher thermal stability than five-membered ring polyimides due to the fact that six-membered rings are thermodynamically more stable than five-membered rings. Six-membered ring polyimides are less strained and comprise higher thermal and chemical stability in comparison with analogous five-membered ring counterparts. However, reactivity of an amine group toward six-membered ring anhydrides is lower than that of five-membered analogues.³¹

Estimation of crystallinity in the prepared polymers was achieved using wide-angle X-ray diffraction in the region of $2\theta = 5^\circ\text{--}70^\circ$ at room temperature. Low crystallinity was observed for all the polymers and therefore they were almost amorphous. One sample wide-angle X-ray diffraction was brought in Figure 10. The amorphous nature of polyimides was also reflected in their excellent solubility behavior. The introduction of bulky fluorene group decreased the chain-to-chain interactions, which interrupted the close packing of polymer chains, thereby leading to an enhancement in solubility and decreasing in crystallinity which was in agreement with the general rule that the solubility decreases with increasing crystallinity.¹⁵

CONCLUSIONS

A new diamine with bulky pendant fluorene group was prepared from two successive reactions. Reactions of 9-hydroxy fluorene with 3,5-dinitrobenzoylchloride and then reduction of its nitro groups with SnCl_2 in the presence of fuming hydrochloric acid

afforded the diamine. Related thermally stable polyimides were synthesized from reaction of prepared diamine with commercially available tetracarboxylic dianhydrides including five- and six-membered rings via one-step and two-step methods. Similar polyimides prepared from one-step method had higher thermal stability because of better growing of molecular weight in comparison to two-step method. Also, the polymers derived from six-membered imide rings showed higher thermal stability than five-membered ones that was as a result of more thermal stability of nonsteric six-membered rings than five-membered rings. So, one-step method of imidization using six-membered ring structures give polyimides with higher thermal stability. Also, the prepared polyimides had improved solubility in respect to common polyimides because of the presence of bulky pendant fluorene ring, flexible ester in the backbones of polyimides, and *meta*-catenation of the diamine.

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