

Synthesis and Characterization of Novel Heat Resistance Poly(amide-imide)s from *N,N'*-[2,5-bis(4-aminobenzylidene)cyclopentanone] Bistrimellitimidic Acid and Various Aromatic Diamines

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ABSTRACT: A new-type of dicarboxylic acid was synthesized from the reaction of 2,5-bis(4-aminobenzylidene)cyclopentanone with trimellitic anhydride in a solution of glacial acetic acid/pyridine (Py) at refluxing temperature. Six novel heat resistance poly(amide-imide)s (PAIs) with good inherent viscosities were synthesized, from the direct polycondensation reaction of *N,N'*-[2,5-bis(4-aminobenzylidene)cyclopentanone]bistrimellitimidic acid with several aromatic diamines, by two different methods such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (Py) and direct polycondensation in a *p*-toluene sulfonyl chloride (tosyl chlo-

ride, TsCl)/pyridine (Py)/*N,N*-dimethylformamide (DMF) system. All of the above polymers were fully characterized by ¹H NMR, FTIR, elemental analysis, inherent viscosity, solubility tests, UV-vis spectroscopy, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), and derivative of thermogravimetric (DTG). The resulted poly(amide-imide)s (PAIs) have showed admirable good inherent viscosities, thermal stability, and solubility. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2877–2885, 2011

Key words: heat resistance; poly(amide-imide); polycondensation; trimellitic anhydride

INTRODUCTION

Polyimides and polyamide-imides are of high interest for many engineering applications due to their excellent thermal and mechanical properties. The aerospace, automobile, and microelectronics industries have developed many important applications.¹ Additionally, introduction of alicyclic moieties into the main chains of polyimides restrains the formation of intermolecular charge-transfer complexes to lower the dielectric constant, a property that is highly desirable for microelectronics applications. In addition to low dielectric constant, some excellent properties such as good optical clarity, low refractive index, and good mechanical properties are observed in mixed or fully nonaromatic polyimides.²

However, the major limitation of polyimides for the versatile applications is their insolubility in common organic solvents. In fact, unless carefully designed, polyimides are often insoluble in the fully imidized form.^{3,4} Thus, their commercial applications are limited in some fields. Therefore, prepara-

tion of soluble polyimides without perceptible loss of favorable properties has been a major research interest, and a great deal of efforts has been made to improve the processing characteristics of this class of polymers. One of the successful approaches to improve solubility is the incorporation of other functional groups such as amide,^{4–11} ester,^{12,13} urethane,^{14,15} and urea^{16,17} linkages along the polymer skeleton.

Aromatic poly(amide-imide)s possess desirable characteristics with the merits of both polyamides and polyimides, for example, high thermal stability and good mechanical properties as well as easy processability. Conventionally, aromatic poly(amide-imide)s can be prepared in several ways starting from trimellitic anhydride (TMA), such as two-step polycondensation from the acid chloride of TMA with aromatic diamines involving polyaddition and subsequent cyclodehydration,¹⁸ low temperature solution polycondensation of TMA-derived imide ring-preformed diacid chloride and aromatic diamines,¹⁹ polycondensation of TMA or TMA-derived imide ring-containing dicarboxylic acids with diisocyanates,²⁰ and phosphorylation polyamidation between TMA-derived imide ring-preformed dicarboxylic acids and aromatic diamines.²¹

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A triphenyl phosphite (TPP)-activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides was reported by Yamazaki et al.²² We describe here the preparation and basic characterization of heat resistance poly(amide-imide)s 8a-f based on dibenzalacetone moiety from the direct polycondensation reaction of *N,N'*-[2,5-bis(4-aminobenzylidene)cyclopentanone]bistrimellitimidic acid 6 as a new diacid monomer with six aromatic diamines such as 4,4'-diaminodiphenylether 7a, 4,4'-diaminodiphenylsulfone 7b, 3,3'-diaminodiphenylsulfone 7c, 1,4-phenylenediamine 7d, 1,5-naphthalenediamine 7e, 4,4'-diaminobenzidiazole 7f, by two different methods such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl₂)/pyridine (py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (py)/*N,N*-dimethylformamide (DMF) system. Because of present dibenzalacetone moiety containing rigid ring in the main chain of synthesized polymers, these polymers can be photosensitive²³ and have high thermal stability.

EXPERIMENTAL

Materials

Cyclopentanone, 4-nitrobenzaldehyde, trimellitic anhydride, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, 1,4-phenylenediamine, 1,5-naphthalenediamine, 4,4'-diaminobenzidiazole, (Merck) were used without previous purification. Solvent: *N*-methyl-2-pyrrolidone (NMP; Fluka), pyridine (Acros), triphenyl phosphite (TPP; Merck), tosyl chloride (TsCl; Merck) and *N,N*-dimethylformamide (DMF; Merck) were used as received. Commercially available calcium chloride (CaCl₂; Merck) was dried under vacuum at 150°C for 6 h.

Techniques

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Mass spectrum was recorded on an Agilent Technology (HP), 5973 network mass selective detector on the electron impact (EI), 70 eV. Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were reported in wave number (cm⁻¹). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure by using a Technico Regd Trad Mark Viscometer. UV-vis absorptions were recorded at 25°C in the 190–790 nm spectral regions with a Perkin–Elmer

Lambda 15 spectrophotometer on DMF solution by using cell lengths of 1 cm. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N₂ atmosphere at rate of 10°C/min and differential scanning calorimeter (DSC) was conducted with a DSC Mettler 110 (Switzerland) at a heating and heating rate of 10°C min⁻¹ in a nitrogen atmosphere. Elemental analyses were performed by Vario EL equipment by Arak University.

Monomer synthesis

2,5-bis(4-nitrobenzylidene)cyclopentanone 3

0.475 g (5.6 mmol) cyclopentanone 1, 1.691 g (11.2 mmol) 4-nitrobenzaldehyde 2, 12 mL a mixture of ethanol and water (2 : 1), and a stirring bar were placed into a 100-mL round-bottom flask. Then this mixture was heated in 50°C for 1 h and 5 mL of NaHCO₃ (1%) was added slowly at this temperature and refluxed for 3 h. Then the reaction mixture was cooled to ambient temperature and 50 mL cooled water was added. A light brown crud product formed and was collected by filtration, washed thoroughly with water, and dried to afford 1.62 g (82%). Mp: 265–267°C. FTIR (KBr): 3088 (w), 2908 (w), 1685 (s), 1604 (s), 1518 (s), 1415 (m), 1344 (s), 1253 (s), 1184 (s), 1113 (s), 983 (m), 856 (s), 756 (m), 677 (m), 507 (m), 416 (m) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆, TMS): δ; 8.30–8.32 (d, 2H, J = 6 Hz), 7.96–7.98 (d, 2H, J = 6 Hz), 7.57 (s, 2H), 3.19 (s, 4H) ppm. Elemental analysis: calculated for C₁₉H₁₄N₂O₅: C, 65.14; H, 4.03; N, 8.00; found: C, 65.09; H, 4.01; N, 8.00.

2,5-bis(4-aminobenzylidene)cyclopentanone 4

This compound was prepared according to our previous works.²⁴

N,N'-[2,5-bis(4-aminobenzylidene)cyclopentanone]bistrimellitimidic acid 6

Into a 50-mL, round-bottom flask, 0.2 g (0.68 mmol) 2,5-bis(4-aminobenzylidene)cyclopentanone 4, 0.26 g (1.36 mmol) trimellitic anhydride 5, 20 mL of a mixture of acetic acid and pyridine (3 : 2) and a stirring bar were placed. The mixture was stirred at room temperature overnight and then was refluxed for 4 h. After this time the solvent was removed under reduced pressure, and the residue was dissolved in 100 mL of cold water; then, 5 mL of concentrated HCl was added. The solution was stirred until a brown precipitate was formed, and then the precipitate was filtered off and dried in vacuum to give 0.391 g (89%) of dicarboxylic acid 6: mp: 310–312°C. FTIR(KBr): 2500–3400 (m, br), 1782 (s), 1722 (s, sh), 1693 (s, sh), 1624 (s), 1512 (s), 1421 (m), 1383 (s),

1253 (m), 1178 (m), 1097 (m), 987 (w), 927 (m), 802 (m), 721 (m), 528 (s) cm^{-1} . ^1H NMR (300 MHz, DMSO- d_6 , TMS): δ : 13.89 (s, br, 2H), 8.41-8.44 (d, 2H, $J = 9.2$ Hz), 8.32 (s, 2H), 8.08-8.11 (d, 2H, $J = 9.2$ Hz), 7.86-7.88 (d, 4H, $J = 6$ Hz), 7.59-7.61 (d, 4H, $J = 6$ Hz), 7.52 (s, 2H), 3.34 (s, 4H) ppm. MS (EI): $m/z = 620$ [$\text{M}^+ - 18$], 523, 368, 313, 297, 137, 110, 94, 81, 69, 58 (base peak), 42. Elemental analysis: calculated for $\text{C}_{37}\text{H}_{22}\text{N}_2\text{O}_9$: (638.5). C, 69.59; H, 3.47; N, 4.39; found: C, 69.48; H, 3.41; N, 4.37.

Polymer synthesis

Poly(amide-imide)s **8a-f** were synthesized by two different methods that as an example the preparation of PAI **8a** explains in the following. PAI **8a** was prepared from the reaction of *N,N'*-[2,5-bis(4-aminobenzylidene)cyclopentanone]bistrimellitimidic acid **6** with 4,4'-diaminodiphenylether **7a** by two different methods.

Method A: Direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl_2)/pyridine (Py)

0.175 g (0.275 mmol) dicarboxylic acid **6**, 0.055 g (0.275 mmol) 4,4'-diaminodiphenylether **7a**, 0.1 g (0.9 mmol) calcium chloride, 0.84 mL (3.00 mmol) triphenyl phosphite, 0.1 mL of pyridine and 2 mL *N*-methyl-2-pyrrolidone (NMP) were placed into a 25-mL round-bottomed flask, which was fitted with a stirring bar. The reaction mixture was heated under reflux on an oil bath at 110°C for 7 h. Then, the reaction mixture was poured into 50 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly with hot methanol and dried at 60°C for 12 h under vacuum to leave 0.201 g (91%) yellow solid polymer **8a**.

Method B: Direct polycondensation in a tosyl chloride (TsCl)/pyridine (Py)/*N,N*-dimethylformamide (DMF) system

A solution of 0.1 mL pyridine, 0.0078 g (0.411 mmol) TsCl after 30 min stirring at room temperature was treated with 0.1 mL (1.36 mmol) DMF for additional 30 min. The reaction mixture was added dropwise to a solution 0.087 g (0.137 mmol) of dicarboxylic acid **6** in 0.1 mL pyridine. The mixture was maintained at room temperature for 30 min, and then to this mixture, a solution 0.027 g (0.137 mmol) 4,4'-diaminodiphenylether **7a** in 0.4 mL of Pyridine was added dropwise and the whole solution was stirred at room temperature for 30 min and at 100°C for 2 h. As the reaction proceeded, the solution became viscous, then was precipitated in 30 mL

of methanol and filtered off, dried under vacuum to leave 0.087 g (79%) brown solid polymer **8a**.¹⁰

Polymer **8a**, FT-IR Peaks (cm^{-1})

3310 (m, br), 3061 (w), 1778 (w), 1718 (s, br), 1670 (s, sh), 1589 (m), 1541 (m), 1481 (m), 1381 (m), 1356 (m), 1248 (m), 1182 (w), 690 (m), 503 (w).

Polymer **8b**, FT-IR Peaks (cm^{-1})

3330 (m, br), 3054 (m), 2934 (w), 1776 (m), 1720 (s, br), 1685 (s, sh), 1590 (s), 1543 (s), 1487 (s), 1383 (s, sh), 1240 (m), 1161 (m), 1080 (m), 730 (m), 506 (m).

Polymer **8c**, FT-IR Peaks (cm^{-1})

3313 (m, br), 3067 (w), 2972 (w), 1777 (m), 1720 (s, br), 1678 (s, sh), 1589 (m), 1541 (m), 1483 (m), 1356 (m, sh), 1244 (m), 1165 (m), 1080 (w), 692 (w), 501 (w).

Polymer **8 days**, FT-IR Peaks (cm^{-1})

3321 (m, br), 3028 (w), 2960 (w), 1778 (w), 1718 (s, br), 1681 (s), 1589 (m), 1541 (m), 1383 (m), 1351 (m, br), 1240 (m), 1160 (m), 1082 (w), 691 (w), 506 (w).

Polymer **8e**, FT-IR Peaks (cm^{-1})

3329 (w, br), 3056 (w, sh), 1776 (m), 1721 (s, br), 1684 (m, sh), 1589 (m), 1541 (m), 1381 (m), 1356 (m), 1246 (w), 1109 (m), 698 (m), 501 (w).

Polymer **8f**, FT-IR Peaks (cm^{-1})

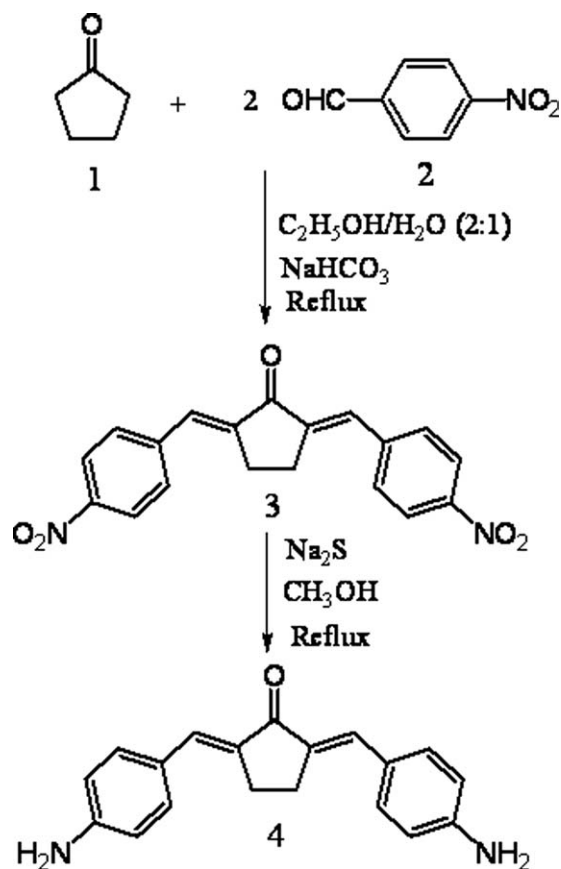
3316 (m, br), 3068 (w), 1776 (w), 1718 (s, br), 1673 (s, sh), 1589 (m), 1541 (m), 1481 (m), 1381 (m), 1356 (m), 1249 (m), 1188 (w), 695 (m), 509 (w).

RESULTS AND DISCUSSION

Monomer synthesis

2,5-bis(4-aminobenzylidene)cyclopentanone **4** was synthesized by using a two-step reaction. At first 2,5-bis(4-nitrobenzylidene)cyclopentanone **3** was prepared from the reaction of two equimolar 4-nitrobenzaldehyde **2** and one equimolar cyclopentanone **1** in ethanol/water (2 : 1) and NaHCO_3 . Then dinitro compound **3** was reduced by using Na_2S (Scheme 1).

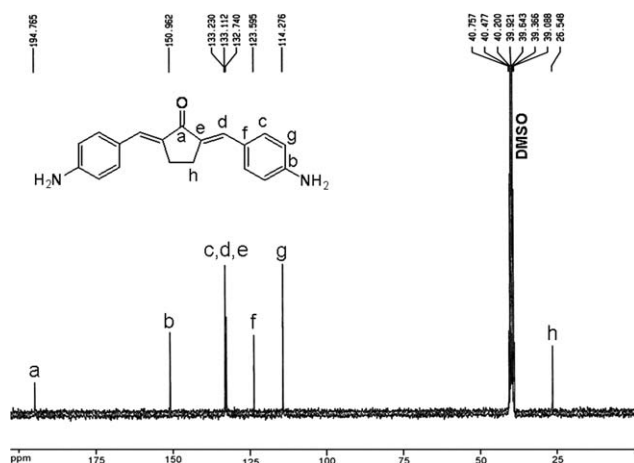
The chemical structure and purity of dinitro compound **3** were proved with elemental analysis, ^1H NMR and FTIR spectroscopy and diamine compound **4** were proved with elemental analysis, FTIR, ^1H NMR, and ^{13}C NMR spectroscopy. The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones,



Scheme 1 Synthesis of diamine 4.

demonstrating that the expected compounds were obtained.

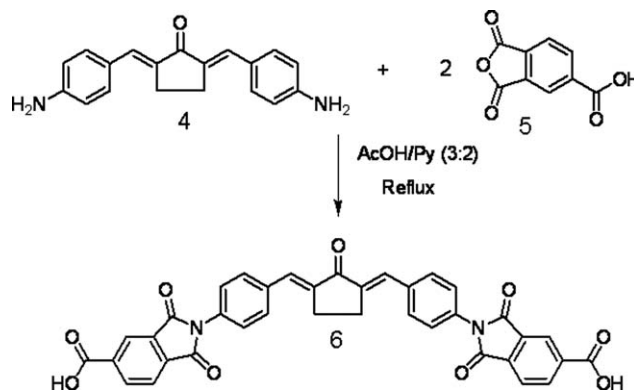
The FTIR spectrum of diamine compound 4 showed two peaks at 3319 and 3217 cm^{-1} , which were assigned to the NH_2 groups. Also ^1H NMR spectrum of diamine compound 4 showed a peak as a doublet of doublet at 7.36–7.38 ppm and 6.62–6.65 ($J = 7.5$ Hz) were assigned to the H(a) and H(c) related to aromatic protons and a peak as a singlet

Figure 1 ^1H NMR spectrum of 2,5-bis(4-aminobenzylidene)cyclopentanone 4.Figure 2 ^{13}C NMR spectrum of 2,5-bis(4-aminobenzylidene)cyclopentanone 4.

at 7.23 ppm, which was assigned to the H(b) related to olefin protons. Also a singlet peak at 5.83 ppm which was assigned to the H(d) protons of the NH_2 groups. Peak at 2.95 ppm (as a singlet) which were assigned to the H(e) protons of the methylene groups (Fig. 1). Also ^{13}C NMR spectrum of diamine compound 4 showed eight different carbon atoms (Fig. 2).

The condensation reaction between the amines and anhydride groups, as well as the subsequent cyclodehydration reaction was carried out in the heterogeneous solution. As shown in Scheme 2, the dicarboxylic acid 6 was obtained by the condensation of the appropriate diamine 4 with two mole equivalents of trimellitic anhydride 5 in refluxing mixture of glacial acetic acid and pyridine. The chemical structure and purity of dicarboxylic acid 6 was proved with elemental analysis, FTIR, ^1H NMR, and mass spectroscopy.

As shown in Figure 3, The FTIR spectrum of the dicarboxylic acid 6 showed absorption bands around 2500–3600 cm^{-1} (acidic H's), 1782 cm^{-1} (asymmetric imide $\text{C}=\text{O}$ stretching), 1722 (asymmetric imide $\text{C}=\text{O}$ stretching and acid $\text{C}=\text{O}$ stretching), and



Scheme 2 Synthesis of dicarboxylic acid 6.

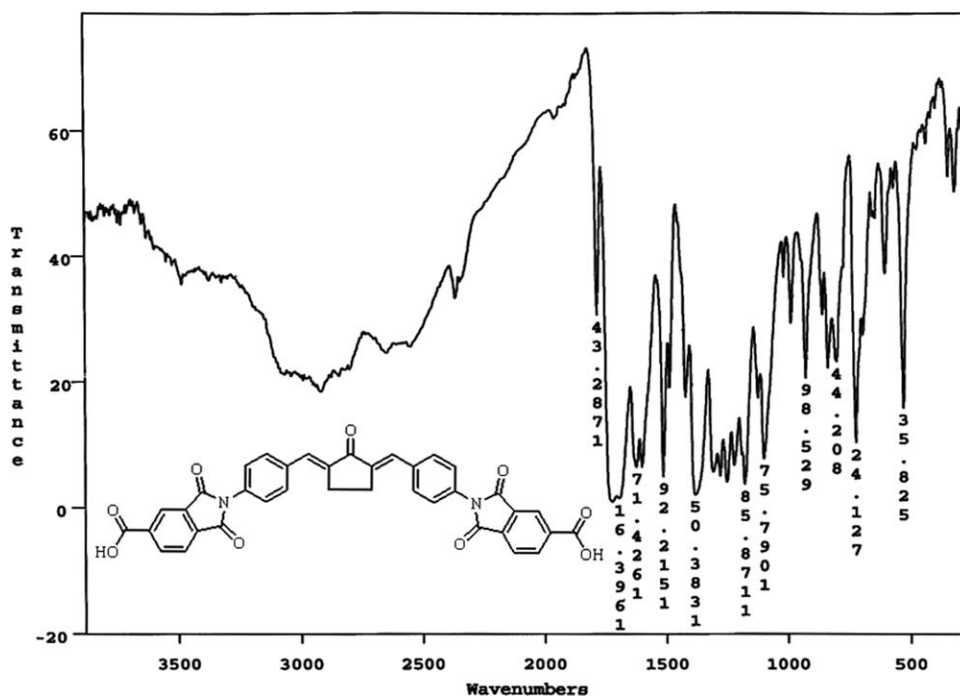


Figure 3 FTIR spectrum of dicarboxylic acid 6.

1383 cm^{-1} (imide ring vibration) confirming the presence of imide ring and carboxylic acid groups in the structure.

The ^1H NMR spectroscopic data of the dicarboxylic acid 6 related to aromatic protons are in the range of 7.52–8.44 ppm, which protons of the

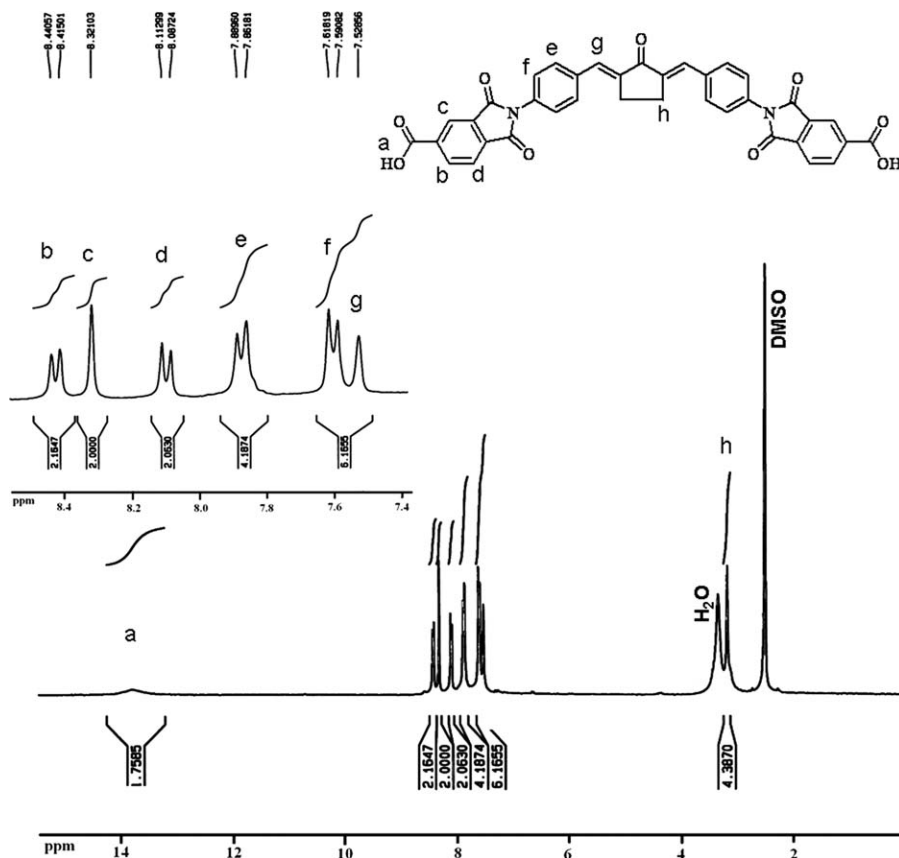
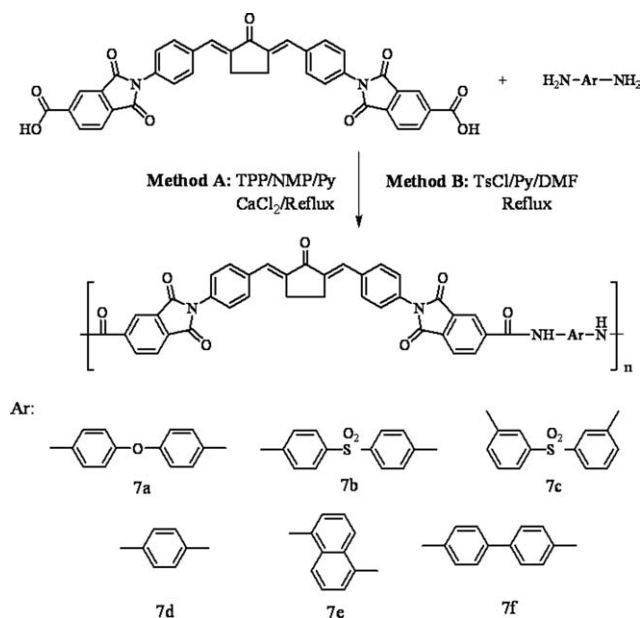


Figure 4 ^1H NMR spectrum of dicarboxylic acid 6.



Scheme 3 Synthesis of poly(amide-imide)s 8a-f.

trimellitoyl groups create resonance signals around downfield regions (above 8 ppm). Peaks related to diamine moiety in the center of this compound were appeared in 7.52–7.88 ppm regions (below 8 ppm). Also a broad singlet peak at 13.89 ppm which was assigned to the H(a) protons of the acidic groups in this compound (Fig. 4). These peaks in FTIR, ^1H NMR, and mass spectra along with elemental analyses data confirmed the proposal structure of dicarboxylic acid 6.

Polymer synthesis

The direct polycondensation of a dicarboxylic acid and diamine is one of the well-known methods for PAI synthesis. In this article, we synthesized PAIs 8a-f containing dibenzalacetone moiety by the direct polycondensation reactions of N,N' -[2,5-bis(4-amino-benzylidene)cyclopentanone]bistrimellitamide acid 6 as a new diacid monomer with six aromatic diamines 7a-f by two different methods (method A and B Scheme 3).

TABLE I
Synthesis and Some Physical Properties
PAIs 8a-f by Method A

Diacid	Polymer	Yield (%)	η_{inh} (dL/g) ^a
7a	8a	91	0.78
7b	8b	94	0.65
7c	8c	90	0.64
7d	8d	93	0.59
7e	8e	95	0.71
7f	8f	91	0.73

^a Measured at a concentration of 0.5g/dL in DMSO at 25°C.

TABLE II
Synthesis and Some Physical Properties
PAIs 8a-f by Method B

Diamine	Polymer	Yield (%)	η_{inh} (dL/g) ^a
7a	8a	79	0.33
7b	8b	80	0.41
7c	8c	78	0.40
7d	8d	74	0.35
7e	8e	81	0.39
7f	8f	75	0.36

^a Measured at a concentration of 0.5g/dL in DMSO at 25°C.

In method A for direct polycondensation used TPP/Py/ CaCl_2 as activating agent according to a typical procedure that was shown in Scheme 3. The syntheses and some physical properties of these new PAIs 8a-f are given in Table I. The entire polycondensation reaction readily proceeds in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in good yields. The resulting polymers have a range of color between cream and dark orange (Table I).

In method B for the direct polycondensation of diacid 6 and aromatic diamines 7a-f, a Vilsmeier adduct was prepared by dissolving TsCl in a mixed solvent of Py and DMF. The polycondensation was carried out as the following way: TsCl was dissolved in Py and after a certain period of time (aging time), the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py. After 30 min, a solution of diamine in Py was added and the whole solution was maintained at room temperature, and then elevated temperature for 2 h.

Less than this time, the polymers obtained will have lower inherent viscosities, and more than this time, the materials will be degraded. The syntheses and some physical properties of these new PAIs 8a-f are given in Table II. The entire polycondensation

TABLE III
Elemental Analysis of PAIs 8a-f

Polymer	Formula		C%	H%	N%
8a	$\text{C}_{49}\text{H}_{30}\text{N}_4\text{O}_8$	Calcd	73.31	3.77	6.98
	$(802.78)_n$	Found	72.48	3.68	6.97
8b	$\text{C}_{49}\text{H}_{30}\text{N}_4\text{O}_9\text{S}$	Calcd	69.17	3.55	6.58
	$(850.17)_n$	Found	68.24	3.53	6.48
8c	$\text{C}_{49}\text{H}_{30}\text{N}_4\text{O}_9\text{S}$	Calcd	69.17	3.55	6.58
	$(850.17)_n$	Found	68.41	3.48	6.55
8d	$\text{C}_{43}\text{H}_{26}\text{N}_4\text{O}_7$	Calcd	72.67	3.69	7.88
	$(710.69)_n$	Found	71.59	3.66	7.86
8e	$\text{C}_{47}\text{H}_{28}\text{N}_4\text{O}_7$	Calcd	74.20	3.71	7.36
	$(760.75)_n$	Found	73.51	3.69	7.36
8f	$\text{C}_{49}\text{H}_{30}\text{N}_4\text{O}_7$	Calcd	74.80	3.84	7.12
	$(786.79)_n$	Found	73.98	3.82	7.10

TABLE IV
Solubility of PAIs 8a-f

Solvent	8a	8b	8c	8d	8e	8f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	-	-	-	-	-	-
CHCl ₃	-	-	-	-	-	-
Acetone	-	-	-	-	-	-
EtOH	-	-	-	-	-	-
MeOH	-	-	-	-	-	-

+, soluble at room temperature, -, Insoluble at room temperature.

reaction readily proceeds in a homogeneous solution, tough and stringy precipitates formed when the viscous PAIs solution was obtained in moderate yields. Also the resulting polymers have a range of color between red and brown (Table II). Although PAIs 8a-f obtained in a shorter period by method B, but these polymers obtained with higher inherent viscosities and good yields by method A.

Polymer characterization

The elemental analyses of the resulting PAIs 8a-f were in good agreement with the calculated values for the proposed structure (Table III).

The solubility of PAIs 8a-f was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in DMSO, DMF, and NMP and are insoluble in solvents such as chloroform, ac-

etone, methanol and ethanol (Table IV, +: Soluble at room temperature, -: Insoluble at room temperature).

The structure of these polymers was confirmed as PAIs by means of FTIR spectroscopy and elemental analyses. The representative FTIR spectrum of PAI 8a was shown in Figure 5. The polymer exhibited characteristic absorption bands at 1718 and 1778 cm^{-1} for the imide ring (symmetric and asymmetric C=O stretching vibration), 1670 cm^{-1} for the amide group (C=O stretching vibration) in the main chain, 1381 cm^{-1} (C-N stretching vibration). The absorption bands of amide groups appeared at 3310 cm^{-1} (N-H stretching).

The ^1H NMR spectrum of PAI 8b showed peaks that confirm its chemical structure. Figure 6 displays ^1H NMR spectrum of PAI 8b that the aromatic protons and two olefin protons related diamine 4 appeared in the region of 7.00–8.50 ppm and the peak in the region of 10.91 ppm is assigned for N-H amide groups in the polymer backbone.

UV-vis absorption characteristics

The UV-vis absorption of the novel poly(amide-imide)s 8a-f in the DMF solution was studied by a UV spectrophotometer. All polymer solutions exhibit two same positions of absorption maximum in UV-vis spectra at 330–335 nm and 265–270 nm. The UV-vis absorption spectrum of PAI 8f in *N,N*-dimethylformamide is shown in Figure 7. The spectrum of PAI 8f exhibited two typical peaks at 266 nm and 335 nm.

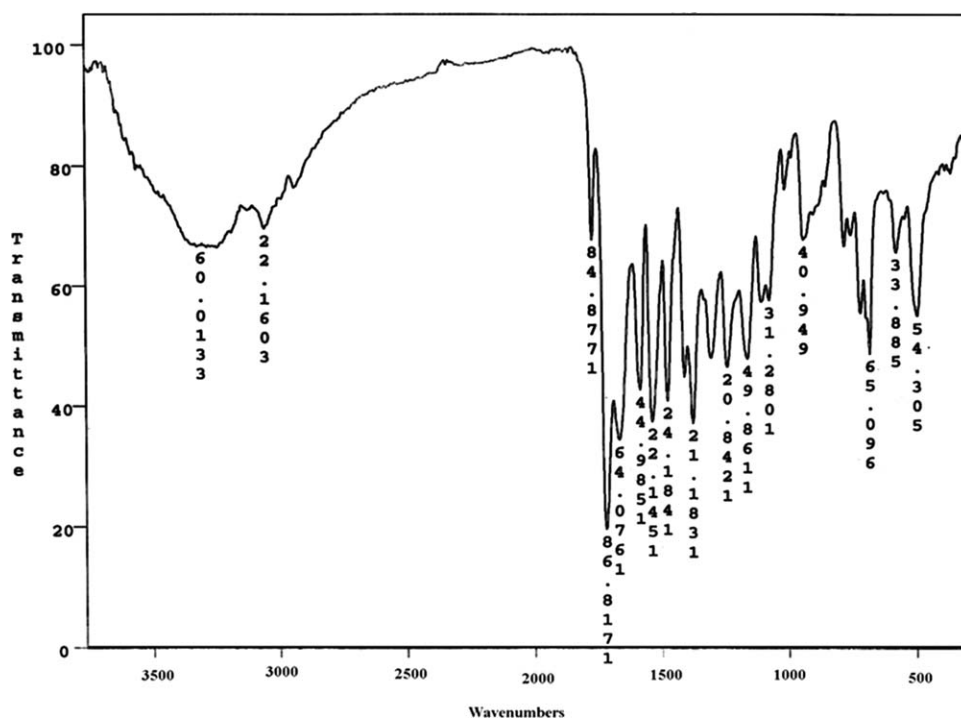


Figure 5 FTIR Spectrum of PAI 8a.

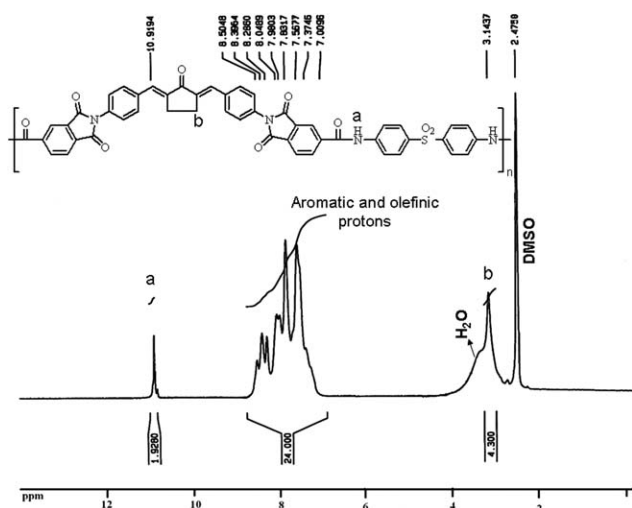


Figure 6 ^1H NMR Spectrum of PAI 8b.

Also the UV-vis absorption spectral change of PAI 8f in DMF solution was studied when this polymer was irradiated with UV light at 340 nm for different times such as 30, 50, 70, 90, and 100 min. The UV absorption of polymer 8f decreased when this polymer irradiated with UV light. This decrease in UV absorption is due to *trans* to *cis* conversion of dibenzalacetone groups in the polymer structure.

The UV-vis spectra of PAI 8f in DMF showed an intense dibenzalacetone π - π^* band at $\lambda_{\text{max}} = 340$ nm. The irradiation of PAI 8f solution with UV light led to a decrease in the absorbance of dibenzalacetone π - π^* band, which indicated the *trans*-to-*cis* isomerization of PAI 8f (Fig. 8).

Thermal properties

TGA and derivative of thermogravimetric (DTG) analysis at a rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere were utilized to examine the thermal properties of these PAIs, and the obtained results are summarized in Table V. Figure 9 show TGA results of PAIs 8a-f, respectively.

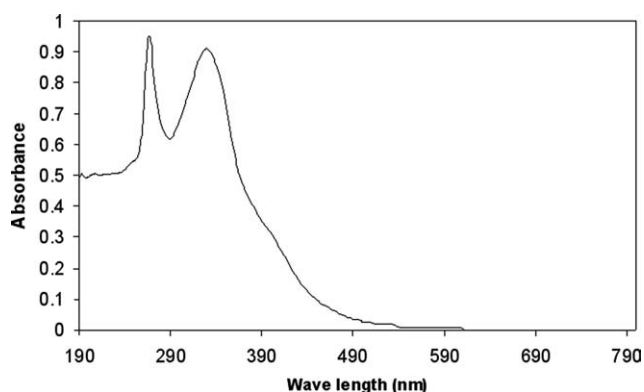


Figure 7 UV-vis absorption spectrum of PAI 8f in DMF solution.

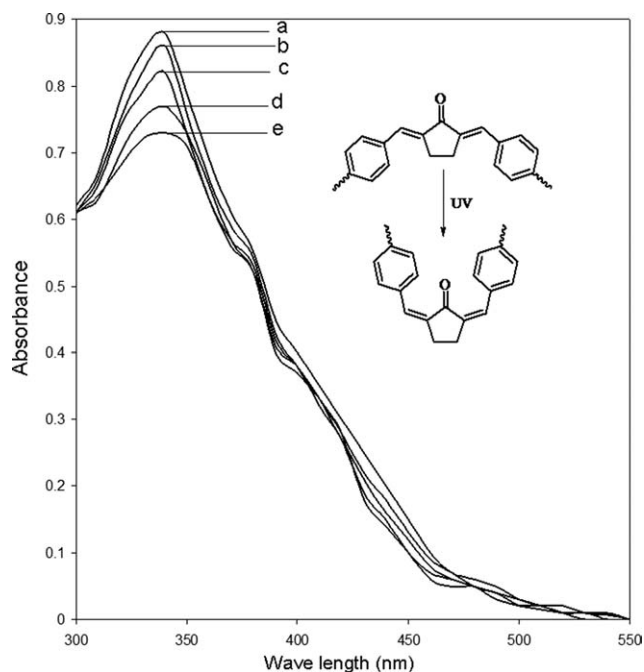


Figure 8 UV-vis absorption spectral change of PAI 8f in DMF solution upon irradiation with UV light for (a) 30 minutes, (b) 50 minutes, (c) 70 minutes, (d) 90 minutes, (e) 100 minutes.

The thermal stability of the polymers was studied on the basis of 5 and 10% weight losses (T_5 and T_{10} , respectively) of the polymers and the residue at 800°C (char yield). The results revealed that the PAIs were thermally stable up to 370°C . TGA data showed that the resulting polymers were good thermally stable. Also the DSC analyses for PAIs showed T_g around 184 – 215°C (Table V).

CONCLUSIONS

In this article, we have successfully synthesized a new dicarboxylic acid 6, containing dibenzalacetone moiety group. A series of novel thermally stable PAIs 8a-f were prepared by the direct polycondensation from dicarboxylic acid 6 with various aromatic

TABLE V
Thermal Behavior of PAIs 8a-f

Polymer	T_g^a	T_5 ($^\circ\text{C}$) ^b	T_{10} ($^\circ\text{C}$) ^b	Char yield ^c
8a	185	390	410	45.47
8b	191	410	420	55.82
8c	195	400	425	43.35
8d	184	370	410	42.96
8e	180	360	410	53.55
8f	215	390	400	40.84

^a Glass transition temperature was recorded at a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere.

^b Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10°C/min under N_2 .

^c Weight percentage of material left after TGA analysis at 800°C under N_2 .

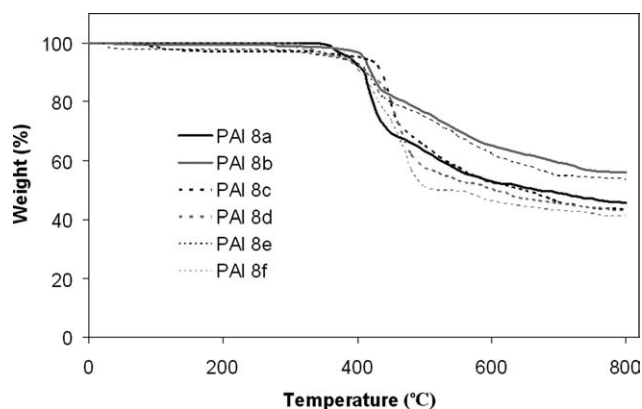


Figure 9 TGA curves of PAIs 8a-f.

diamines **7a-f** by two different methods such as direct polycondensation in a medium consisting of *N*-methyl-2-pyrrolidone (NMP)/triphenyl phosphite (TPP)/calcium chloride (CaCl_2)/pyridine (py) and direct polycondensation in a tosyl chloride (TsCl)/pyridine (py)/*N,N*-dimethylformamide (DMF) system. The results presented herein also clearly demonstrate that incorporating the imide group into the polymer main chain as well as combination of the wholly aromatic backbone and several functional groups remarkably enhanced the thermal stability of the new polymers. Also due to present amide groups in the main chain these polymers have good solubility in organic solvents. These properties could make these PAIs attractive for practical applications such as processable high-performance engineering plastics.

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