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Synthesis of poly (amide-imide)s by polycondensation reaction of [*N,N'* -(4,4' -carbonyldiphtaloyl)-bis-L-amino diacid]s and 1,5-bis (4-aminophenyl) penta-1,4-dien-3-one

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ABSTRACT

Six dicarboxylic acids 3a-3f were synthesized by the reaction of 3,3' ,4,4' - benzophenonetetracarboxylic dianhydride 1 with L-aminoacids 2a-2f in a solution of glacial acetic acid/pyridine at refluxing temperature. Then six new poly (amide-imide)s PAIs were synthesized from the direct polycondensation reaction of (*N,N'* -(4,4' - carbonyldiphtaloyl)-bis-L-amino diacid)s with 1,5-bis (4-aminophenyl) penta-1,4-dien-3-one (APPD). The polymerization reactions produced a series of new optically active poly (amide-imide)s with high yield and good inherent viscosity. Also these PAIs are optically active and soluble in various organic solvents. These resulting new polymers can be used in column chromatography for the separation of enantiomeric mixtures. The resulted polymers were fully characterized by means of FTIR and ^{1}H-NMR spectroscopy, elemental analysis, inherent viscosity measurements, solubility tests and thermogravimetric analysis (TGA).

KEYWORDS

Polyamide-imides;
N,N' -(4,4' - Carbonyldiphtaloyl)-Bis-L-Amino Diacids;
1,5-Bis (4-Aminophenyl) Penta-1,4-Dien-3-One;
Spectroscopic study;
Viscosity;
Thermogravimetric analysis.

INTRODUCTION

The development of heat resistant high performance polymers in the past decades has been quite dramatic and has drawn the attention of many polymer scientists all over the world. Aromatic polyimides have got a reputation as high-performance materials because of their excellent thermal stability, chemical resistance and outstanding mechanical properties[1]. Polyimides have become an increasingly important class of polymers, finding a wide range of applications in the aerospace and microelectronics industries[2,3]. However, polyimides are often insoluble and intractable resulting in processing difficulties that limit their applications[4]. Modification of high performance materials by enhancing the solubility and lowering the transition temperatures while maintaining thermal stability is of particular interest. Copolycondensation is one of the possible ways for modifying the polymer characteristics. Thus, for the processing of polyimides many copolyimides, such as poly (amide-imide)s, poly (ester-imide)s and other copolymers have been prepared[5-9]. Poly (amide-imide)s are an attractive polymer family which has received attention due to its natural biodegradability[10-12]. Photosensitivity of polymers means that the polymers are sensitive to the irradiated light leading to some changes in property or structure. Polymers containing photosensitive moieties such as cinnamate, chalcone, coumarine, dibenzalacetone and their derivatives both in main chain or side chain[13-15] have attracted great interest owing to their potential use in various applications, most of these including devices for optical data storage, photoresists and photolithographic assemblies[16,17]. Optically active polymers are advanced technological substances with various engineering applications. Their uses like chiral stationary phases in HPLC techniques for resolution of racemates and asymmetric mediums in enantioselective synthesis have already been reported[18-22]. Thus, polymers containing naturally occurring amino acids in their backbones may be expected to have bioactivity and biocompatibility.

We wanted to report the preparation and basic characterization of photosensitive and thermally stable poly (amide-imide)s PAIs 5a-5f from the direct polycondensation reaction of [*N*,*N*' -(4,4' -carbonyldiphtaloyl)- bis-L-amino acid]s with 1,5-bis (4-aminophenyl)penta-1,4-dien-3-one (APPD) in a medium containing *N*- methyl-2-pyrrolidone (NMP), triphenyl phosphite (TTP), calcium chloride (CaCl2) and pyridine. Previou study reported that APPD has been synthesized through a two-step reaction starting from 4-nitrobenzaldehyde and acetone in ethanol/water and finally by a catalytic reduction of 1,5-bis (4-nitrophenyl) penta-1,4-dien-3-one using Na2S, NaHCO3 in methanol.

EXPERIMENTAL

Materials

3,3' ,4,4' -Benzophenonetetracarboxylic dianhydride (1, Aldrich), L-alanine (2a), L-valine (2b), L-leucine (2c), L-isoleucine (2d), L-phenylalanine (2e) and L-2-aminobutyric (2f) acids (Merck) were used without previous purification. Diamine APPD (mp., 295-297°C) was prepared according to the previous work (23, 24). Solvents NMP (Fluka), Py (Acros) and TPP (Merck) were used as received. Commercially available CaCl2 (Merck) was dried under vacuum at 150°C for 6 hours.

Techniques

1H-NMR spectra were recorded on a Bruker AVANCE DRX- 400 MHz (Germany). Chemical shifts are shown in δ values (ppm) with tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FTIR) spectra were recorded on a 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 using a Technico Regd Trad Mark Viscometer. UV-Vis absorptions were recorded at 25°C in the 250-750 nm spectral regions with a Perkin-Elmer Lambda 15 spectrophotometer on DMF solutions by using a cell length of 1 cm. Specific rotations were measured by an A-Kruss polarimeter. Thermal gravimetric analysis (TGA and DTG) data for polymers were taken on a Mettler TA 4000 System under N2 atmosphere at a rate of 10 k/min. Elemental analysis were performed on a Vario EL equipment.

Monomer synthesis

[N,N' -(4,4' -carbonyldiphtaloyl)-bis-L-amino diacid]s 3a-3f

4.36 g (20.00 mmol) of 3,3' ,4,4' -benzophenonetetracarboxylic dianhydride 1, 40.00 mmol of L-amino acids 2a-2f, 80 ml of mixture of acetic acid/pyridine and a stirring bar were placed into a 250 ml round-bottomed flask. The mixture was stirred at room temperature overnight and refluxed for 4-10 hours. The solvent was removed under reduced pressure and the residue was dissolved in 100 ml of cold acidic water. A white precipitate was formed, filtered off and dried to give compounds [*N*,*N*' -(4,4' -carbonyldiphtaloyl)-bis-L-amino diacid]s 3a-3f.

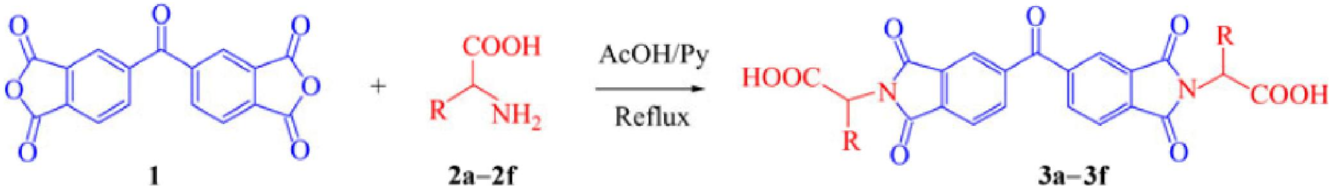
Polymer synthesis

A mixture of diacid 3a-3f (1 mmol), diamine APPD 4 (1 mmol), calcium chloride (0.350 g), TPP (0.8 ml), pyridine (1.2 ml) and NMP (4.0 ml) was refluxed for 10 hours. After cooling, the reaction mixture was poured into methanol (50 ml) to precipitate the corresponding polymer. The precipitated polymer was then separated by vacuum filtration and washed with methanol (30 ml) and hot water (100 ml) and dried at 120°C under vacuum for 24 hours. IR and NMR spectroscopic results of the obtained polymers will be discussed in the results and discussion section

RESULTS AND DISCUSSION

Monomer synthesis

The asymmetric diacids 3a-3f were synthesized by the condensation reaction of 3,3′ ,4,4′ -benzophenonetetracarboxylic dianhydride 1 with two equimolars of L-alanine 2a, L-valine 2b, L-leucine 2c, L- isoleucine 2d, L-phenyl alanine 2e and L-2-aminobutyric 2f acids in an acetic acid/pyridine solution. In this work we used six diacids 3a-3f for direct polycondensation (Scheme 1). The diacids 3a, 2c and 2e were synthesized previously[19-21]. The yields and some physical properties of these compounds are shown in TABLE 1. The chemical structure and purity of the optically active diacids 3a-3f were proved by using elemental analysis, FTIR and 1H-NMR spectroscopic techniques.



	2a	2b	2c	2d	2e	2f
R	Alanine	Valine	Leusine	Isoleusine	Phenylalnine	2-Aminobutyric acid
	CH_3	$CH (CH_3)_2$	$CH_2CH (CH_3)_2$	$CH_3CHC_2H_5$	CH_2Ph	CH_2CH_3

Scheme 1 : Synthesis of diacids 3a+3f

TABLE 1 : Synthesis of chiral diacids 3a-3f

Entry	Amino acid	Yield (%)	Mp (°C)	$[\alpha]_D^{25a}$	Color
3a	L-alanine	94	262–264	–7.5	White
3b	L-valine	92	283–285	+4.5	White
3c	L-leucine	82	265–267	+2.1	Grey
3d	L-isoleucine	91	278–280	-8.2	Pale yellow
3e	L-phenyl alanine	94	264–266	-6.5	Grey
3f	L-2 aminobutyric acid	88	241–243	+14.6	White

[a] Measured at a concentration of 0.5 g/dl in DMF at 25°C

As an example, the 1H-NMR spectrum of diacid 3f showed peaks between 0.84 and 0.89 ppm as a triplet, which were assigned for two CH3 (b), peaks between 2.05 and 2.18 ppm as a multiplet, which was assigned to the CH2 (c) and peaks between 4.70 and 4.75 ppm as a doublet of doublet, which was assigned to the CH (d) protons, which are chiral centers. The peak at 8.1-8.25 ppm was assigned to aromatic protons (e). Also a broad peak at 13.25 ppm was assigned to COOH groups as shown in Figure 1. The measured results in elemental analysis of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

Polymer synthesis

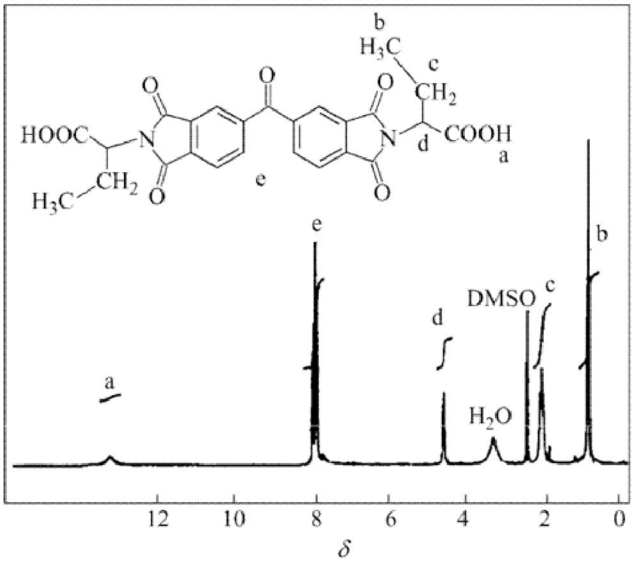
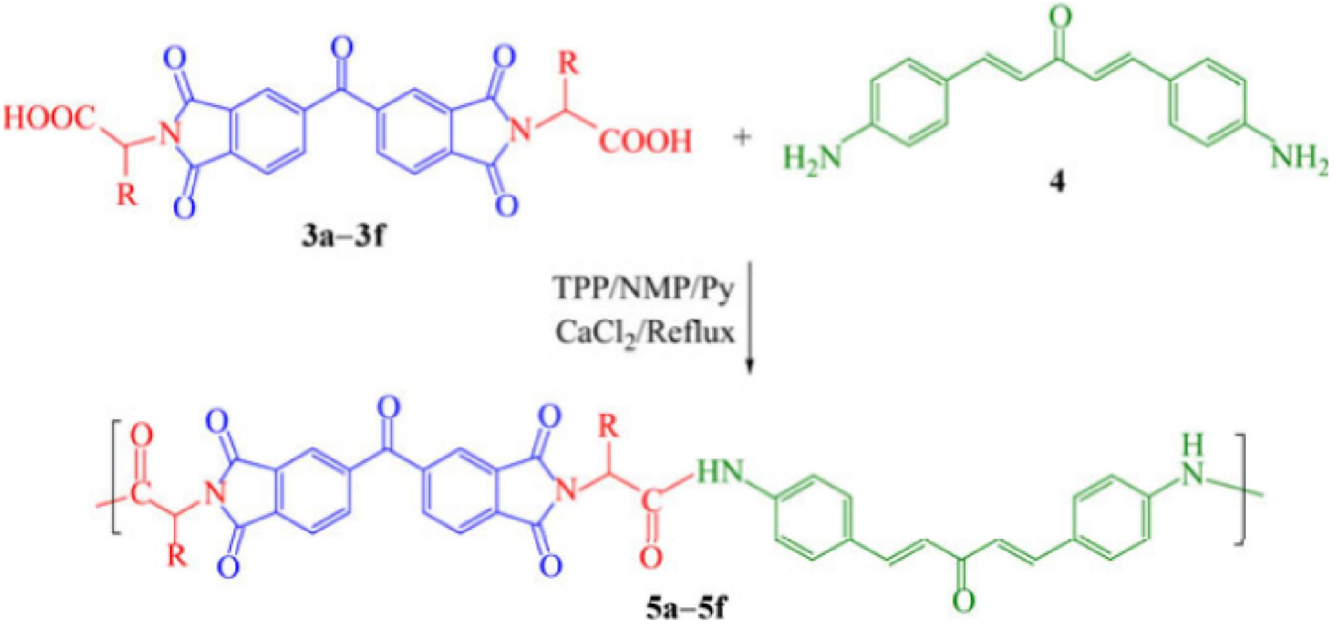


Figure 1 : ^{1}H-NMR spectrum of diacid 3a- 3f

In this work, the direct polycondensation of a dicarboxylic acid and diamine is one of the well-known methods for PAI synthesis. We synthesized PAIs 5a-5f containing dibenzalacetone moiety by direct polycondensation reactions of six chiral [*N*,*N*′ -(4,4′ -carbonyldiphtaloyl)-bis-L-amino acid]s 3a-3f with diamine APPD 4 by using triphenyl phosphate (TPP) and pyridine as condensing agents (Scheme 2).

All the polycondensations proceeded readily in a homogeneous solution. Tough and stringy precipitates



Scheme 2 : Synthesis route of PAIs 5a-5f

formed when the viscous polymer solutions were trickled into the stirring methanol.

The synthesis and some physical properties of these new PAIs 5a-5f are given in TABLE 2. All the polymers were obtained in high yields (82%-94%) and the inherent viscosities were 0.45-0.58 dl/g measured in DMF solutions. Some physical properties of PAIs 5a-5f are given in TABLE 2. Also the resulting polymers have a range of color between cream and brown.

TABLE 2 : Synthesis and some physical properties of PAIs 5a-5f

Diacid	Polymer	Yield (%)	η_{inh} (dL/g)^a	$[\alpha]D^{25a}$	Color
3a	5a	91	0.45	+110	Cream
3b	5b	90	0.54	+115	Cream
3c	5c	83	0.50	+99.5	Brown
3d	5d	85	0.51	+118.5	Pale Brown
3e	5e	94	0.48	+112.5	Cream
3f	5f	82	0.58	+123.5	Cream

^{a} **Measured at a concentration of 0.5 g/dl in DMF at 25°C**

Polymer characterization

The structure of polymers was confirmed as PAIs by means of FTIR spectroscopy and elemental analysis, the representative FTIR spectrum of PAI 5b is shown in Figure 2. The polymer showed the C=O asymmetric stretching of imide at 1776 cm^{-1}, the C=O symmetric stretching of imide at 1720 cm^{-1}, C-N stretching at 1379 cm^{-1}. All of these PAIs exhibited strong ab-

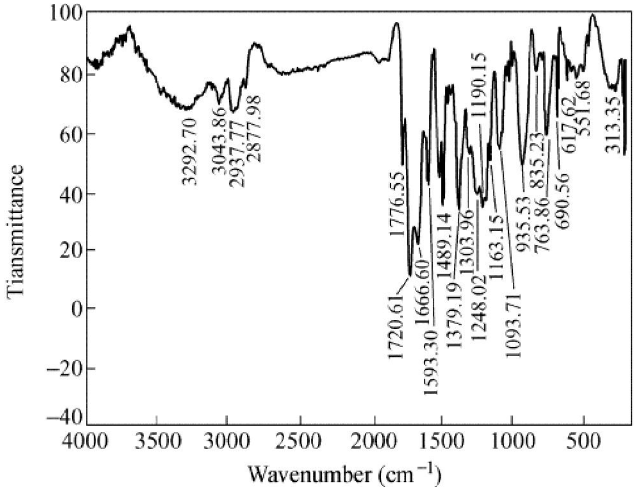


Figure 2 : FTIR spectrum of PAI 5b

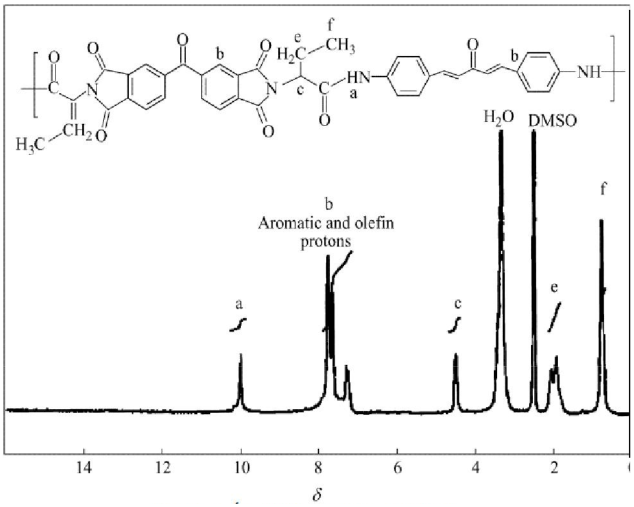


Figure 3 : ^{1}H-NMR spectrum of PAI 5f

TABLE 3 : FTIR characterization of PAIs 5a-5f FT-IR peaks (cm^{-1})

Polymer	
5a	3071 (w), 2916 (w), 1780 (w), 1722 (s), 1610 (m), 1514 (s), 1388 (s), 1290 (m), 1247 (m), 1175 (w), 1095 (w), 1050 (w), 823 (w), 725 (s), 524 (m)
5b	3075 (w), 2915 (w), 1780 (w), 1722 (s), 1610 (w), 1512 (s), 1388 (m), 1249 (m), 1125 (w), 1057 (w), 825 (m), 730 (s), 527 (w)
5c	3071 (w), 2914 (w), 1778 (m), 1722 (s, br), 1610 (m), 1514 (s), 1386 (s), 1249 (s), 1176 (w), 1097 (w), 1053 (w), 825 (w), 725 (s), 617 (w), 524 (w)
5d	3065 (w), 2969 (m), 1776 (w), 1716 (s), 1678 (m), 1639 (w), 1591 (m), 1465 (m), 1385 (s), 1321 (w), 1201 (m), 1113 (w), 723 (w).
5e	3075 (w), 2954 (w), 1780 (w), 1720 (s, br), 1610 (m), 1512 (s), 1388 (s), 1292 (m), 1248 (m), 1176 (w), 1099 (w), 1055 (w), 825 (w), 721 (s), 524 (m).
5f	3073 (w), 2925 (m), 1780 (m), 1722 (s), 1611 (w), 1514 (s), 1387 (s), 1248 (m), 1122 (w), 1055 (w), 825 (m), 723 (s), 526 (w)

sorption around 1380 and 763 cm^{-1}, which shows the presence of the heterocyclic imide groups. FTIR spectroscopy data for all of PAIs 5a-5f are listed in TABLE 3.

The 1H-NMR spectrum of PAI 5f shows peaks confirm its chemical structure as shown in Figure 3. The aromatic and olefin protons related to polymer backbone appeared in the region of 7.22-7.73 ppm. The peaks in the region at 1.90-2.04 ppm are assigned to diasterotopic protons in the polymer chain. The peak in region 9.97 ppm is assigned to N-H amide groups in the polymer chain. The peak in the region at 4.50 ppm is assigned to the proton of the chiral center. Also, the 1H-NMR spectrum of PAI 5b showed peaks that confirm its chemical structure see Figure 4. The elemental analysis of the resulting PAIs 5a-5f were in good agreement with the calculated values for the proposed structure as shown in TABLE 4.

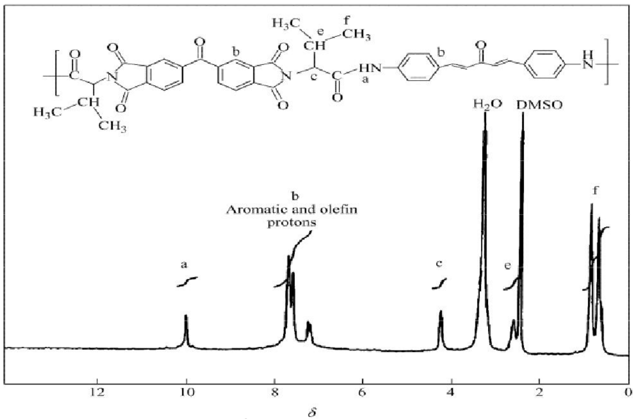


Figure 4 : ^{1}H-NMR spectrum of 5b

Solubilityof PAIs 5a-5f

The solubility of PAIs 5a-5f was investigated as 0.01 g of polymeric sample in 2 ml of solvent. These poly (amide-imide)s have good solubility in aprotic organic solvents. Remarkably, all of these PAIs were easily soluble at room temperature in aprotic polar solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-

TABLE 4 : Elemental analysis of PAIs 5a-5f

Polymer	Formula		% C	% H	% N
5a	$C_{34}H_{27}N_4O_7$	Calcd	67.69	4.47	9.27
	$(603.23)_n$	Found	66.89	3.93	8.96
5b	$C_{36}H_{31}N_4O_7$	Calcd	68.49	4.91	8.86
	$(631.25)_n$	Found	68.31	4.66	8.80
5c	$C_{37}H_{33}N_4O_7$	Calcd	68.86	5.11	8.67
	$(645.26)_n$	Found	68.72	4.89	8.49
5d	$C_{37}H_{33}N_4O_7$	Calcd	68.86	5.11	8.67
	$(645.26)_n$	Found	67.98	4.97	8.31
5e	$C_{40}H_{31}N_4O_7$	Calcd	70.72	4.56	8.23
	$(679.29)_n$	Found	69.89	4.65	8.02
5f	$C_{35}H_{29}N_4O_7$	Calcd	68.10	4.69	9.06
	$(617.24)_n$	Found	67.88	4.61	8.89

TABLE 5 : Solubility of PAIs 5a-5f

Solvent	5a	5b	5c	5d	5e	5f
H_2SO_4	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
MeOH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–
H_2O	–	–	–	–	–	–

+ soluble at room temperature “ insoluble at room temperature dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF) and insoluble in solvents such as chloroform, ethanol and methanol as shown in TABLE 5.

UV-vis absorption characteristics

The photosensitive property of the new poly (amide-imide)s 5a-5f in the DMF solution was studied by a UV

spectrophotometer. All polymer solutions exhibit the same position of absorption maximum in UV-Vis spectra 310-330 nm. The maximum absorption at around 300 nm corresponds to $n \rightarrow \pi^*$ transition of the nonbonding electrons which was present in nitrogen and oxygen atoms in the polymer backbone. The UV-Vis absorption spectrum of PAI 5c in *N,N′*-dimethylformamide is shown in Figure 5.

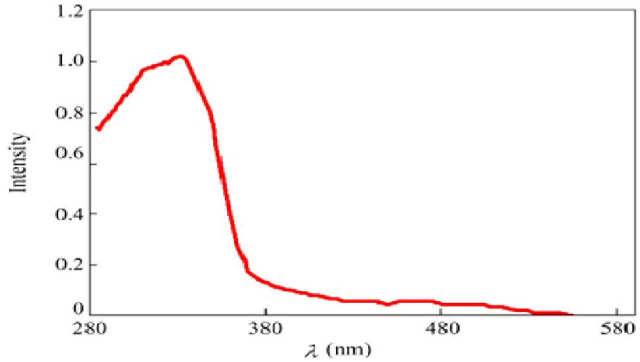


Figure 5 : UV-vis absorption spectrum of PAI 5a-5f in DMF solution

Thermal properties

The thermal properties of 5b and 5d were evaluated by means of TGA/DTG in a tmosphere at a heating rate of 10 k/min. The temperature of 5% and 10% weight loss together with char yield at 800ºC has been calculated by means of thermograms and used as a criterion for the evaluation of thermal stability of these polymers. The thermoanalyses of the polymers are summarized in TABLE 6. Figure 6 shows TGA results of PAIs 5b and 5d respectively.

The char yield of the polymers at 800°C was above 35% which show a high intrinsic fire resistance. The char yield can be applied as a decisive factor for estimating the limited oxygen index (LOI) of polymers using Van Krevelen and Hoftyzer's equation[25].

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

Where as CR is char yield.

PAIs 5b and 5d had LOI values around 32, which were calculated from their char yield. On the basis of the LOI values, such macromolecules can be classified as self-extinguishing polymers.

TABLE 6 : Thermal behavior of PAIs 5b and 5d

Polymer	T$_5$ (°C)^a	T$_{10}$ (°C)^a	Char yield^b	LOI^c
5b	330	390	41.1	33.9
5d	245	383	35.4	31.6

aTemperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 k/min under N_2.
bWeight percentage of material left after TGA analysis at a maximum temperature of 800°C under N_2.
cLimiting oxygen index.

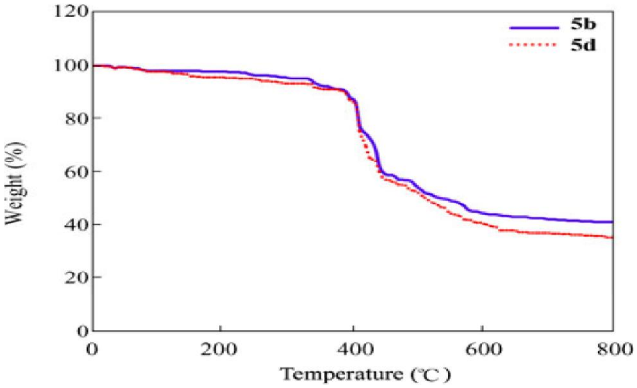


Figure 6 : TGA curves of PAIs 5b and 5d

CONCLUSIONS

In this article, we have successfully synthesized new dicarboxylic acid 6 containing L-amino acids. A series of new optically active and thermally stable PAIs 5a-5f were prepared from [*N,N*′-(4,4′-carbonyldiphtaloyl)-bis-L- amino diacid]s 3a-3f with 1,5-bis (4-aminophenyl) penta-1,4-dien-3-one by direct polycondensation method. The photosensitive properties of new PAIs 5a-5f in the DMF solution were studied by a UV-Vis spectrophotometer. These PAIs are photosensitive polymers because of dibenzalacetone moieties in the backbone of polymers. The results presented here also clearly demonstrate that incorporating the imide group into the polymer main chain as well as combination of the aromatic backbone and several functional groups remarkably increased the thermal stability of the new polymers. These polymers are expected to have higher solubility due to the presence of alkyl groups in the polymer chain. These properties could make these PAIs attractive for practical applications such as processable high-performance engineering plastics that may be subject of further investigations.

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