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ORIGINAL PAPER

L-Aspartic acid incorporated optically active poly(amide-imide)s: synthesis and characterization

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Abstract *N*-trimelliticimido-L-aspartic acid (**1**) was prepared from the reaction of trimellitic anhydride with L-aspartic acid in a mixture of glacial acetic acid and pyridine solution (3/2 ratio) under refluxing conditions. The solution polycondensation of the corresponding activated monomer with eight aromatic diamines were carried out in DMAc. The resulting poly(amide-imide)s were obtained in quantitative yields, showed admirable inherent viscosities (0.20–0.36 dl g^{-1}), good optical activity (+7.32° to +15.24°), and were readily soluble in polar aprotic solvents. They start to decompose ($T_{10\%}$) above 170 °C and display glass-transition temperatures at 120–237 °C. All of the above polymers were fully characterized by UV, FT–IR, and ^{1}HNMR spectroscopy, elemental analysis, thermogravimetric analyses, DSC, inherent viscosity measurement, and specific rotation.

Keywords L-Aspartic acid · Poly(amide-imide) · Optical active · Biodegradable

Introduction

Owing to the increasing demands for high-performance polymers as a potential candidate for ceramics or metals in the microelectronic device, aerospace and automotive industries, thermally stable polymers have received much more interest over the past decade. Polyamides are positively one of the most useful classes but they suffer at least from disadvantages such as infusible, insoluble, and having high melting and/or glass transition temperatures, which cause restriction their processing. However, these problems can be solved or reduced by copolymerization [1, 2].

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Poly(amide-imide)s were developed from high-performance polymers which combine and inherit desirable characteristics from both polyamides and polyimides. They possess good thermal properties in comparison with polyamides, and better melting processability than polyimides. To improve further solubility in organic solvents, flexible, or asymmetrical linkages have been introduced into the polymer [3–8].

Optically active polymers are one of the most important classes of high performance engineering materials which are suitable candidates for use as the chiral stationary phases in high-performance liquid chromatography (HPLC) [9–12]. Synthesis and application of these polymers is a considerable topic, which has been paid more attention recently [13]. In polycondensation reactions, we used amino acids as chiral inducting agents. These materials are naturally existing compounds, and therefore, synthetic polymers based on amino acids are expected to be biodegradable and biocompatible [14]. These properties have caused them to be good candidate for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials, and also as chiral purification media [15]. So, more considerations to improve different synthetic procedures of optically active polymers exist. Recently, we have synthesized optically active polymers by different methods [8, 16]. In this research, we report the synthesis and characterization of eight novel poly(amide-imide)s based on L-aspartic acid through Solution polycondensation. These polymers showed good optical activity (+7.32° to +15.24°). The outstanding characteristics of these polymers include thermal stability, good solubility and optical activity.

Experimental

Materials and instruments

The trimellitic anhydride (Merck) was recrystallized from acetic anhydride. L-Aspartic acid (Merck) was used without further purification. 1,3-phenylene diamine and 1,4-phenylene diamine were purified by sublimation under the reduced pressure. 4,4′-diamino diphenyl sulfone, 4,4′-diamino diphenyl ether and 4,4′-diamino biphenyl were recrystallized from EtOH/H_2O. DMAc was purified by distillation under reduced pressure over barium oxide. The other chemicals (Merck) were used as received. NMR spectra were recorded on a 400 MHz (Bruker Avance) instrument, using DMSO-d_6 as solvent. IR spectra were recorded on a Bruker Tensor-27 FT–IR instrument using KBr pellets. UV spectra were recorded on a Perkin-Elmer lambada 5 instrument. Specific rotations were measured by an A. Kruss. Optronic P3002 RS (Germany) Polarimeter in DMF as solvent. Thermogravimetric analyses (TGA) were recorded on a Mettler TA4000 with heating rate of 10 °C min^{-1} under air atmosphere. DSC analyses were preformed on a Mettler DSC-30 under nitrogen atmosphere. Inherent viscosities of polymers were measured by a standard procedure using a Cannon–Fenske Routine Viscometer (Germany) at 25 °C using DMF as solvent. Melting points were measured in open capillaries with a IA9000 series digital Melting Point Apparatus. Elemental analyses were preformed in a Heraeus CHNS-RAPID instrument.

Monomer synthesis

*N-trimelliticimido-L-aspartic acid (**1**)*

Into a 25 mL round-bottomed flask with a stirring bar were placed 1.920 g (10.0 mmol) of trimellitic anhydride, 1.330 g (10.0 mmol) of L-aspartic acid, a mixture of acetic acid/pyridine (10 mL, 3:2) and a stirring bar were placed. The mixture was stirred at room temperature for 5 h and then refluxed for 6 h. The solvent was removed under reduced pressure. 5 mL of cold concentrated HCl was added. A white precipitate was formed and filtered off. Yield: 2.45 g (79%); m.p.: 230 °C, $[\alpha]_D^{25} = +5.07°$; IR (cm^{-1}): 3400–2400, 1785, 1728, 1487, 1388, 1299, 1199, 1104, 890, 727; ^{1}HNMR (400 MHz, DMSO-d_6) δ(ppm): 2.95(dd, 1H), 3.14(dd, 1H), 5.19(br, 1H), 8.05(d, 1H), 8.28(d, 1H), 8.42(d, 1H), 13.26(br, 3H). ^{13}CNMR (400 MHz, DMSO-d_6) δ(ppm): 34.19, 48.55, 123.95, 124.38, 132.01, 134.82, 136.23, 137.20, 166.15, 166.67, 166.71, 170.20, 171.88.

*N-trimelliticimido-L-aspartic anhydride acyl chloride (**2**)*

Into a 25 mL round-bottomed flask, equipped with a reflux condenser 0.558 g (1.81 10–3 mol) of compound **1**, 7 mL (an excess amount) of thionyl chloride and a stirring bar were placed. The mixture was stirred for 20 min and then refluxed for 2 h. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with *n*-hexane, to leave 0.486 g (87%) of white crystals. $[\alpha]_D^{25} = +3.23°$; IR (KBr cm^{-1}): 2953, 1862, 1785, 1724, 1394, 1226, 1072, 932, 852, 748, 690, 653.

Preparation of poly(amide-imide)s

In a two necked flask equipped with reflux condenser and gas inlet tube, a mixture consisting of DMAc (4.0 mL), *N*-trimelliticimido-L-aspartic anhydride acyl chloride (0.3075 g, 1.0 mmol), and triethyl amine (0.11 mL) was prepared. Then 4,4′-diamino diphenyl ether (0.200 g, 1.0 mmol) in DMAc (2.0 mL) was added to the flask. The mixture was stirred under a stream of N_2 5 °C for 4 h and then kept under stirring for 24 h in room temperature. The resulting polyamic acid was heated stepwise at 100, 120, and 150 °C for 60, 60, and 30 min, correspondingly. The solution was poured into stirring methanol. The solid was collected by filtration, washed several times with methanol and vacuum dried to leave **PAIa**: Pale green; Yield (%) = 90; $\acute{\eta}_{inh}$ (dl g^{-1}) = 0.30; $[\alpha]_D^{25} = +11.45$; UV (λ max) = 344; FT–IR spectra show (KBr cm^{-1}): 3377, 1778, 1721, 1696, 1500, 1383, 1222, 1105, 834, 727, 652. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.83–2.98 (2H), 5.53 (1H), 6.98–8.51 (11H), 10.66 (1H).

The other polymers were prepared according to the above mentioned procedure.

PAIb: Pale yellow; Yield (%) = 87; $\acute{\eta}_{inh}$ (dl g^{-1}) = 0.25; $[\alpha]_D^{25} = +8.56$; UV (λ max) = 337; FT–IR spectra show (KBr cm^{-1}): 3359, 1778, 1721, 1690, 1545, 1381, 1205, 1106, 788, 725, 652. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.81–2.99 (2H), 5.54 (1H), 7.382–8.54 (7H), 10.76 (1H).

PAIc: Green; Yield (%) = 90; $\acute{\eta}_{\mathrm{inh}}$ (dl g^{-1}) = 0.36; $[\alpha]_{\mathrm{D}}^{25}$ = +12.70; UV (λ max) = 358; FT–IR spectra show (KBr cm^{-1}): 3372, 1777, 1720, 1650, 1501, 1380, 1184, 1105, 821, 725. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.80–2.98 (2H), 5.54 (1H), 7.39–8.56 (11H), 10.75 (1H).

PAId: Brown; Yield (%) = 85; $\acute{\eta}_{\mathrm{inh}}$ (dl g^{-1}) = 0.22; $[\alpha]_{\mathrm{D}}^{25}$ = +13.20; UV (λ max) = 360; FT–IR spectra show (KBr cm^{-1}): 3329, 2925, 1780, 1719, 1650, 1515, 1383, 1315, 1175, 1106, 832, 727, 654. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.81–2.97 (2H), 5.50 (1H), 6.64–8.55 (7H), 10.69 (1H).

PAIe: Gray; Yield (%) = 87; $\acute{\eta}_{\mathrm{inh}}$ (dl g^{-1}) = 0.24; $[\alpha]_{\mathrm{D}}^{25}$ = +15.24; UV (λ max) = 331; FT–IR spectra show (KBr cm^{-1}): 3372, 1780, 1723, 1690, 1591, 1530, 1382, 1321, 1152, 1106, 839, 728. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.80–2.98 (2H), 5.50 (1H), 7.57–8.49 (11H), 11.0 (1H).

PAIf: Brown; Yield (%) = 84; $\acute{\eta}_{\mathrm{inh}}$ (dl g^{-1}) = 0.26; $[\alpha]_{\mathrm{D}}^{25}$ = +7.32; UV (λ max) = 308; FT–IR spectra show (KBr cm^{-1}): 3430, 1780, 1720, 1630, 1513, 1383, 1204, 728. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.89–3.0 (2H), 3.87(2H), 5.49 (1H), 7.13–8.49 (11H), 10.64 (1H).

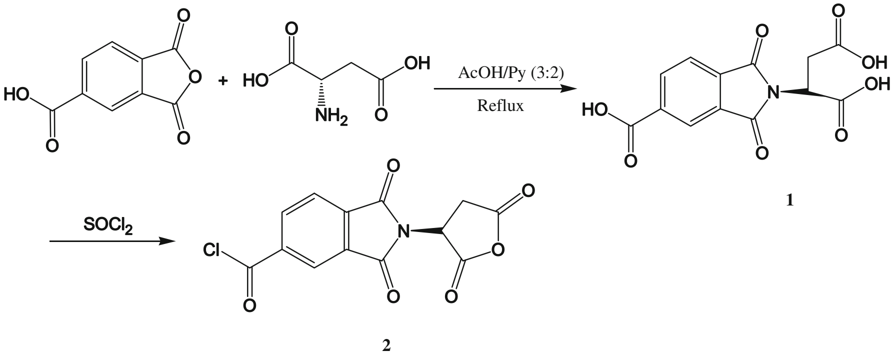
PAIg: Bright yellow; Yield (%) = 81; $\acute{\eta}_{\mathrm{inh}}$ (dl g^{-1}) = 0.20; $[\alpha]_{\mathrm{D}}^{25}$ = +8.10; UV (λ max) = 341; FT–IR spectra show (KBr cm^{-1}): 3376, 2925, 1780, 1721, 1690, 1524, 1383, 1188, 1107, 728. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.3 (3H), 2.89–3.0 (2H), 5.49 (1H), 7.13–8.49 (6H), 10.64 (1H).

PAIh: Violet; Yield (%) = 70; $\acute{\eta}_{\mathrm{inh}}$ (dl g^{-1}) = 0.21; $[\alpha]_{\mathrm{D}}^{25}$ = +8.00; UV (λ max) = 343; FT–IR spectra show (KBr cm^{-1}): 3396, 2924, 1780, 1720, 1625, 1590, 1380, 1200, 826, 765. ^{1}HNMR (DMSO-d_6, δ in ppm): 2.83–2.98 (2H), 5.53 (1H), 6.98–8.51 (9H), 10.66 (1H).

Results and discussion

Trimellitic anhydride and L-aspartic acid were reacted in a mixture of acetic acid/pyridine to prepare the corresponding triacid. This compound was reacted in excess amount of thionyl chloride to yield *N*-trimelliticimido-L-aspartic anhydride acyl chloride (**2**) (Scheme 1). IR spectrum of compound **2** shows the characteristic absorptions at around 1830 cm^{-1}, peculiar to acyl chloride, two peaks at around 1862 and 1785 cm^{-1}, peculiar to symmetrical and unsymmetrical carbonyl stretching of anhydride, two absorption bands at 1770 and 1705 cm^{-1} due to the symmetrical and asymmetrical imide carbonyl stretching vibrations, and strong absorptions at 1388 and 725 cm^{-1}, that indicates the presence of the cyclic imide group. The corresponding peaks included acidic groups at around 13.2 ppm have been detected by ^{1}HNMR. ^{1}HNMR and ^{13}CNMR of diimide-diacid **1** is presented in Fig. 1.

The polycondensation method was used to prepare the polymers (**PAIa–h**) (Scheme 2). The polymers were characterized by FT–IR and ^{1}HNMR analyses.



Scheme 1 Preparation of *N*-trimelliticimido-L-aspartic anhydride acyl chloride

The presence of amidic bands at ca. 3370 cm^{-1} (N–H stretching), 1720 cm^{-1} (C=O stretching) and ca. 1680 cm^{-1} (combined N–H bending and C–N stretching) in the IR spectra and the amidic proton at ca. 10.6 ppm in the ^{1}HNMR spectra confirm the amidic structure. ^{1}HNMR spectra of **PAIa** is shown in Fig. 2.

The color of **PAI**s ranges from brown to pale green. The inherent viscosities of the polymers are in the range of 0.20–0.36 dl/g, indicating moderate to high molecular weight. Transparent, flexile, and tough films could be obtained from these polymers by casting from solution of polymers in DMF solvent, which shows good mechanical strength of the films and consequently high molecular weight. One of the major objectives of this study is to improve the solubility. Table 1 shows that these polymers are readily soluble in common polar aprotic solvents.

The photosensitivity of these new poly(amide-imide)s was studied by a UV–vis spectrophotometer in DMF solution. All of them exhibit two same absorption maximum at around 311–354 nm. The absorption maximum at around 311 nm corresponds to $\pi \rightarrow \pi^*$ transition of the carbon double bonds in aromatic rings in the polymer backbones and the absorption maximum at around 354 nm corresponds to $n \rightarrow \pi^*$ transition of the nonbonding electrons present in nitrogen and oxygen atoms in the polymer backbone. The UV–vis absorption spectrum of **PAIa** in *N*,*N*-dimethylformamide is shown in Fig. 3. The spectrum exhibits two typical peaks at 310 nm ($\pi \rightarrow \pi^*$) and 344 nm ($n \rightarrow \pi^*$).

The thermal properties of **PAI**s were evaluated by means of TGA/DTG under air atmosphere and DSC under nitrogen atmosphere at a heating rate of 10 °C min^{-1} (Table 2). These polymers show similar decomposition behavior. The temperature of 10% weight loss for the polymers range from 170 to 342 °C and the residual weight for these polymers at 600 °C range from 3.80 to 52.10% under air atmosphere. The high char yields of the synthetic polymers could be due to their high aromatic content. Char yield can be used as a factor for estimated limiting oxygen index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation [17]. $\mathrm{LOI} = 17.5 + 0.4\,\mathrm{CR}$, where CR = char yield. On the basis of LOI values, these polymers can be classified as self-extinguishing polymers.

The Tgs of these polymers range from 120 to 237 °C. The TGA/DSC diagram of **PAIa** is shown in Fig. 4.

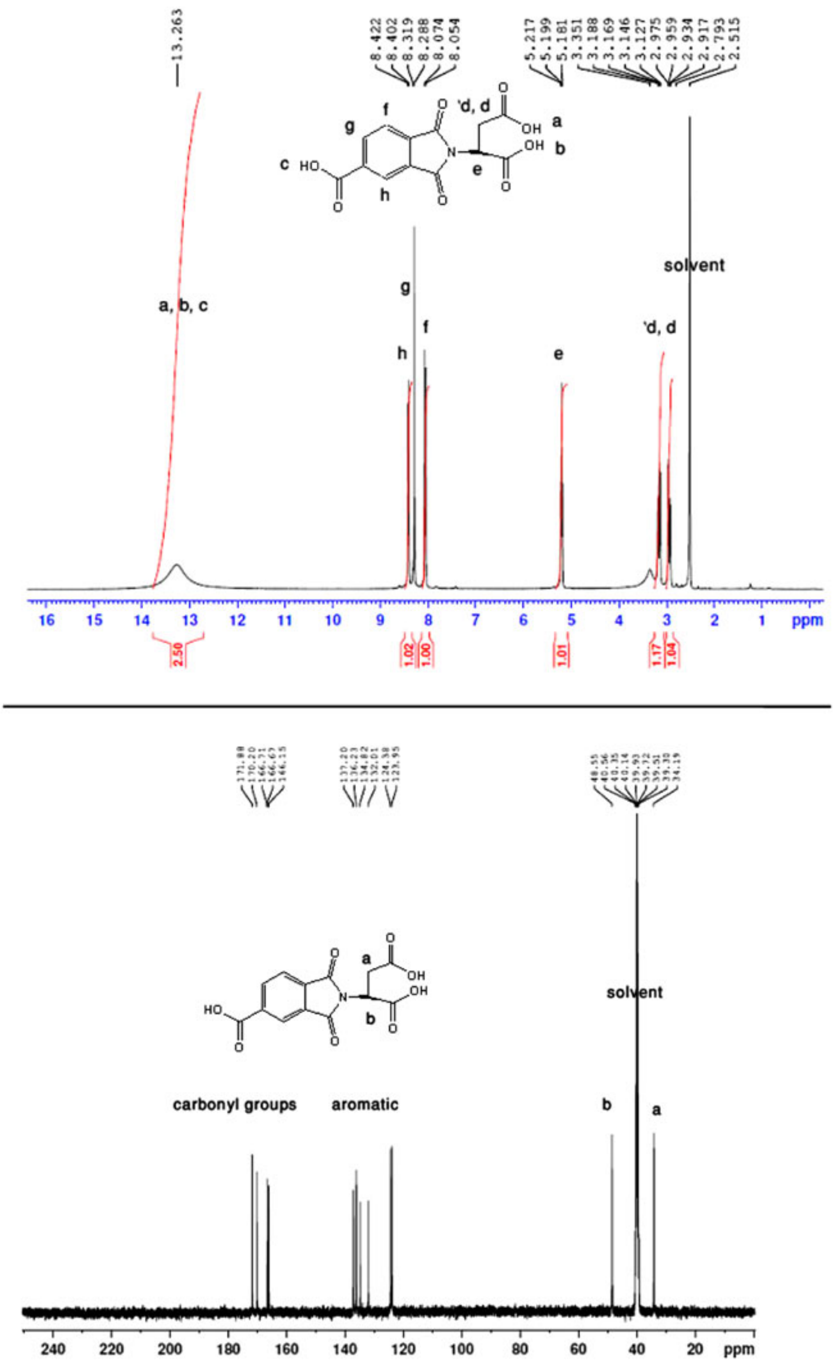
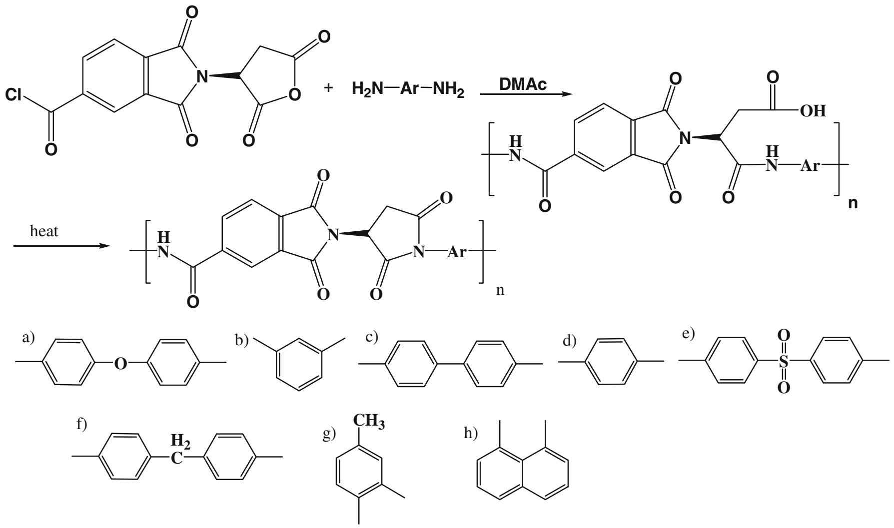


Fig. 1 ^{1}HNMR and ^{13}CNMR of compound **1**



Scheme 2 Preparation of poly(amide-imide)s

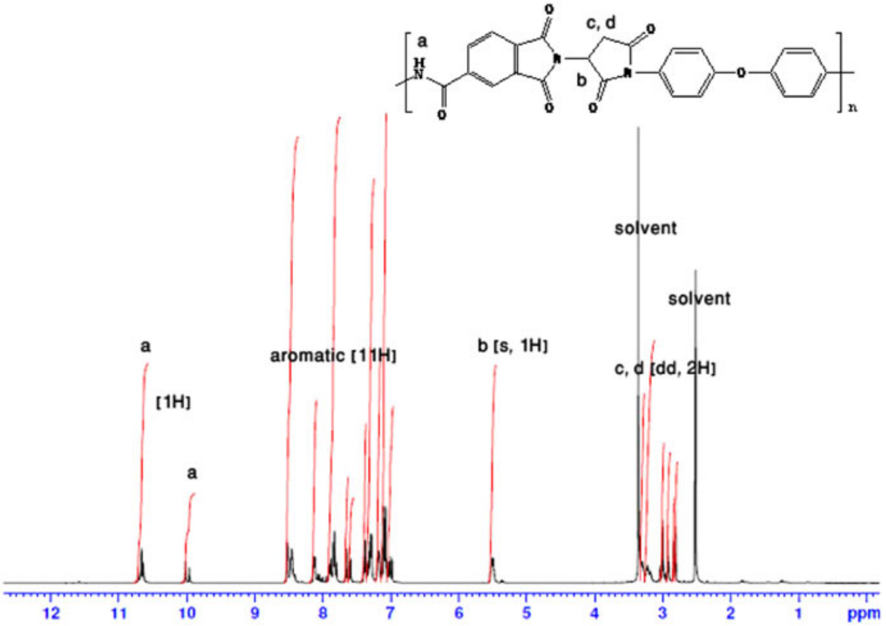


Fig. 2 ^{1}HNMR spectrum of **PAIa**

In continue to our developing study on different natural amino acids we interested to incorporate L-aspartic acid since different study on polymers containing it have been preformed such as on controlled hydrolytic degradation

Table 1 Solubility of **PAIa–h**

Solvents	**PAIa**	**PAIb**	**PAIc**	**PAId**	**PAIe**	**PAIf**	**PAIg**	**PAIh**
NMP	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+
DMAc	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+
H_2SO_4	+	+	+	+	+	+	+	+
CH_2Cl_2	–	–	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–	–	–
EtOH	–	–	–	–	–	–	–	–
MeOH	–	–	–	–	–	–	–	–

+: soluble at room temperature, DMAc: *N,N*-dimethylacetamide, DMF: *N,N*-dimethyl formamide, NMP: *N*-methyl pyrrolidone, DMSO: dimethyl sulfoxide

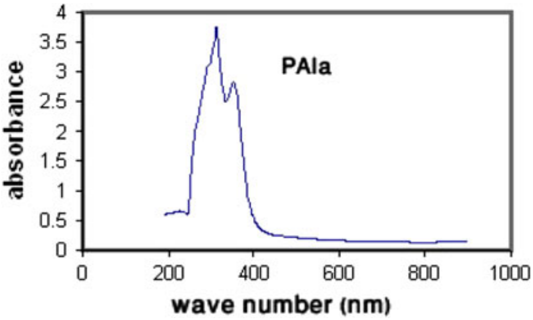


Fig. 3 UV–vis spectrum of **PAIa**

Table 2 Thermal properties of **PAIa–h**

Polymer	T10% (°C)[a]	T_g[b]	Ch.Y[c]
PAIa	342	223	45.3
PAIb	175	130	21.8
PAIc	293	219	52.1
PAId	170	120	9.17
PAIe	236	145	20.1
PAIf	200	123	15.8
PAIg	224	237	3.8
PAIh	223	193	35.7

[a] Temperature of 10% weight loss, obtained from TGA

[b] Glass transition temperature, obtained from DSC

[c] Char yield percentage at 600 °C, obtained from TGA

[18], Photocatalytic decomposition [19] and complexation with poly(ethylene glycol) [20]. In addition, L-aspartic acid is a natural compound that potentially makes the polymers nontoxic, biodegradable, and unlimited sources of chemicals to synthesis new polymers with specific properties.

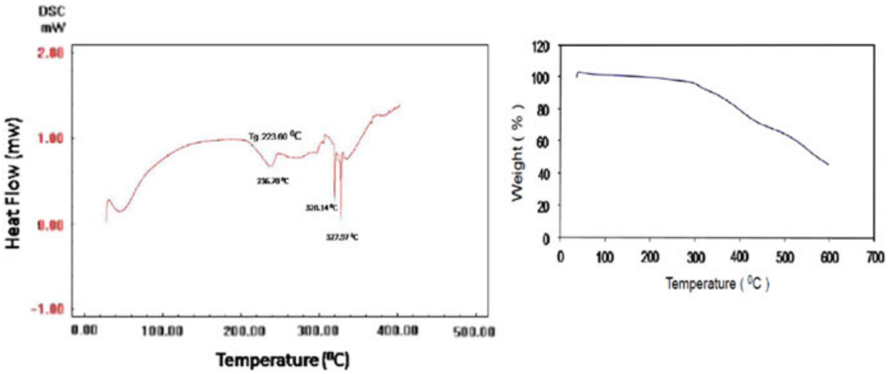


Fig. 4 DSC/TGA spectrum of **PAIa**

Conclusions

Eight new heterocyclic, thermally stable, and optically active **PAI**s with admirable inherent viscosities (0.20–0.36) and optical activity (+7.32° to +15.24°) were synthesized from L-aspartic acid as natural compound by usual solution polycondensation method. These aromatic **PAI**s show optical rotation and are readily soluble in various organic solvents and have good thermal stability.

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