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ORIGINAL ARTICLE

Microwave-assisted synthesis and characterization of optically active poly (ester-imide)s incorporating L-alanine

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Abstract Pyromellitic dianhydride (1) was reacted with L-alanine (2) to result [*N,N′*-(pyromellitoyl)-bis-L-alanine diacid] (3). This compound (3) was converted to *N,N′*-(pyromellitoyl)-bis-L-alanine diacyl chloride (4) by reaction with thionyl chloride. The microwave-assisted polycondensation of this diacyl chloride (4) with polyethyleneglycol-diol (**PEG-200**) and/or three synthetic aromatic diols furnish a series of new **PEI**s and **Co-PEI**s in a laboratory microwave oven (Milestone). The resulting polymers and copolymers have inherent viscosities in the range of 0.31–0.53 dl g^{-1}. These polymers are optically active, thermally stable and soluble in polar aprotic solvents such as DMF, DMSO, NMP, DMAc, and sulfuric acid. All of the above polymers were fully characterized by IR spectroscopy, ^{1}H NMR spectroscopy, elemental analyses, specific rotation and thermal analyses. Some structural characterizations and physical properties of these optically active **PEI**s and **Co-PEI**s have been reported.

Keywords Optically active · Poly (ester-imide) · Microwave-assisted · Pyromellitic dianhydride

Introduction

Due to the increasing demands for high-performance polymers as a replacement for ceramics or metals in the microelectronic, aerospace and automotive industries, thermally stable polymers have received much interest over the past decade. Polyimides and their copolymers are certainly one of the most useful classes of high-performance polymers, which have found many applications in industries (Mittal 1984). Aromatic polyimides are an important class of heterocyclic polymers with remarkable heat resistance and superior mechanical and electrical properties, and also durability (Banihashemi and Abdolmaleki 2004). Poor thermoplastic fluidity and solubility are the major problems in wide application of polyimides. This makes it impossible for most polyimides to be directly processed in their imidized forms; thus, their applications have been restricted in some fields. Processable engineering plastics possessing moderately high softening temperatures and/or solubility in some organic solvents are required for practical use. Therefore, various efforts have been focused on the preparation of soluble and/or thermoplastic polyimides, while still maintaining the excellent thermal and mechanical properties. Typical approaches have been employed to improve the processability of these polyimides including the incorporation of flexible links (Tamai et al. 1996), bulky pendant or cardo groups (Hsiao and Li 1998), kinked or unsymmetrical structures (Li et al. 1999), and spiro-skeletons (Reddy et al. 2003) into the polymer chain. These modifications lower the melting temperature and lead to soluble and amorphous polymers. In general, amorphous polymers have a lower softening temperature (Tg) and improved solubility with respect to their crystalline analogs. Some of the block copolymers composed of polyethers and polyamides have already been

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commercialized as thermoplastic elastomers (Legge et al. 1987). A number of synthetic routes for polyether–polyimide block copolymers have been known (Noshay and McGrath 1977). Ether linkages inserted in the main chains provide them with significantly lower energy of internal rotation.

The synthesis and application of optically active polymers are the newly considerable topics which have been paid more attention recently (Hajipour et al. 2008). Most of the natural polymers are optically active and have special chemical activities, such as catalytic properties that exist in genes, proteins, and enzymes. Some other applications are construction of chiral media for asymmetric synthesis, chiral stationary phases for resolution of enantiomers in chromatographic techniques (Akelah and Sherrington 1981), chiral liquid crystals in ferroelectrics and nonlinear optical devices (Wulff 1989). These synthetic polymers based on optically pure aminoacids can induce crystallinity with their ability to form higher ordered structures that exhibit enhanced solubility characteristics. These properties have caused them to be good candidate for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials, and also as chiral purification media (Mallakpour et al. 1998). So, more considerations to improve different synthetic procedures of optically active polymers exist. Recently, we have synthesized optically active polymers by different methods (Hajipour et al. 2005). Organic reactions assisted by microwave irradiation have gained special attention. The reactions are very fast and are completed within short times (Hajipour et al. 2000). Recently, we have used microwave irradiation to synthesis organic compounds as well as macromolecules (Mallakpour et al. 1998).

In this research, we report the synthesis and characterization of some **PEI**s and **Co-PEI**s by microwave-assisted polycondensation method in a laboratory microwave oven. These polymers showed good optical activity (+25.2 to +60.3) and also because of the presence of benzophenone moiety, the polymers containing it, can potentially be photolabile (Guo et al. 2004). The photolabile polymers are potentially able to be used as affinity columns for protein purification (Guo et al. 2004).

The outstanding characteristics of these polymers include thermal stability, good solubility, improved optical activity and being photolabile. Here, we have also investigated the effect of catalyst, irradiation power, and time of irradiation on optical activity and viscosity of polymers.

Materials and methods

Pyromellitic dianhydride (Merck) and 3,3′,4,4′-benzophenonetetracarboxylic-3,3′,4,4′-dianhydride (Merck) were recrystallized from acetic anhydride. The other chemicals (Merck) were used as received. Micro SYNTH oven (Milestone) was used to perform reactions. ^{1}H NMR spectra were recorded on 300 MHz instrument, using DMSO-d_6 as solvent and tetramethylsilane as shift reference (tube diameter, 5 mm). IR spectra were recorded on a Shimadzu IR-435 instrument, using KBr pellets. Mass spectra were recorded on a Fisons (UK) mass spectrometer Model Trio 1000. Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermogravimetric analyses (TGA) were recorded on a Mettler TGA-50 with heating rate of 10°C min^{-1} under air atmosphere. Differential scanning calorimetry (DSC) analyses were recorded on a Mettler DSC-30 under nitrogen atmosphere. Inherent viscosities of polymers were measured by a standard procedure using a KPG Cannon Fenske routine viscometer at 25°C using DMF as solvent. Melting points were measured in open capillaries with a Qallenkamp instrument.

Monomer synthesis

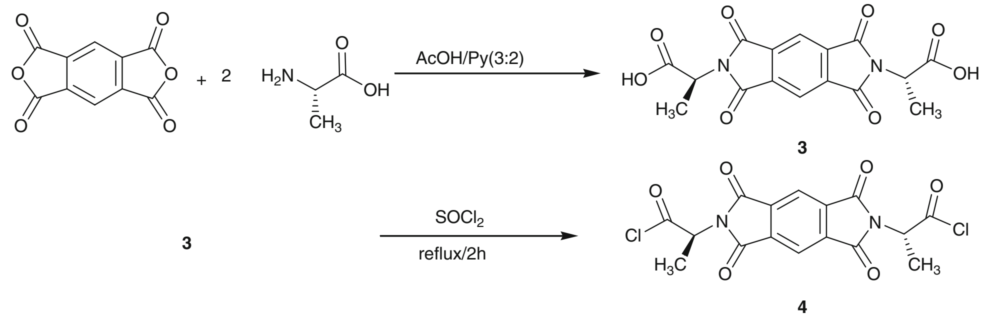
*N,N′-Pyromelliticdiimido-di-L-alanine (**3**)*

Into a 25 ml round-bottomed flask, 2.523 g (7.83×10^{-3} mol) of Pyromellitic dianhydride (1), 1.397 g (1.57×10^{-2} mol) of L-alanine (2), a mixture of acetic acid/pyridine (10 ml, 3:2) and a stirring bar were placed. The mixture was stirred at r.t. for 2 h and then refluxed for 15 h. The solvents were removed under reduced pressure. 5 ml of cold concentrated HCl was added. A white precipitate was formed, filtered off, and washed with hot water. The solid was dried to leave 2.593 g (92%) of diacid 3 (Scheme 1). m.p. (°C) >250. $[\alpha]_D^{25} = +2.8$ (0.050 g in 10 ml DMF). IR (KBr): 3,400–2,700, 1,765–1,570, 1,455, 1,380, 1,365, 1,280, 1,250, 1,170, 1,060, 1,015, 930, 850, 730, 630 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.60 (d, 6H), 4.98 (q, 2H), 8.45 (s, 2H), 13.7 (s, 2H) ppm. MS (m/z): 360, 345, 317, 316, 315 (100%), 288, 271, 244, 243, 199, 173, 172, 145, 135, 128, 75, 74, 45.

*Synthesis of N,N′-(pyromellitoyl)-bis-L-alanine diacyl chloride (**4**)*

Into a 25-ml round-bottomed flask were placed 0.36 g (1.0×10^{-3} mol) of diacid (3), 5 ml (an excess amount) of thionyl chloride and two drops of DMF. The mixture was refluxed for 2 h. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with *n*-hexane, to leave 0.38 g (96.0%) of white crystals (Scheme 1). mp(dp): 150°C. $[\alpha]_D^{25} = +3.2°$ (0.050 g in 10 ml DMF). IR (KBr): 3,450, 2,990, 1,805, 1,780, 1,720, 1,590, 1,465, 1,390, 1,380, 1,180, 1,170, 1,110, 1,080, 920, 905, 830, 730, 600 cm^{-1}. Elemental analysis: Calculated

Scheme 1 Preparation of Diacid **3** and diacyl chloride **4**



for $C_{16}H_{10}N_2O_6Cl_2$, C (48.38%), H (2.54%), N (7.05%); found C (48.29%), H (2.58%), N (6.96%).

*Synthesis of N,N′-(pyromellitoyl)-bis-p-aminophenol (**5**)*

Into a 25 ml round-bottomed flask, 2.523 g (7.83×10^{-3} mol) of Pyromellitic dianhydride (1), 1.711 g (1.57×10^{-2} mol) of *p*-amino phenol, 10 ml of DMF and a stirring bar were placed. The mixture was stirred at r.t. for 2 h and then refluxed for 10 h. The solvents were removed under reduced pressure. A bright yellow precipitate was formed, filtered off, and washed thoroughly with hot water. The solid was dried to leave 2.974 g (95%) of diol (5) (Scheme 2). mp > 300°C. IR (KBr): 3,420, 1,710, 1,705, 1,560, 1,510, 1,490–1,410, 1,405, 1,260, 1,140, 995, 815, 720 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 6.91 (d, 4H), 7.25 (d, 4H), 8.31 (s, 2H), 9.76 (s, 2H) ppm. Elemental analysis: Calculated for $C_{22}H_{12}N_2O_6$, C (66.00%), H (3.02%), N (7.00%); found C (65.9%), H (3.10%), N (6.95%).

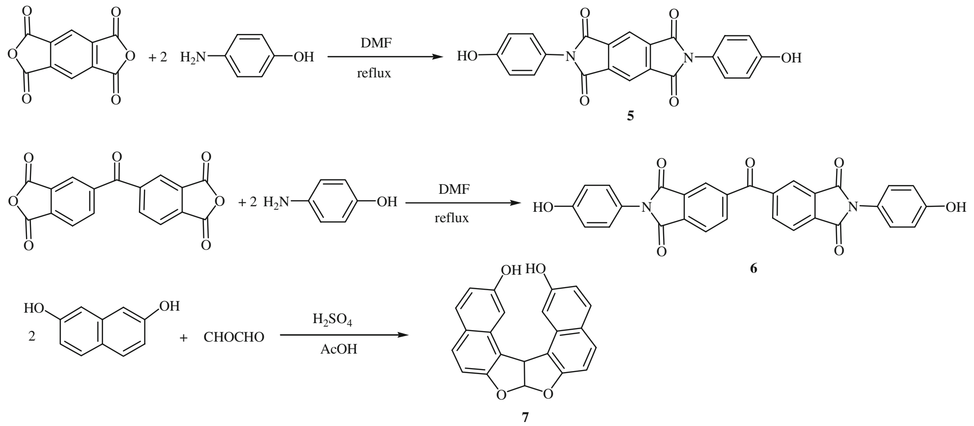
*Synthesis of N,N′-(3,3′,4,4′-benzophenonetetracarboxylic)-3,3′,4,4′-diimido-bis-p-aminophenol (**6**)*

Into a 25 ml round-bottomed flask, 2.521 g (7.83×10^{-3} mol) of 3,3′,4,4′-benzophenonetetracarboxylic-3,3′,4,4′-dianhydride, 1.711 g (1.57×10^{-2} mol) of *p*-amino phenol, 10 ml of DMF and a stirring bar were placed. The mixture was stirred at r.t. for 2 h and then refluxed for 10 h. The solvents were removed under reduced pressure. A yellow precipitate was formed, filtered off, and washed thoroughly with hot water. The solid was dried to leave 3.70 g (94%) of diol (6) (Scheme 2). mp > 300°C. IR (KBr): 3,450, 1,780, 1,708, 1,660, 1,600, 1,518, 1,450, 1,390, 1,250, 1,207, 1,120, 866, 824, 715 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 6.89 (d, 4H), 7.21 (d, 4H), 8.15 (br, 4H), 8.25 (s, 2H), 9.71 (s, 2H) ppm. Elemental analysis: Calculated for $C_{29}H_{16}N_2O_7$, C (69.05%), H (3.20%), N (5.55%); found C (68.94%), H (3.26%), N (5.45%).

*Synthesis of dihydroxy-[7a, 14c] dihydro-naphto[2,1-b] naphtha[1’,2’: 4, 5] furo[3,2-d] furan (**7**)*

Into a 50 ml round-bottomed flask, 3.20 g (0.02 mol) of 2,7-naphthalene diol, 15 ml (0.01 mol) of glyoxal (30%) and 15 ml of AcOH were placed. To the stirring mixture 4 ml of H_2SO_4 (conc.) was added dropwise. It stirred for 24 h and then poured into water to precipitate. After recrystalization from EtOH and drying at 70°C, 2.55 g (74%) of white diol (7) was left (Scheme 2). mp = 301°C. IR (KBr): 3,500–3,200, 1,640, 1,530, 1,460, 1,370, 1,210, 1,070, 830 cm^{-1}. ^1H NMR (250 MHz, DMSO-d_6) δ: 9.82 (s, 2H), 6.98–7.77 (m, 8H), 5.58–5.60 (d, 2H), 3.55 (s, 2H) ppm. ^{13}C NMR (250 MHz, DMSO-d_6) δ: 156.6, 156.5,

Scheme 2 Preparation of diols



132.3, 131, 130.6, 124.8, 117.6, 116.3, 114.9, 108.8, 106.3, 48.8 ppm.

Synthesis of polymers

The **PEI**s (**1**, **2**, and **3**) were prepared by microwave-assisted polycondensation using the following general procedure:

General procedure for polymerization of **PEI**$_1$: Into a porcelain dish, a mixture of diacid chloride (4) (0.397 g, 1.0 mmol) and DABCO (0.222 g, 2.0 mmol) as a catalyst was placed. After grounding the reagents for 5 min, diol 5 (0.400 g, 1.0 mmol) was added and the mixture was ground for further 5 min. 0.25 ml of *O*-cresol as a solvent was added, and the mixture was ground for 5 min. The reaction mixture was irradiated in a laboratory microwave oven (Micro SYNTH, Milestone) for 20 min (600 W, Interval: 10 s/min). The resulting homogenous glassy compound film was isolated by adding methanol/H_2O (80:20) and triturating, followed by filtration. It was washed several times with methanol and vacuum dried. White-gray; Yield (%) = 85; η_{inh} (dl g^{-1}) = 0.35; $[\alpha]_D^{25} = +31.5$; IR (KBr): 3,380, 1,800–1,700, 1,600, 1,510, 1,455, 1,395–1,360, 1,250, 1,205, 1,175, 1,140, 1,100, 1,095, 1,050, 910, 850, 810, 720 cm^{-1}. Elemental analysis: calculated for $C_{38}H_{20}N_4O_{12}$, C (62.81%), H (3.05%), N (7.71%); Found, C (62.69%), H (3.18%), N (7.63%).

The other **PEI**s (**2**, **3**) were prepared by the same procedure using the appropriate diols (Scheme 3).

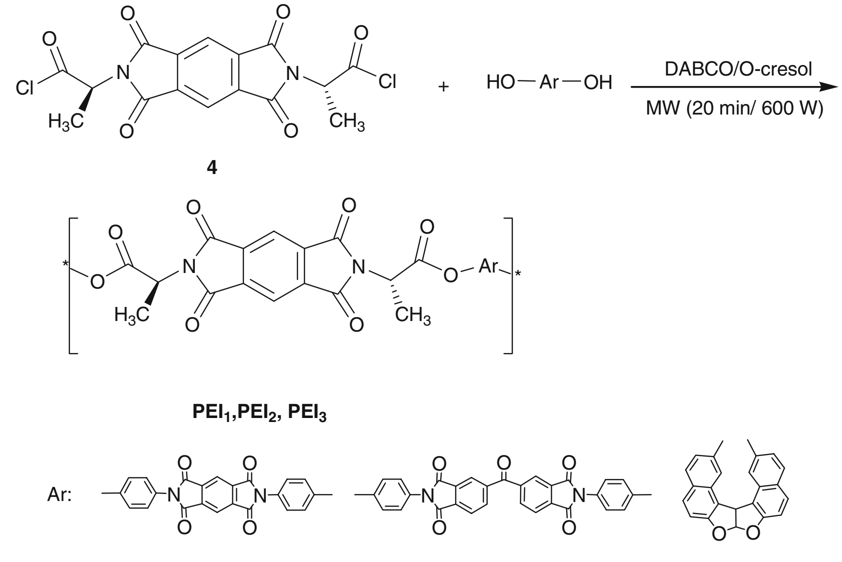
PEI$_2$: Gray; Yield (%) = 80; η_{inh} (dl g^{-1}) = 0.45; $[\alpha]_D^{25} = +45.2$; IR (KBr): 3,385, 1,780, 1,720, 1,705, 1,650, 1,565, 1,510, 1,430, 1,375, 1,240, 1,200, 1,150, 1,105, 820, 720 cm^{-1}. Elemental analysis: calculated for $(C_{45}H_{24}N_4O_{13})_n$ C (65.22%), H (2.92%), N (6.76%); Found C (65.10%), H (3.02%), N (6.93%).

PEI$_3$: White-gray; Yield (%) = 78; η_{inh} (dl g^{-1}) = 0.53; $[\alpha]_D^{25} = +60.3$; IR (KBr): 3,380, 1,785–1,705, 1,630, 1,565, 1,450, 1,380, 1,205, 1,160, 1,055, 955, 920, 825, 720 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 1.70 (br, 6H), 5.45 (br, 3H), 5.75 (br, 1H), 6.95 (br, 2H), 7.30 (br, 2H), 7.65 (br, 2H), 7.95 (br, 4H), 8.32 (br, 2H) ppm. Elemental analysis: calculated for $(C_{38}H_{22}N_2O_{10})_n$ C (68.48%), H (3.30%), N (4.20%); Found C (68.41%), H (3.36%), N (4.18%).

Synthesis of copolymers

The **Co-PEI**s (**4**, **5**, and **6**) were prepared by microwave-assisted polycondensation using the following general procedure:

General procedure for polymerization of **Co-PEI$_4$**: Into a porcelain dish, a mixture of diacid chloride (4) (0.397 g, 1.0 mmol) and DABCO (0.222 g, 2.0 mmol) as a catalyst was placed. After grounding the reagents for 5 min, polyethyleneglycol-diol (**PEG-200**) (0.100 g, 5×10^{-4} mol) was added and the mixture was ground for further 5 min. 0.25 ml of *O*-cresol as a solvent was added, and the mixture was ground for 5 min. The reaction mixture was irradiated in a laboratory microwave oven (Micro SYNTH, Milestone) for 5 min (600 W, Interval: 10 s/min). Diol 5 (0.200 g, 5×10^{-4} mol) and 0.25 ml of *O*-cresol was added and the mixture was ground for further 5 min. The reaction mixture was irradiated in a laboratory microwave oven (Micro SYNTH, Milestone) for 20 min (600 W, Interval: 10 s/min). The resulting homogenous glassy compound film was isolated by adding methanol/H_2O (80:20) and triturating, followed by filtration. It was washed several times with methanol and vacuum dried. Gray; Yield (%) = 81; η_{inh} (dl g^{-1}) = 0.39; $[\alpha]_D^{25} = +38.4$; IR (KBr): 3,380, 1,780–1,750, 1,715, 1,650, 1,600, 1,580, 1,510,



Scheme 3 preparation of polymers (**PEI$_{1\text{–}3}$**)

1,455, 1,400–1,380, 1,240–1,210, 1,160, 1,110, 1,095, 870, 850, 805, 715 cm^{-1}. Elemental analysis: calculated for $C_{62}H_{46}N_6O_{23}$, C (59.90%), H (3.73%), N (6.76%); Found, C (59.96%), H (3.64%), N (6.87%).

The other **Co-PEI**s (**5**, **6**) were prepared by the same procedure using the appropriate diols (Scheme 4).

Co-PEI$_5$: Gray; Yield (%) = 76; η_{inh} (dl g^{-1}) = 0.31; $[\alpha]_D^{25} = +25.2$; IR (KBr): 3,385, 1,785–1,745, 1,715, 1,655, 1,595, 1,570, 1,505, 1,450, 1,390, 1,240–1,205, 1,150, 1,105, 1,075, 880, 845, 800, 720 cm^{-1}. Elemental analysis: calculated for $(C_{69}H_{50}N_6O_{24})_n$ C (61.51%), H (3.73%), N (6.25%); Found C (61.72%), H (3.60%), N (6.40%).

Co-PEI$_6$: Pale green; Yield (%) = 80; η_{inh} (dl g^{-1}) = 0.48; $[\alpha]_D^{25} = +50.2$; IR (KBr): 3,380, 1,780–1,735, 1,720, 1,650, 1,580, 1,560, 1,460, 1,395, 1,215–1,205, 1,150, 1,100, 870, 840, 805, 720 cm^{-1}. Elemental analysis: calculated for $(C_{62}H_{48}N_4O_{21})_n$ C (62.83%), H (4.08%), N (4.73%); Found C(63.15%), H(3.88%), N(4.88%).

Results and discussion

We synthesized the diimide-diacid [*N,N′*-Pyromellitic-diimido-di-L-alanine (3)] by the condensation reaction of dianhydride (**1**) with L-alanine (**2**) in 1:2 molar ratio in refluxing acetic acid/pyridine (3:2). Washing the residue with cold water yields a gummy layer which breaks by adding concentrated HCl into a white solid (Scheme 1).

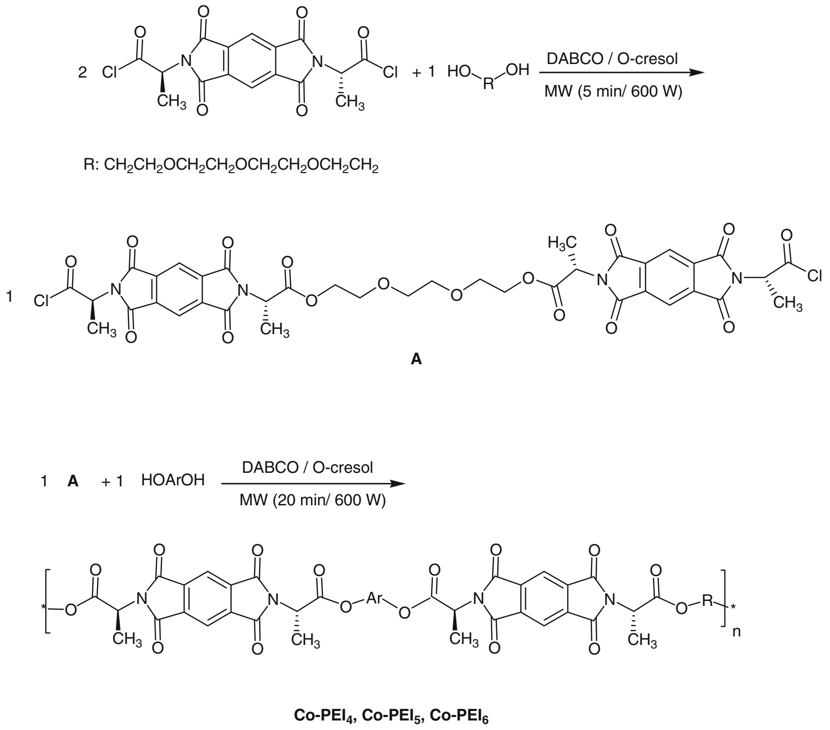
IR spectrum of this diacid shows the characteristic absorptions at around 3,400–2,250 cm^{-1}, peculiar to carboxylic acid groups, two peaks at around 1,765 and 1,700 cm^{-1}, peculiar to carbonyl stretching of imide and acid moieties, and exhibits strong absorptions at 1,380 and 730 cm^{-1}, that indicates the presence of the cyclic imide group. ^{1}H NMR of diimide-diacid **1** is presented in Fig. 1. The corresponding peaks included acidic groups at around 13.7 ppm have been detected by ^{1}H NMR. Mass spectra showed the appropriate molecular ion peaks and/or fragments. The chlorination was completed after 2 h, when the mixture was completely dissolved in refluxing thionyl chloride.

DMF plays a catalytic role in this reaction. The characteristic peak at around 1,805 cm^{-1} is due to the acyl chloride carbonyl group. The acyl chloride will decompose on heating at 150°C, so its mass spectrum did not show the molecular ion peak by EI technique.

This monomer is the source of chirality in the corresponding polymers. Diol **7** was prepared as mentioned in the experimental part (Fig. 2).

The dark purple solids turned to white needle crystals after recrystallization from EtOH (Scheme 2). In the preparation of diols **5** and **6** after stirring at r.t. for 2 h, the corresponding amic acids formed which turned to the corresponding imide rings after 10 h reflux. These diols were yellow powders, which showed high melting points, low solubility, and very low vapor pressure so that we could not run their mass spectra by EI technique.

Scheme 4 Preparation of copolymers (**Co-PEI$_{4–6}$**)



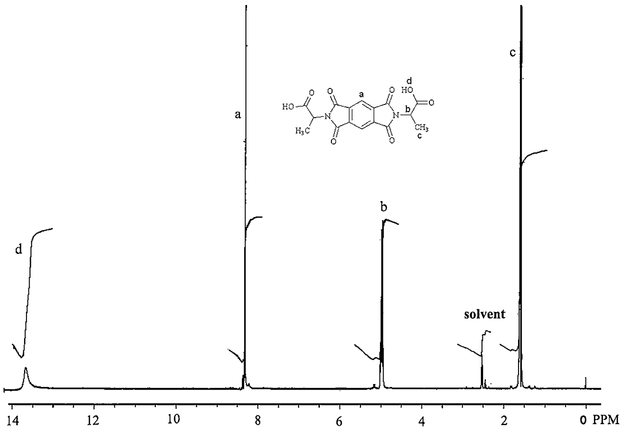


Fig. 1 ^{1}H NMR spectrum of diacid (**3**)

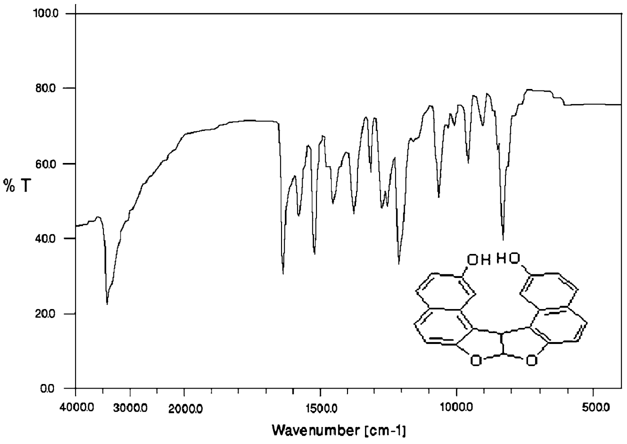


Fig. 2 IR spectrum of diol **7**

In IR spectra, the characteristic peaks at around 3,400 cm^{-1} and in ^{1}H NMR, the peaks at around 9.7 ppm show the phenolic (OH) groups. These diols are good candidates to improve the thermal stability of the corresponding polymers. Figure 3 shows ^{1}H NMR spectrum of diol **6**.

The resulting homogenous glassy compound films were isolated by adding methanol/H_2O (80:20) and triturating, followed by filtration. It was washed several times with methanol and vacuum dried. To optimize the polymerization conditions, we did six experiments on **PEI$_1$**. The optimum condition is as follows: Power = 600 W; Time = 20 min with interval times of 10 s/min of running. It is found that at higher power, the lower viscosity and lower specific rotation are obtained; which can be attributed to polymer degradation. At lower power, the higher specific rotation but lower viscosity is obtained; the results are shown in Table 1.

All the polymers were obtained in quantitative yields with moderate inherent viscosities (0.31–0.53 dl g^{-1}) and optical rotation. The formation of **PEI**s and **Co-PEI**s was confirmed by IR spectroscopy and elemental analysis. As an example, the IR of **Co-PEI$_6$** showed the C=O asymmetric stretching of imide group at 1,780 cm^{-1}, the C=O symmetric stretching of imide and ester groups at 1,725 cm^{-1}, C–N stretching at 1,380 cm^{-1}, C–O–C stretching at 1,280–1,030 cm^{-1}. All of these **PEI**s and **Co-PEI**s exhibited strong absorption at 1,380 and 720 cm^{-1}, which shows the presence of the heterocyclic imide groups. As an example, the ^{1}H NMR spectrum of **PEI$_3$** is presented which shows peaks that confirmed its chemical structure (Fig. 4). The elemental analyses results are also in good agreement with calculated/expected percentages of carbon, hydrogen and nitrogen contents in the polymer-repeating units. The colors of these polymers range from white–grey to grey. Transparent, flexile and tough films could be obtained from these polymers by casting from solution of polymers in DMF, which shows good mechanical strength of the films and consequently high molecular weight.

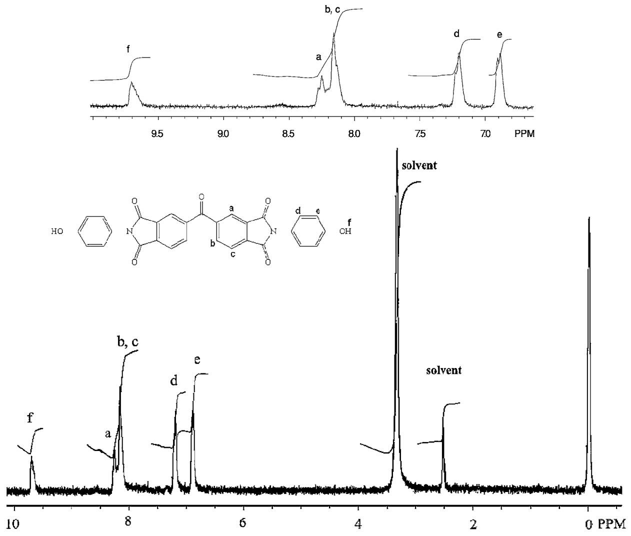


Fig. 3 ^{1}H NMR spectrum of diol **6**

One of the major objectives of this work is to study the solubility and the flexibility of these polymers by incorporating the soft segment in the polymer backbone. Their solubility was tested qualitatively in various solvents and the results are summarized in Table 2. Having soft

Table 1 Optimization of microwave-assisted polycondensation on **PEI$_1$**

Power	Time (min)	Interval (10 s/min)	η_{inh} (dl g^{-1})	$[\alpha]_D^{25}$
800	10	–	0.17	+16.7
800	10	+	0.22	+20.6
600	10	+	0.30	+23.0
600	20	+	0.35	+31.5
400	20	+	0.29	+33.1
300	20	+	0.20	+35.7

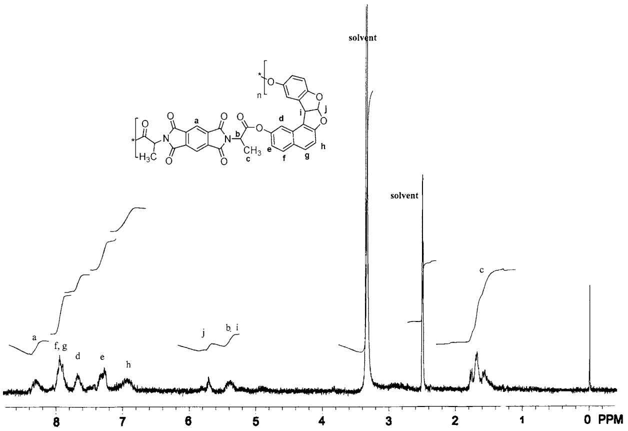


Fig. 4 ^{1}H NMR spectrum of **PEI$_3$**

Table 2 Solubility of **PEI**s and **Co-PEI**s

Solvents	PEI$_1$	PEI$_2$	PEI$_3$	Co-PEI$_4$	Co-PEI$_5$	Co-PEI$_6$
NMP	+	+	++	++	++	++
DMSO	+	+	++	++	++	++
DMAc	+	+	++	++	++	++
DMF	+	+	++	++	++	++
H_2SO_4	++	++	++	++	++	++
CH_2Cl_2	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
MeOH	–	–	–	–	–	–
H_2O	–	–	–	–	–	–

Concentration: 5 mg ml^{-1}; ++, soluble at room temperature; +, soluble upon heating; –, insoluble

segments in the polymer backbone will increase the solubility, so here **Co-PEI**s showed very good solubility; all of them are soluble in polar aprotic solvents such as DMF, DMAc, DMSO, NMP and also H_2SO_4 at room temperature. They are insoluble in solvents, such as chloroform, methylene chloride, methanol, ethanol and water. These polymers showed good optical activity (+25.2 to +60.3) and also because of the presence of benzophenone moiety, the polymers containing it, can potentially be photolabile. In compare to **PEIs**, **Co-PEIs** showed higher viscosities and better solubility. The thermal properties of these polymers were evaluated by means of TGA/DTG (under air atmosphere) and DSC (under nitrogen atmosphere). These polymers show similar decomposition behavior. They showed two different decomposition maxima. Table 3 summarizes the thermal properties of them. These polymers exhibited good resistance to thermal decomposition. (5% weight loss: 355–400°C and 10% weight loss: 365–430°C). Tg values of **Co-PEI**s are from 170–190°C. TGA/DTG thermogram of **PEI$_1$** is represented in Fig. 5.

Table 3 Thermal behavior of **PEI**s and **Co-PEI**s

Polymer	Decomposition temperature (°C) $T^a_{5\%}$	Decomposition temperature (°C) $T^b_{10\%}$	Char yield (%)^c	Tg (°C)^d
PEI$_1$	400	430	0.2	–
PEI$_2$	395	415	2.0	–
PEI$_3$	380	390	0.4	–
Co-PEI$_4$	355	365	0.0	170
Co-PEI$_5$	370	380	0.0	190
Co-PEI$_6$	375	385	0.0	180

[a] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min under air atmosphere

[b] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min under air atmosphere

[c] Percentage weight of material left after TGA analysis at maximum temperature 600°C under air atmosphere

[d] Glass transition temperature

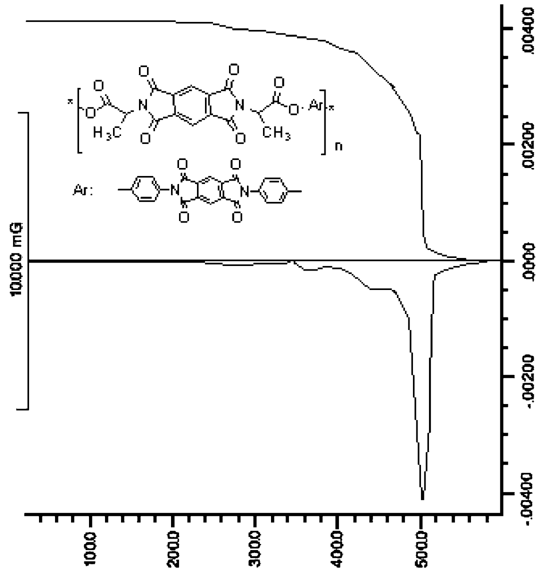


Fig. 5 TGA/DTG thermogram of **PEI$_1$** under air atmosphere

TGA and DSC thermograms of **Co-PEI$_4$** are represented in Fig. 6. DSC thermogram of **PEI$_1$** did not show a clear Tg, but expectedly that of **Co-PEI$_4$**, since soft segment in the polymer backbone which cause an increase in phase separation along with decreasing thermooxidative stability have shown a Tg value of about 170°C.

Conclusions

A series of optically active **PEI**s and **Co-PEI**s, having inherent viscosities of 0.31–0.53 dl g^{-1} were synthesized for the first time by microwave-assisted polycondensation

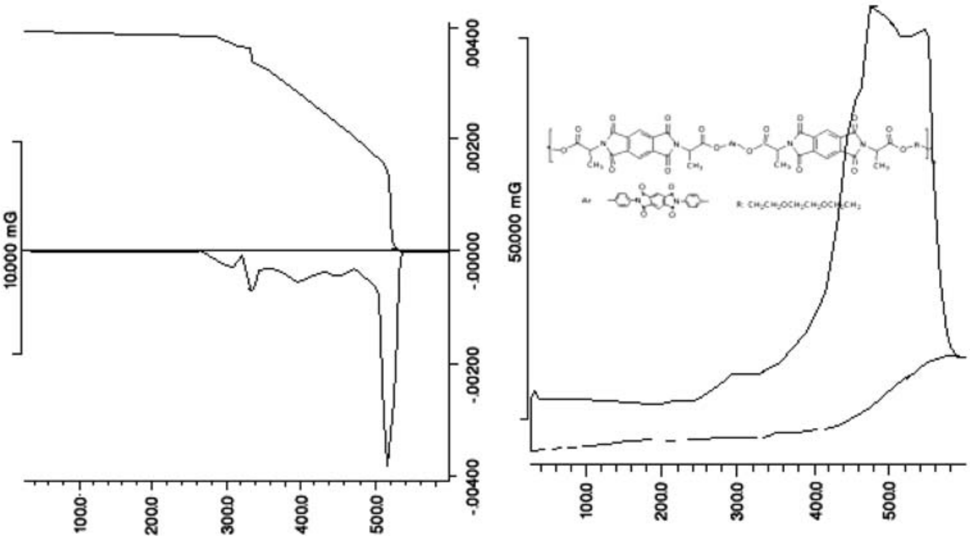


Fig. 6 TGA/DTG and DSC thermograms of **Co-PEI$_4$**

of optically active *N,N′*-Pyromelliticdiimido-di-L-alanine (**3**) as a diacid having a preformed imide rings as an "enlarged" monomer containing two chiral L-alanine groups with polyethyleneglycol-diol (**PEG-200**) and/or three synthetic aromatic diols. These polymers showed optical activity (+25.2 to +60.3) and also because of the presence of benzophenone moiety, the polymers containing it, can potentially be photolabile. **Co-PEI**s showed better solubility than **PEI**s. These polymers showed good thermal stability.

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References

Akelah A, Sherrington DC (1981) Application of functionalized polymers in organic synthesis. Chem Rev 81:557–587

Banihashemi A, Abdolmaleki A (2004) Novel aromatic polyimides derived from benzofuro[2, 3-b]benzofuran-2, 3, 8, 9-tetracarboxylic dianhydride (BBTDA). European Polymer Journal 40:1629–1635

Guo LW, Hajipour AR, Gavala ML, Grant JE, Ruoho AE (2004) FASEB J 18:A587

Hajipour AR, Mallakpour SE, Khoee S (2000) An efficient, fast and selective oxidation of aliphatic and benzylic alcohols to the corresponding carbonyl compounds under microwave irradiation. Synlett 5:740–742

Hajipour AR, Zahmatkesh S, Zarei A, Khazdooz L, Ruoho AE (2005) Synthesis and characterization of novel optically active poly (amide-imide)s via direct amidation. Eur Polym J 41:2290–2296

Hajipour AR, Zahmatkesh S, Parniyan Roosta, Ruoho AE (2009) Synthesis and characterization of new optically active poly (azo-ester-imide)s via interfacial polycondensation. Amino acids 36(3):511–518

Hsiao SH, Li CT (1998) Synthesis and characterization of new adamantane-based polyimides. Macromolecules 31(21):7213–7217

Legge NR, Holden G, Schroeder HE (1987) Thermoplastic elastomers. Hanser, New York

Li F, Ge JJ, Honigfort PS, Fang S, Chen JC, Harris FW et al (1999) Dianhydride architectural effects on the relaxation behaviors and thermal and optical properties of organo-soluble aromatic polyimide films. Polymer 40:4987–5002

Mallakpour SE, Hajipour AR, Khoee S, Sheikholeslami B (1998) A new method for producing optically active polybutadiene. Polym Int 47:193–197

Mittal KL (1984) Polyimides: synthesis, characterization and application. Plenum, New York

Noshay A, McGrath IE (1977) Block copolymers. Academic Press, New York

Reddy DS, Chou CH, Hsu CF, Lee GH (2003) Synthesis and characterization of soluble poly(ether imide)s based on 2, 2′-bis(4-aminophenoxy)-9, 9′-spirobifluorene. Polymer 44:557–563

Tamai S, Yamaguchi A, Ohta M (1996) Melt processible polyimides and their chemical structures. Polymer 37:3683–3692

Wulff G (1989) Main-chain chirality and optical activity in polymers consisting of CC chains. Angew Chem Int Engl Ed 28:21–37