

L-Lysine-derived optically active poly(hydrazide-imide)s: synthesis, characterization and their application in removal of heavy metal ions

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Abstract Six novel poly(hydrazide-imide)s (**PHI_{a-f}**) were prepared from the reaction of a novel L-lysine-derived chiral diacid, ethyl L-lysine-*N,N'*-ditrimellitoyl diacid (**1**), with six synthetic dihydrazides by solution polycondensation. These polymers have inherent viscosities in the range of 0.22–0.45 dl g⁻¹, display optical activity, and are readily soluble in polar aprotic solvents. They start to decompose (*T*_{10%}) above 248 °C and display glass-transition temperatures at 164.37–210.20 °C. All the above polymers were fully characterized by UV, FT-IR, and ¹H NMR spectroscopy, TGA, DSC, inherent viscosity measurement and specific rotation.

Keywords Optically active · L-lysine · Thermally stable · Poly(hydrazide-imide)

Introduction

The interest for developing new biodegradable and/or biocompatible polymers, especially polyesters and polyamides, has largely encouraged the use of monomers based on naturally occurring products [1, 2]. Both carbohydrate [3, 4] and amino acid [1] derived monomers are being currently used as building blocks to generate novel polymeric structures with enhanced biodegradability.

Polyamides were developed from high performance polymers, which possess good thermal properties [5–7]. L-lysine in particular has been repeatedly used for making polyamides with potential as biomaterials, [8–12]. For instance, L-lysine with good functionalities has been used to prepare some poly(amide-imide)s [13].

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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) [14–18], as well as asymmetric catalysis applications [19–23]. The synthesis and application of these polymers is a considerable topic, which has been paid more attention recently [24]. 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 [25], chiral liquid crystals in ferroelectrics and nonlinear optical devices [26, 27]. These synthetic polymers based on optically pure amino acids can induce crystallinity with their ability to form higher ordered structures that exhibit enhanced solubility characteristics. These properties have caused them to be a good candidate for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials, and also as chiral purification media [28]. Therefore, more considerations to improve different synthetic procedures of optically active polymers exist.

Polyhydrazides [29] have been extensively studied, since they increase the dye ability of synthetic fibbers and improve elasticity over other polymer types. They have been cyclized to give polyoxadiazoles and polytriazoles. They also provide a synthetic base for the chelate polymers [30], since the hydrazide group ($-\text{CO}-\text{NH}-\text{NH}-\text{CO}-$) can react with metal ions to form complexes. Recently, we have synthesized optically active polymers by different methods [31, 32]. In this research, we report the synthesis and characterization of six novel poly(hydrazide-imide)s based on L-lysine through solution polycondensation. The outstanding characteristics of these polymers include thermal stability, good solubility, and optical activity, chelating ability and potentially being ion exchangeable.

Experimental

Materials and instruments

The trimellitic anhydride (Merck) was recrystallized from acetic anhydride. The other chemicals (Merck) were used as received. ^1H NMR spectra were recorded on 300 or 500 MHz and ^{13}C NMR on an 125 MHz (Bruker Avance) instrument, using DMSO- d_6 as solvent and tetramethylsilane as shift reference (tube diameter, 5 mm). IR spectra were recorded on a Shimadzu FT-IR-680 instrument, using KBr pellets. UV spectra were recorded on a Perkin–Elmer lambda 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 $6\text{ }^\circ\text{C min}^{-1}$ under air atmosphere. DSC analyses were performed 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 $25\text{ }^\circ\text{C}$ using DMF as solvent. Melting points were measured in open capillaries with a IA9000 series digital Melting Point Apparatus. Elemental analyses were performed in a Heraeus CHNS-RAPID instrument.

Monomer synthesis

Synthesis of Ethyl L-lysine dihydrochloride [13]

According to the reported procedure: Yield: 90 %; m.p.: 136–137 °C; IR (cm^{-1}): 3,421, 3,350–2,514, 2,019, 1,740, 1,603, 1,583, 1,501, 1,217, 851, 740; ^1H -NMR (D_2O , ppm): 1.07 (3H, t, 7 Hz), 1.29 (2H, br), 1.49 (2H, br), 1.76 (2H, br), 2.78 (2H, br), 3.91 (1H, t, 4.3 Hz), 4.08 (2H, br); elemental analysis for $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_2 \cdot 2\text{HCl}$, calculated: C (38.87 %), H (8.16 %), N (11.33 %), found: C (38.62 %), H (8.31 %), N (11.40 %).

Synthesis of ethyl L-lysine-*N,N'*-ditrimellitoyl diacid (1) (Since Alborzi [13])

According to the reported procedure: Yield: 80 %; m.p.: 168 °C; $[\alpha]_D^{25} = +3.14^\circ$ (0.050 g in 10 ml DMF); IR (cm^{-1}): 3,400–2,400, 1,702, 1,498, 1,418, 1,296, 1,148, 1,069, 1,018, 916, 803, 750, 748; ^1H -NMR (500 MHz, CDCl_3 , ppm): 1.2 (3H, t, 7.06 Hz), 1.3 (2H, br), 1.7 (1H, br), 1.8 (1H, br), 2.1 (1H, br), 2.2 (1H, br), 3.7 (2H, t, 4.1 Hz), 4.2 (2H, q, 3.9 Hz), 4.8 (1H, t, 4 Hz), 7.9 (1H, s), 8.0 (1H, s), 8.1 (1H, s), 8.2 (1H, s), 8.4 (1H, s), 8.5 (1H, s), 10.2 (2H, s); ^{13}C NMR (125 MHz, CDCl_3 , ppm): δ 14.4, 23.6, 27.7, 28.2, 38.0, 52.4, 62.5, 123.8, 124.1, 124.8, 125.2, 132.2, 132.4, 134.9, 135.1, 136.2, 136.4, 136.5, 136.6, 166.8, 166.9, 167.6, 167.7, 169.3, 170.1, 170.2

Synthesis of ethyl L-lysine-*N,N'*-ditrimellitoyl diacylchloride (2) [13]

According to the reported procedure: dp: 175 °C. $[\alpha]_D^{25} = +4.08^\circ$ (0.050 g in 10 ml DMF). IR (KBr, cm^{-1}): 3,023, 2,784, 1,862, 1,785, 1,720, 1,464, 1,384, 1,226, 1,017, 922, 877, 754, 718, 680, 507.

Dihydrazide synthesis (3–8)

General procedure: In a 25-ml round-bottomed flask equipped with a reflux condenser, a mixture of corresponding dimethyl ester (1.00 mol), hydrazine mono hydrate (2.50 mol), and ethanol (10 ml) were placed and refluxed for 5 h. Upon cooling, crystals separated, which were filtered and washed with ethanol.

Dihydrazide 3 White; yield (%) = 95; m.p. (°C) >300; IR (cm^{-1}): 3,324, 3,033, 1,623, 1,605, 1,540, 1,489, 1,340, 1,291, 1,103, 1,016, 927, 886, 736, 713, 638; ^1H NMR (300 MHz) δ : (ppm): 4.51 (s, 4H), 7.90 (s, 4H), 9.90 (s, 2H).

Dihydrazide 4 White; yield (%) = 98; m.p. (°C) = 244–246; IR (cm^{-1}): 3,289, 3,055, 1,663, 1,625, 1,585, 1,524, 1,321, 1,108, 996, 923, 819, 723, 687, 625; ^1H NMR (300 MHz) δ : (ppm): 4.51 (s, 4H), 7.50 (t, 1H), 7.91 (dd, 2H), 8.30 (t, 1H), 9.80 (s, 2H).

Dihydrazide 5 White–gray; yield (%) = 75; m.p. (°C) = 240–241; IR (cm^{-1}): 3,282, 3,181, 3,007, 1,679, 1,611, 1,534, 1,360, 1,269, 1,097, 998, 793, 537; ^1H NMR (300 MHz) δ : (ppm): 4.11 (s, 4H), 9.60 (s, 2H).

Dihydrazide 6 Yellow; yield (%) = 80; m.p. (°C) = 148–149; IR (cm⁻¹): 3,304, 3,201, 3,131, 3,034, 2,873, 1,667, 1,647, 1,532, 1,363, 1,248, 1,203, 1,052, 955, 788, 694; ¹H NMR (300 MHz) δ : (ppm): 2.90 (s, 2H), 4.20 (s, 4H), 9.11 (s, 2H).

Dihydrazide 7 White; yield (%) = 83; m.p. (°C) = 169–170; IR (cm⁻¹): 3,313, 3,291, 3,200, 3,181, 3,042, 2,874, 2,779, 1,627, 1,531, 1,353, 1,241, 1,012, 949, 752, 664; ¹H NMR (300 MHz) δ : (ppm): 2.30 (s, 4H), 4.11 (s, 4H), 8.90 (s, 2H).

Dihydrazide 8 White; yield (%) = 87; m.p. (°C) = 176–177; IR (cm⁻¹): 3,315, 3,180, 3,046, 2,965, 2,927, 1,636, 1,532, 1,379, 1,330, 1,157, 1,016, 1,001, 954, 711, 618; ¹H NMR (300 MHz) δ : (ppm): 1.75 (quin, 2H), 2.00 (t, 4H), 3.51 (s, 4H), 8.90 (s, 2H).

Poly(hydrazide-imide)s synthesis, general procedure

General procedure: A stoichiometric mixture of the diacyl chloride and an aromatic or aliphatic dihydrazide (1.0 mmol) was dissolved in NMP (5 ml). Then a suitable value of triethyl amine was added. The solution was stirred at 5 °C for 4 h under nitrogen atmosphere, and then kept under stirring for 24 h in room temperature. After completion of the reaction, **PHIs** were recovered by precipitation from methanol. Polymers were isolated by filtration and dried under vacuum.

PHI_a Yellow; yield (%) = 91; $[\alpha]_D^{25} = +32.40$; UV (λ_{\max}) = 298; IR (cm⁻¹): 3,640–3,180, 2,925, 1,780, 1,715, 1,387, 1,258, 864, 731; ¹H NMR (500 MHz, DMSO-d₆) δ : (ppm): 1.1 (3H, br), 1.2 (2H, br), 1.4 (2H, br), 1.7 (2H, br), 2.1 (2H, br), 4.1 (2H, br), 4.8 (1H, br), 7.2–8.5 (10H, br), 10.8 (4H, br).

PHI_b Yellow; yield (%) = 83; $[\alpha]_D^{25} = +5.20$; UV (λ_{\max}) = 268; IR (cm⁻¹): 3,630–3,180, 2,924, 1,770, 1,716, 1,379, 726, 689; ¹H NMR (500 MHz, DMSO-d₆) δ : (ppm): 1.1 (3H, br), 1.2 (2H, br), 1.4 (2H, br), 1.7 (2H, br), 3.6 (2H, br), 4.2 (2H, br), 4.9 (1H, br), 7.6–8.5 (10H, br), 10.9 (4H, br).

PHI_c White; yield (%) = 87; $[\alpha]_D^{25} = +10.30$; UV (λ_{\max}) = 260; IR (cm⁻¹): 3,630–3,170, 1,780, 1,716, 1,389, 1,243, 730, 689; ¹H NMR (500 MHz, DMSO-d₆) δ : (ppm): 1.1 (3H, br), 1.2 (2H, br), 1.4 (2H, br), 1.7 (2H, br), 2.1 (2H, br), 4.2 (2H, br), 4.8 (1H, br), 7.8–8.5 (6H, br), 11.2 (4H, br).

PHI_d White-gray; yield (%) = 82; $[\alpha]_D^{25} = +15.50$; UV (λ_{\max}) = 262; IR (cm⁻¹): 3,600–3,200, 2,942, 1,770, 1,716, 1,387, 1,294, 733; ¹H NMR (500 MHz, DMSO-d₆) δ : (ppm): 1.1 (5H, br), 1.6 (2H, br), 2.1 (2H, br), 3.6 (4H, br), 4.1 (2H, br), 4.8 (2H, br), 7.7–8.5 (6H, br), 10.4 (2H, br), 10.9 (2H, br).

PHI_e Pale yellow; yield (%) = 80; $[\alpha]_D^{25} = +8.30$; UV (λ_{\max}) = 268; IR (cm⁻¹): 3,630–3,130, 1,790, 1,716, 1,388, 1,251, 731, 688; ¹H NMR (500 MHz, DMSO-d₆) δ : (ppm): 1.1 (3H, br), 1.2 (2H, br), 1.7 (2H, br), 2.2 (6H, br), 3.6 (2H, br), 4.2 (2H, br), 4.8 (1H, br), 7.9–8.5 (6H, br), 11.1 (4H, br).

PHI_f Yellow; yield (%) = 77; $[\alpha]_D^{25} = +12.40$; UV (λ_{\max}) = 269; IR (cm⁻¹): 3,630–3,150, 1,770, 1,716, 1,388, 1,251, 731, 688; ¹H NMR (500 MHz, DMSO-d₆) δ : (ppm): 1.1 (3H, br), 1.2 (2H, br), 1.7 (4H, br), 2.1 (6H, br), 2.4 (2H, br), 4.2 (2H, br), 4.8 (1H, br), 7.7–8.4 (6H, br), 10.8 (2H, br).

Polymer heavy metal uptake

Chelation of heavy metal ions from solution was investigated in batch experiments. A solution of PHI_a (0.10 gr) in DMF (20 ml) was added to metal nitrate (10 mmol) solution in DMF (30 ml). The reaction mixture was stirred overnight and filtered. The collected solid was washed several times with deionized water (4×10 ml), ethanol (2×10 ml) followed by ether (2×5 ml) and then dried in vacuum at 60°C for 24 h. Then, into a 50-ml round-bottomed flask, 0.10 g of the mentioned precipitation, 25-ml nitric acid (4 molar), and a stirring bar were placed. The mixture was stirred at r.t. for 20 min and filtered off. The filtrate pH was maintained in a range of 3–4 units, and then this solution was used to analyze the heavy metal absorption capacity of PHI_a by AAS (Atomic Absorption Spectroscopy).

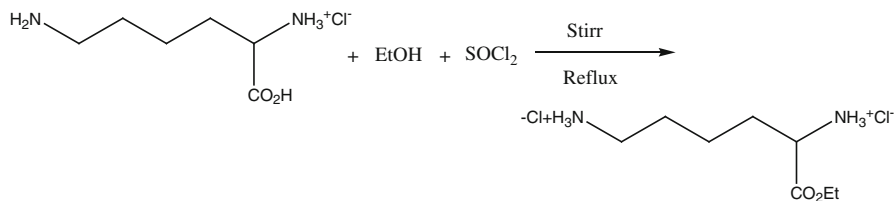
Results and discussion

Ethyl L-lysine dihydrochloride was prepared with the reaction of a mixture of EtOH and thionyl chloride with L-lysine hydrochloride. L-lysine hydrochloride was added to the mixture dropwise at -10°C , and then refluxed for 6 h. The dark solid was washed three times with diethyl ether to leave a bright white solid (87 %). FT-IR spectroscopy shows a strong and broad peak at $3,350\text{--}2,514\text{ cm}^{-1}$ corresponding to the Ammonium N–H stretching and a strong peak at $1,740\text{ cm}^{-1}$ corresponding to the C=O stretching of ester moiety. ^1H NMR (D_2O , ppm) spectroscopy shows the corresponding peaks such as 3.91 (1H) due to the chiral center and 1.07 (3H) and 2.78 (2H) peaks due to the ethyl moiety (Scheme 1).

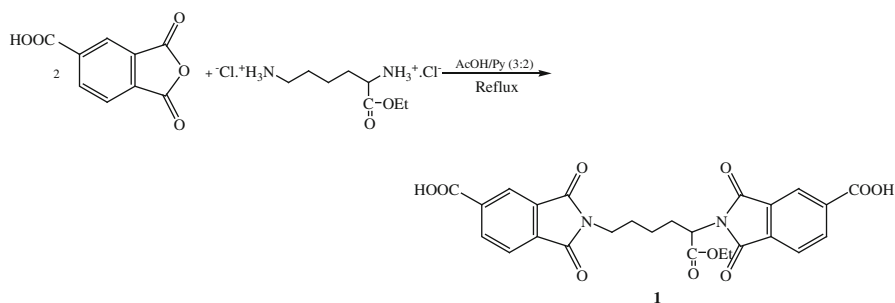
The best solvent to prepare ethyl L-lysine-N,N'-ditrimellitoyl diacidide (**1**) was acetic acid/pyridine mixture, since we have the salt form of chiral diamine as starting material here. The best method for purification of this synthetic diacid was found to be extraction with chloroform (Scheme 2).

The chemical structure of diacid **1** was confirmed by spectroscopic analysis (Figs. 1, 2, and 3).

FT-IR spectroscopy shows a strong and broad peak at $3,600\text{--}2,700\text{ cm}^{-1}$ corresponding to the COOH stretching, a strong and broad peak at $1,740\text{--}1,700\text{ cm}^{-1}$ corresponding to the C=O stretching of carbonyl groups, and also two peaks at $1,411$ and 750 cm^{-1} due to the cyclic imide groups. ^1H NMR (CDCl_3 , ppm) spectroscopy shows 14 peaks and the corresponding peaks such as



Scheme 1 Protection of L-lysine acidic group



Scheme 2 Diacid **1** synthesis

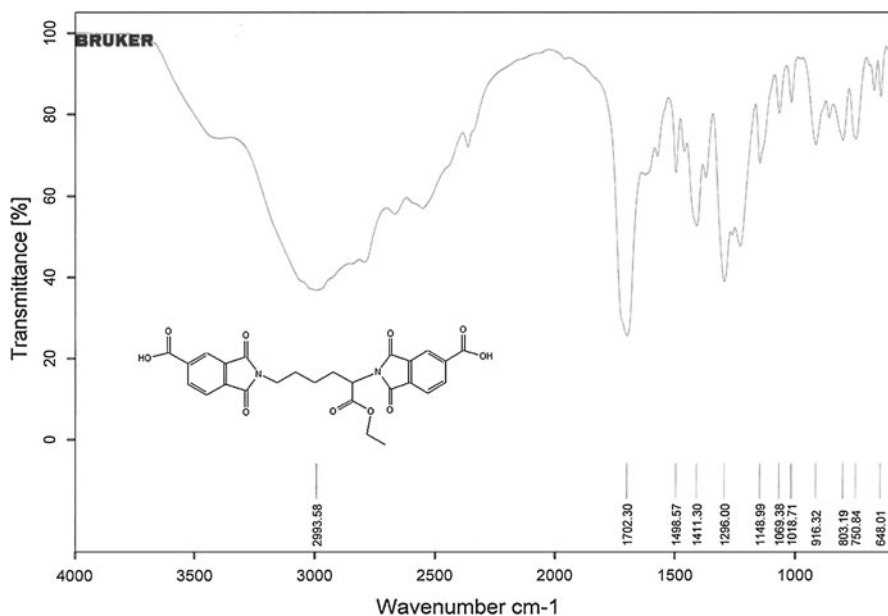


Fig. 1 IR spectrum of diacid **1**

4.8 (1H) due to the chiral center, and 10.21 (2H) due to the acidic moiety. ^{13}C NMR (CDCl_3 , ppm) spectroscopy shows 26 peaks due to the 26 different carbons. Corresponding white diacyl chloride (**2**) was prepared in refluxing SOCl_2 for 2 h (Scheme 3).

FT-IR spectroscopy shows the corresponding carbonyl stretching of acyl chloride at $1,862\text{ cm}^{-1}$. Synthesis of dihydrazides (**3–8**) is presented in Scheme 4.

FT-IR spectroscopy shows the corresponding carbonyl stretching at $1,663\text{ cm}^{-1}$ and that of NH at $3,050\text{--}3,289\text{ cm}^{-1}$.

Solution polymerization was applied to prepare the poly(hydrazide-imide)s (Scheme 5).

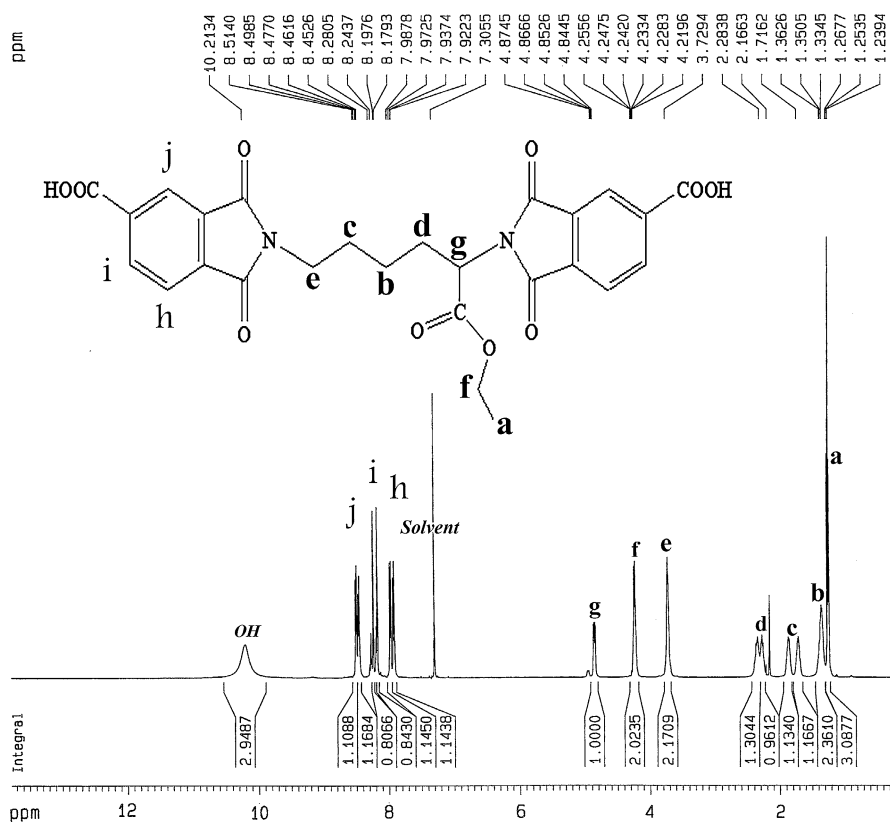


Fig. 2 ^1H NMR spectrum of diacid **1**

All the very probable atactic polymers were obtained from an inexpensive starting material in quantitative yields with moderate inherent viscosities ($0.23\text{--}0.42\text{ dl g}^{-1}$) and optical rotation ($+5.20^\circ$ to $+32.40^\circ$) (Table 1).

As there is no obvious regioselectivity between alpha and epsilon acyl chloride groups of the lysine ester containing diacid during the polymerisation step then random orientation of lysine moieties along the polymer backbone can be predicted, and the concept of “tacticity” cannot be addressed in this research. Head-to-tail regiorandomness may likely affect some physical properties of the polymers such as crystallinity. All polymers have been obtained in good yields (77–91 %) and being thermally stable ($T_{(10\%)}: 0.239.5\text{--}301^\circ\text{C}$). The color of these polymers was white to yellow. Transparent, flexible, and tough films of these polymers were obtained which showed good mechanical strength of the films and consequently high molecular weight. High speed and high yield are the advantages of this polymerization method. One of the major objectives of this work is to study the solubility and the versatility of these polymers by incorporating the soft segment in the polymer backbone. These polymers are organo soluble in common polar aprotic solvents (Table 2).

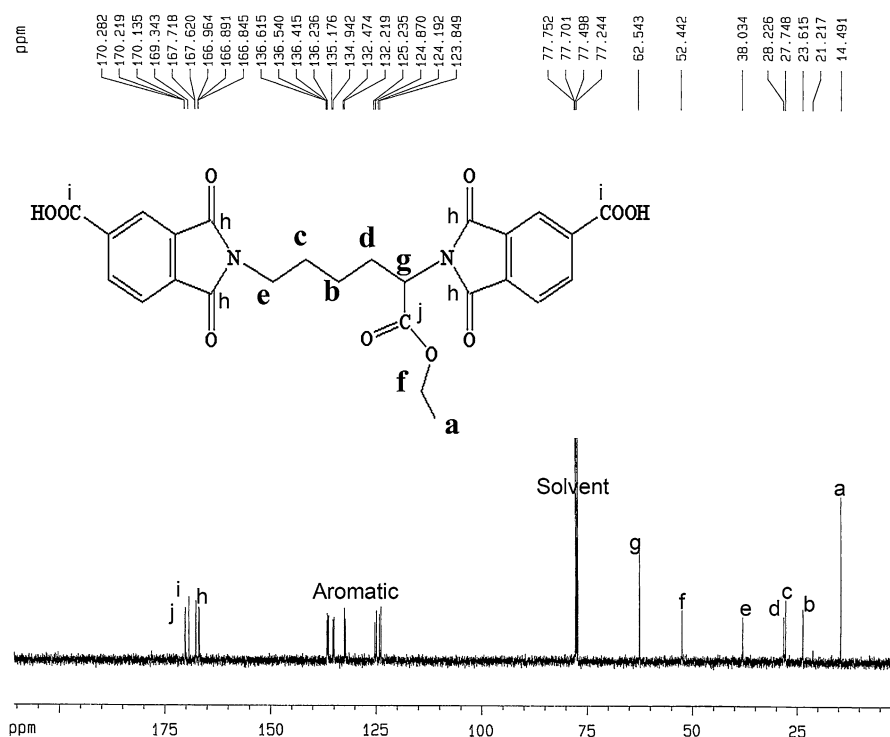
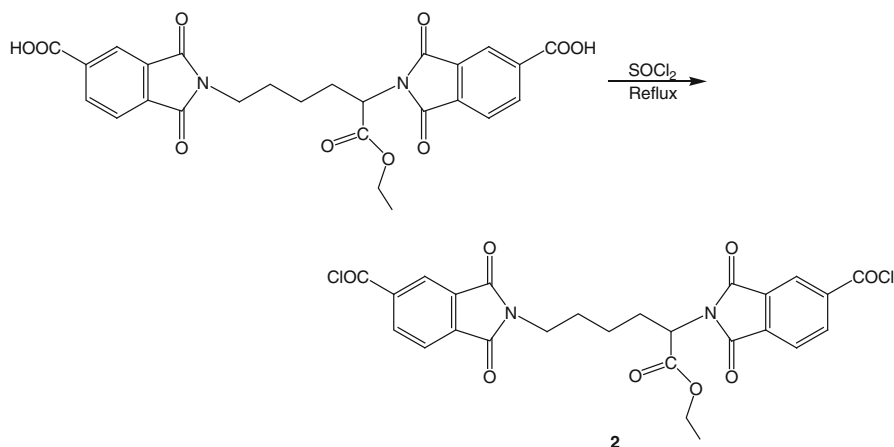
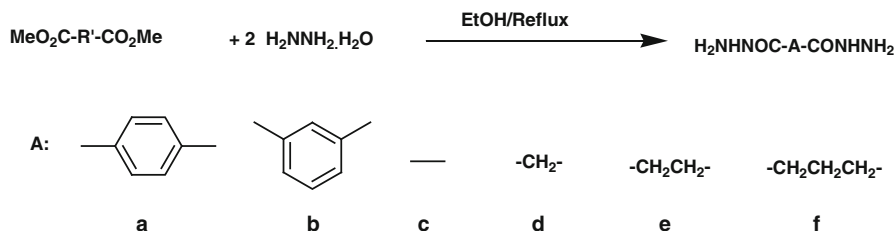
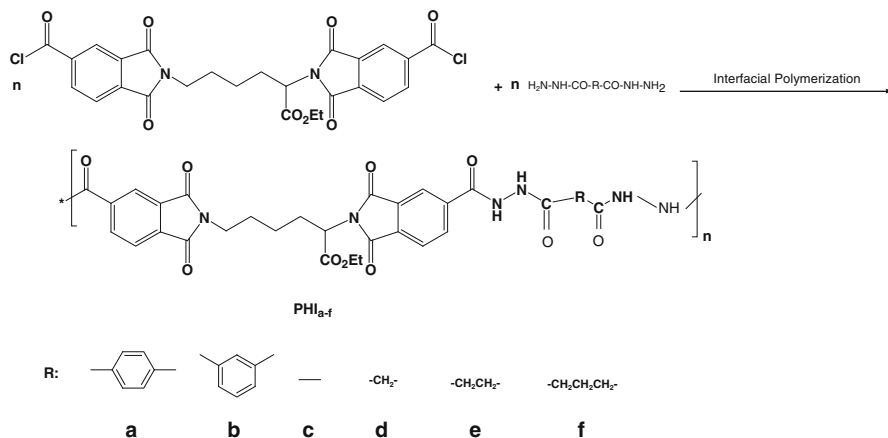


Fig. 3 ¹³C NMR spectrum of diacid **1**



Scheme 3 Diacyl chloride **2** synthesis

The novel polymers were fully characterized by spectroscopic analysis (UV, FT-IR, ¹H NMR), thermal analysis (TGA, DSC), viscometric measurements, optical rotation measurements and solubility tests. As an example, the corresponding spectra of **PHI_a** are represented in Figs. 4, 5, 6, and 7, respectively.

**Scheme 4** Synthesis of dihydrazides (**3–8**)**Scheme 5** Interfacial polymerization**Table 1** Polymer properties

Polymer code	Color	Yield (%)	η_{inh} (dl g ⁻¹)	$[\alpha]_D^{25}$	Film quality ^a
PHI _a	Yellow	91	0.28	+32.40°	Flexible
PHI _b	Yellow	83	0.42	+5.20°	Flexible
PHI _c	White	87	0.23	+10.30°	Flexible
PHI _d	White–gray	82	0.25	+15.50°	Flexible
PHI _e	Bright yellow	80	0.30	+8.30°	Flexible
PHI _f	Yellow	77	0.35	+12.40°	Flexible

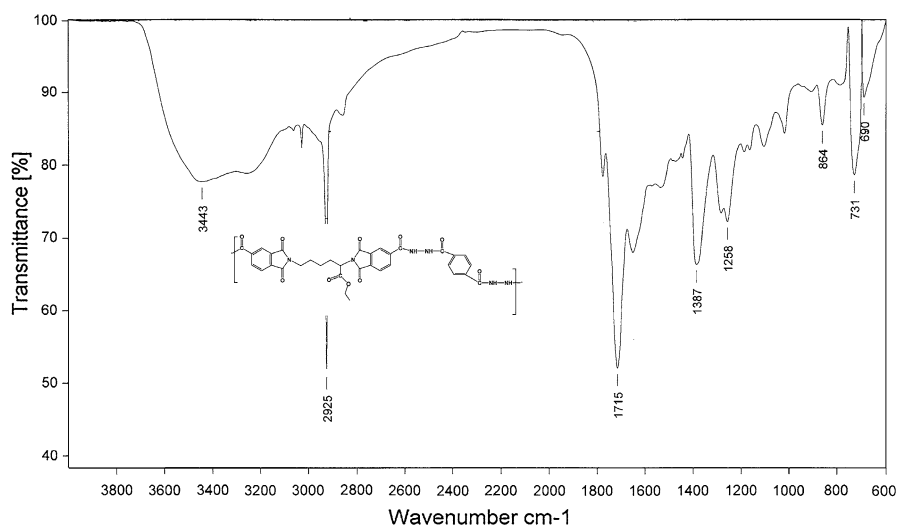
^a Films were casted by slow evaporation of polymer solution in DMAc

In FT-IR spectra of these polymers some characteristic peaks could be seen, including the N–H stretching of hydrazide group at around 3,443 cm⁻¹, C=O asymmetric and symmetric stretching of imide groups at 1,716 cm⁻¹, C=O stretching of hydrazide group at 1,630 cm⁻¹. All these **PHIs** exhibited strong absorption at around 1,380 and 720 cm⁻¹, which shows the presence of the heterocyclic imide groups. The ¹H NMR spectra of **PHIs** show a peak at 4.8 ppm due to the chiral center. The polymers show a maximum absorption in UV spectra at around 248–262 nm.

Table 2 Solubility of polymers

Solvents	PHI _a	PHI _b	PHI _c	PHI _d	PHI _e	PHI _f
NMP	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMF	+	+	+	+	+	+
H ₂ SO ₄	+	+	+	+	+	+
CH ₂ Cl ₂	–	–	–	–	–	–
CHCl ₃	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
MeOH	–	–	–	–	–	–
H ₂ O	–	–	–	–	–	–

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

**Fig. 4** FT-IR spectrum of PHI_a

Thermal properties of these polymers are investigated by TGA/DTG under air atmosphere at 6 °C min^{−1} and by DSC under nitrogen atmosphere at 10 °C min^{−1} (Table 3).

Polyhydrazides are desired chelating agents to adsorb heavy metal ions. In fact, hydrazide functional group can react with heavy metal ions to compose complexes of metals. A report has shown that heavy metals can be up taken very well by hydrazide groups, which are pendent on their polymer backbones. Indeed, poly(hydrazide-imide)s, which have been synthesized in this study, include hydrazide and polar functional groups in their backbone; meanwhile, the chain of the polymers represents enough flexibility by single carbon–carbon bond of L-lysine. These specifications of the polymers may enhance adsorption of heavy

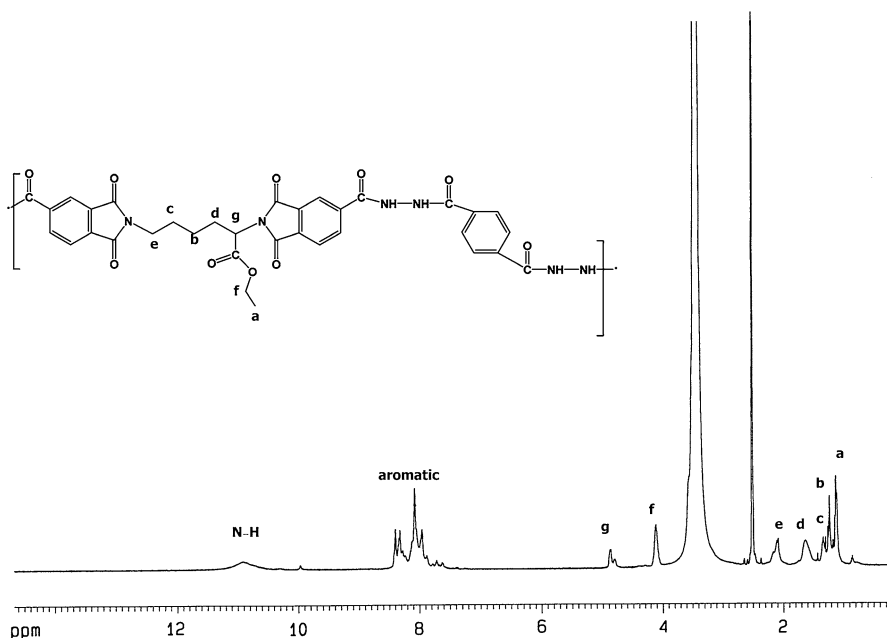


Fig. 5 ^1H NMR spectrum of PHI_a

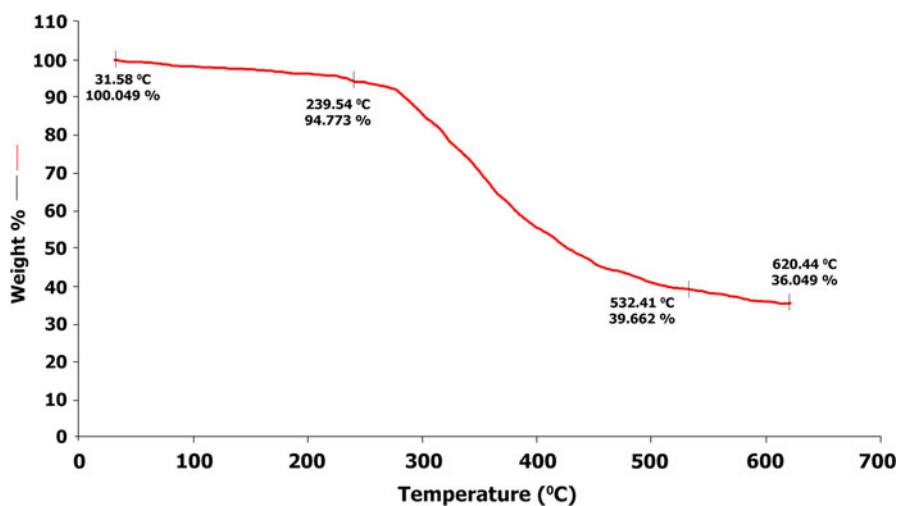


Fig. 6 TGA spectrum of PHI_a

metals on the polymers. The capacity of PHI_a to uptake heavy metals (Pb, Cd, Cu, Zn, Hg) has been shown in Table 4 in the acidic media. Among heavy metals, lead exhibits maximum adsorption (0.99 mmol g^{-1}). Cadmium ions are adsorbed with capacity of 0.75. In fact, this polymer can remove Pb and Cd cations from media.

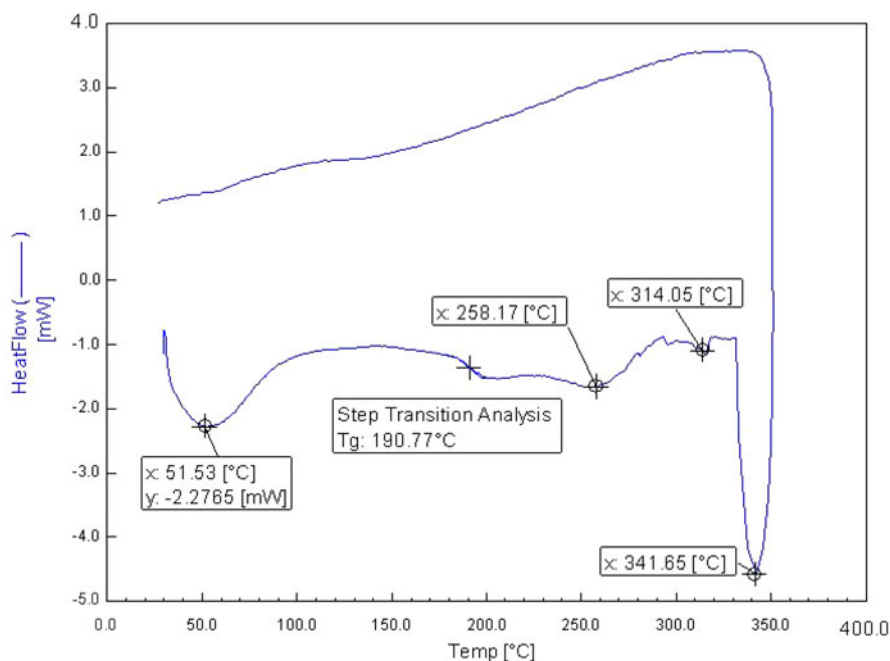


Fig. 7 DSC spectrum of **PHI_a**

Table 3 Thermal behavior of polymers

^a Temperature at which 10 % weight loss was recorded by TGA at a heating rate of 10 °C min⁻¹ under air atmosphere. ^b Percentage weight of material left after TGA analysis at maximum temperature 600 °C under air atmosphere

Polymer	Decomposition temperature (°C) $T_{10\%}^a$	Char yield (%) ^b
PHI_a	299.6	19.31
PHI_b	292.6	21.22
PHI_c	239.5	36
PHI_d	248	40.49
PHI_e	301	13.22
PHI_f	250	34.32

Table 4 The capacity of **PHI_a** to uptake heavy metals (Pb, Cd, Cu, Zn, Hg) in the acidic media

Metal ion	AAS (mg l ⁻¹)	pH value	q (mmol g ⁻¹)
Pb	816.25	3–4	0.99
Cd	170.76	3–4	0.75
Cu	57/98	3–4	0.47
Zn	48/59	3–4	0.31
Hg	9/885	3–4	0.037

Sorption capacity q was determined using the following equation: $q = \frac{V(C_0 - C_f)}{g}$ where C_0 and C_f are the initial and final concentrations of the metal in solution, V is the volume of the solution, and g is the mass of polymer

Conclusions

A fast and effective procedure to prepare a series of optically active poly(hydrazide-imide)s containing ethyl L-lysine ester has been introduced. Since there is no obvious regioselectivity between alpha and epsilon acyl chloride groups of the lysine ester containing diacid during the polymerization step, the random orientation of lysine moieties along the polymer backbone can be predicted. These polymers are very soluble, optically active, potentially ion exchangeable, and thermally stable. The resulting polymers are identified by FT-IR, UV, ^1H NMR spectroscopy and elemental analysis; and characterized by yield of reaction, inherent viscosity, and specific rotation. Metal ion removal capacities of polymers were measured. Among heavy metals, lead exhibits maximum adsorption (0.99 mmol g^{-1}). Cadmium ions are adsorbed with capacity of 0.75. In fact, this polymer can remove Pb and Cd cations from media.

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