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ORIGINAL ARTICLE

Microwave-assisted synthesis and characterization of L-lysine-derived optically active poly (hydrazide-imide)s

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KEYWORDS

Chiral;
Optically active;
L-Lysine;
Poly (hydrazide-imide);
Microwave-assisted polymerization

Abstract L-Lysine hydrochloride was transformed to ethyl L-lysine dihydrochloride. This salt was reacted with trimellitic anhydride to yield the corresponding diacid (**1**). Interfacial polycondensation results a series of novel poly (hydrazide-imide)s (**PHI$_{a-f}$**). These polymers have inherent viscosities in the range of 0.10–0.37 dl g^{-1}, display optical activity, and are readily soluble in polar aprotic solvents. They start to decompose ($T_{10\%}$) above 245 °C and display glass-transition temperatures at around 125.9 °C. All of the above polymers were fully characterized by UV, FT-IR and ^{1}H NMR spectroscopy, elemental analysis, TGA, DSC, inherent viscosity measurement and specific rotation.

1. Introduction

The interest for developing new biodegradable and/or biocompatible polymers has largely encouraged the use of monomers based on naturally occurring products (Gonsalves and Mungara, 1996; Steinbu, 2002). Both carbohydrate (Thiem and Bachmann, 1994; Varela and Orgueira, 1999) and amino-acid (Gonsalves and Mungara, 1996) derived monomers are being currently used as building blocks to generate novel polymeric structures with enhanced biodegradability.

L-Lysine in particular has been repeatedly used for making polyamides with potential as biomaterials (Gachard et al., 1997; Saotome and Schultz, 1967; Crescenzi et al., 1968; Katsarawa et al., 1985). For instance L-lysine with good functionalities has been used to prepare some polytartaramides (Majo et al., 2004).

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) Nakano, 2001; Cirilli et al., 2003; Coa et al., 2007; Mallakpour and Kowsari, 2005; Yuan et al., 2005 as well as asymmetric catalysis applications (Itsuno, 2005; Hu et al., 2001, 2002; Hb et al., 2000; Canali et al., 1999). The synthesis and application of these polymers is a considerable topic, which has been paid more attention recently (Hajipour et al., 2005). 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;

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Fontanille and Guyot, 1987). 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., 2008, 2009; Zahmatkesh and Hajipour, 2009, 2010).

Polyhydrazides have been extensively studied since they increase dye ability of synthetic fibers and improve elasticity over other polymer types. They possess fair absorption characteristics when the hydrazide link is in the main chain or polymer backbone. They have been cyclized to give polyoxadiazoles and polytriazoles. They also provide a synthetic base for the chelate polymers, since the hydrazide group (–CO–NH–NH–CO–) can react with metal ions to form complexes. Moreover, the 1,3,4-oxadiazole ring has special interest owing to its superior thermostability in an oxaidative atmosphere (Hajipour et al., 2007). Aromatic polyhydrazides are generally synthesized by the low-temperature solution polycondensation of an aromatic dihydrazide with an aromatic diacid chloride in a solvent such as NMP in the presence of an inorganic salt like lithium chloride (Dobinson et al., 1979).

Organic reactions assisted by microwave irradiation have gained special attention. The reactions are very fast and are completed within short times. Recently we have used microwave irradiation to synthesize different types of macromolecules (Zahmatkesh and Hajipour, 2009, 2010).

The present work outlines a fast and effective procedure to synthesize six new atactic optically active polyhydrazides based on L-lysine through microwave-assisted polycondensation. A major aim of this work was to study the effect of inclusion of aliphatic or aromatic moieties in polymers, and their properties, were also investigated. These polymers showed good optical activity (+6.30 to +18.00). The outstanding characteristics of these polymers include thermal stability, good solubility, optical activity, potentially being ion exchangeable.

2. Material and methods

The trimellitic anhydride (Merck) was recrystallized from acetic anhydride. The other chemicals (Merck) were used as received. ^{1}H NMR spectra were recorded on 300 or 500 MHz and ^{13}C NMR on a 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 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 a heating rate of 6 °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 an IA9000 series digital Melting Point Apparatus.

2.1. Monomer synthesis

2.1.1. Synthesis of Ethyl L-lysine dihydrochloride (*9*)

In a 50 ml round-bottomed flask equipped with a reflux condenser and a stirring bar, 8 ml of thionyl chloride was added dropwise to the stirring absolute ethanol (2.5 ml) at −10 °C. L-lysine hydrochloride (7.3 g, 0.04 mol) was added to the mixture and refluxed for 6 h. The solvent was evaporated under reduced pressure and the residue was washed with diethyl ether three times. Yield: 87%; m.p.: 136–137 °C; IR (cm^{-1}): 3421, 3350–2514, 2019, 1740, 1603, 1583, 1501, 1217, 851, 740; ^{1}H NMR (D_2O, ppm): 1.07 (3H), 1.29 (2H), 1.49 (2H), 1.76 (2H), 2.78 (2H), 3.91 (1H), 4.08 (2H); Elemental analysis for $C_8H_{18}N_2O_2{\cdot}2HCl$, Calculated: C (38.87%), H (8.16%), N (11.33%), Found: C (38.62%), H (8.31%), N (11.40%).

2.1.2. Synthesis of Ethyl L-lysine-N,N′-ditrimellitoyl diacide (*1*)

Into a 25 ml round-bottomed flask, 2.000 g (10.42 mmol) of trimellitic anhydride, 1.282 g (5.21 mmol) of Ethyl L-lysine dihydrochloride, a mixture of acetic acid/pyridine (5 ml, 3:2) and a stirring bar were placed. The mixture was stirred at r.t. for 2 h and then refluxed for 6 h. The solvents were removed under reduced pressure. 5 ml of cold concentrated HCl was added. A white precipitate was formed and filtered off. The white diacid (**1**) was extracted from this crude product with chloroform. Yield: 2.32 g (79%); m.p.: 168 °C; $[\alpha_D^{25}] = +3.14°$ (0.050 g in 10 ml DMF); IR (cm^{-1}): 3400–2400, 1702, 1498, 1418, 1296, 1148, 1069, 1018, 916, 803, 750, 748; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 1.2 (3H), 1.3 (2H), 1.7 (1H), 1.8 (1H), 2.1 (1H), 2.2 (1H), 3.7 (2H), 4.2 (2H), 4.8 (1H), 7.9 (1H), 8.0 (1H), 8.1 (1H), 8.2 (1H), 8.4 (1H), 8.5 (1H); ^{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.

2.1.3. Synthesis of Ethyl L-lysine-N,N′-ditrimellitoyl diacylchloride (*2*)

Into a 25 ml round-bottomed flask were placed 0.558 g (1.0 mmol) of diacid (**1**), 5 ml (an excess amount) of thionyl chloride and two drops of DMF. 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 (82%) of white crystals. dp: 175 °C; $[\alpha_D^{25}] = +4.08°$ (0.050 g in 10 ml DMF). IR (KBr, cm^{-1}): 3023, 2784, 1862, 1785, 1720, 1464, 1384, 1226, 1017, 922, 877, 754, 718, 680, 507.

2.1.4. Synthesis of dihydrazides (*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) was placed and refluxed for 5 h. Upon cooling, crystals separated, which were filtered and washed with ethanol.

2.1.4.1. Dihydrazide **3** **.** White; Yield (%) = 95; m.p. (°C) > 300; IR (cm^{-1}): 3324, 3033, 1623, 1605, 1540, 1489, 1340, 1291, 1103, 1016, 927, 886, 736, 713, 638; ^{1}H NMR (300 MHz) δ: (ppm): 4.51 (s, 4H), 7.90 (s, 4H), 9.90 (s, 2H).

2.1.4.2. Dihydrazide **4**. White; Yield (%) = 98; m.p. (°C) = 244–246; IR (cm^{-1}): 3289, 3055, 1663, 1625, 1585, 1524, 1321, 1108, 996, 923, 819, 723, 687, 625; ^{1}H 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).

2.1.4.3. Dihydrazide **5**. White–Gray; Yield (%) = 75; m.p. (°C) = 240–241; IR (cm^{-1}): 3282, 3181, 3007, 1679, 1611,

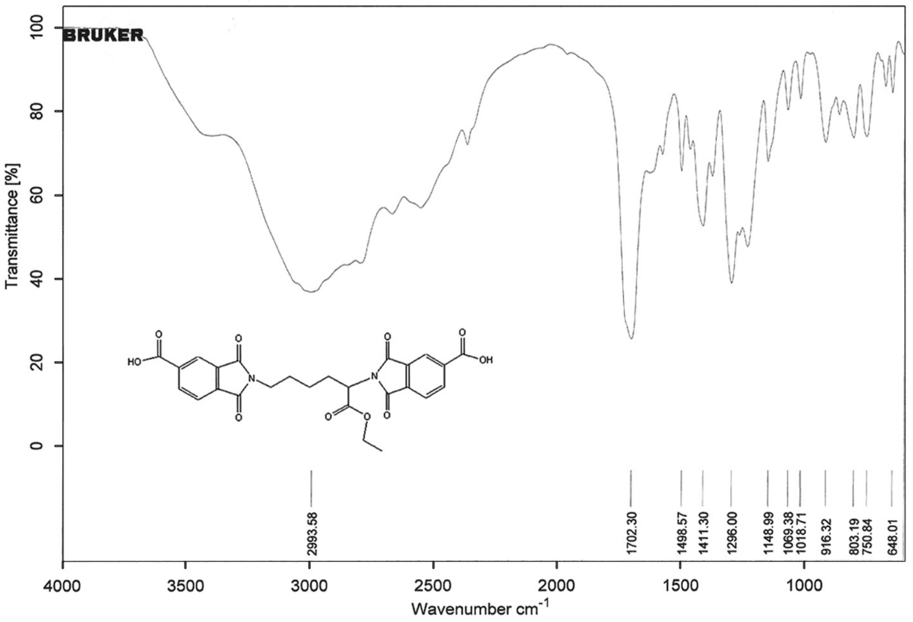
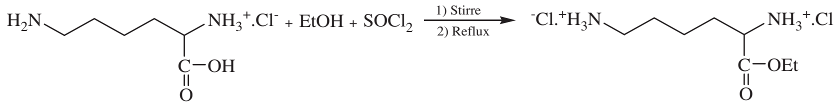
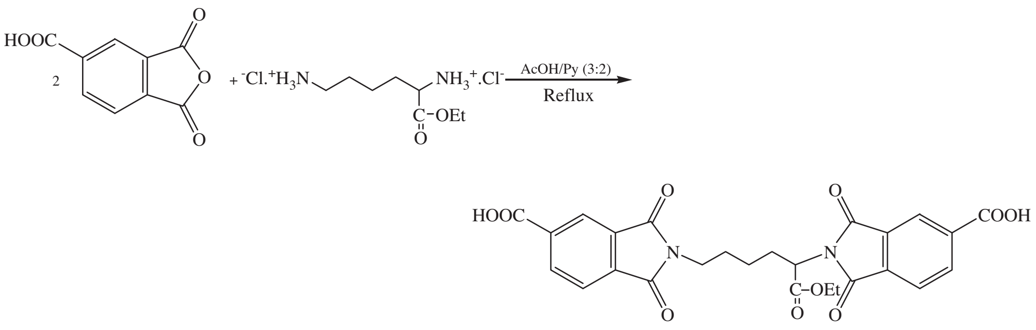


Figure 1 IR spectrum of diacid 1.



Scheme 1 Protection of L-lysine acidic group.



1

Scheme 2 Diacid **1** synthesis.

1534, 1360, 1269, 1097, 998, 793, 537; ^{1}H NMR (300 MHz) δ: (ppm): 4.11 (s, 4H), 9.60 (s, 2H).

2.1.4.4. Dihydrazide 6. Yellow; Yield (%) = 80; m.p. (^{o}C) = 148–149; IR (cm^{-1}): 3304, 3201, 3131, 3034, 2873, 1667, 1647, 1532, 1363, 1248, 1203, 1052, 955, 788, 694; ^{1}H NMR (300 MHz) δ: (ppm): 2.90 (s, 2H), 4.20 (s, 4H), 9.11 (s, 2H).

2.1.4.5. Dihydrazide 7. White; Yield (%) = 83; m.p. (^{o}C) = 169–170; IR (cm^{-1}): 3313, 3291, 3200, 3181, 3042, 2874, 2779, 1627, 1531, 1353, 1241, 1012, 949, 752, 664; ^{1}H NMR (300 MHz) δ: (ppm): 2.30 (s, 4H), 4.11 (s, 4H), 8.90 (s, 2H).

*2.1.4.6. Dihydrazide **8**.* White; Yield (%) = 87; m.p. (^{o}C) = 176–177; IR (cm^{-1}): 3315, 3180, 3046, 2965, 2927, 1636, 1532, 1379, 1330, 1157, 1016, 1001, 954, 711, 618; ^{1}H NMR (300 MHz) δ: (ppm): 1.75 (quin, 2H), 2.00 (t, 4H), 3.51 (s, 4H), 8.90 (s, 2H).

2.2. Microwave-assisted polymerization

2.2.1. General procedure

Into a porcelain dish, a mixture of diacyl chloride (1.0 mmol) and DABCO (1.0 mmol) as a catalyst was placed. After grinding the reagents for 5 min, dihydrazide (1.0 mmol) was added and the mixture was ground for

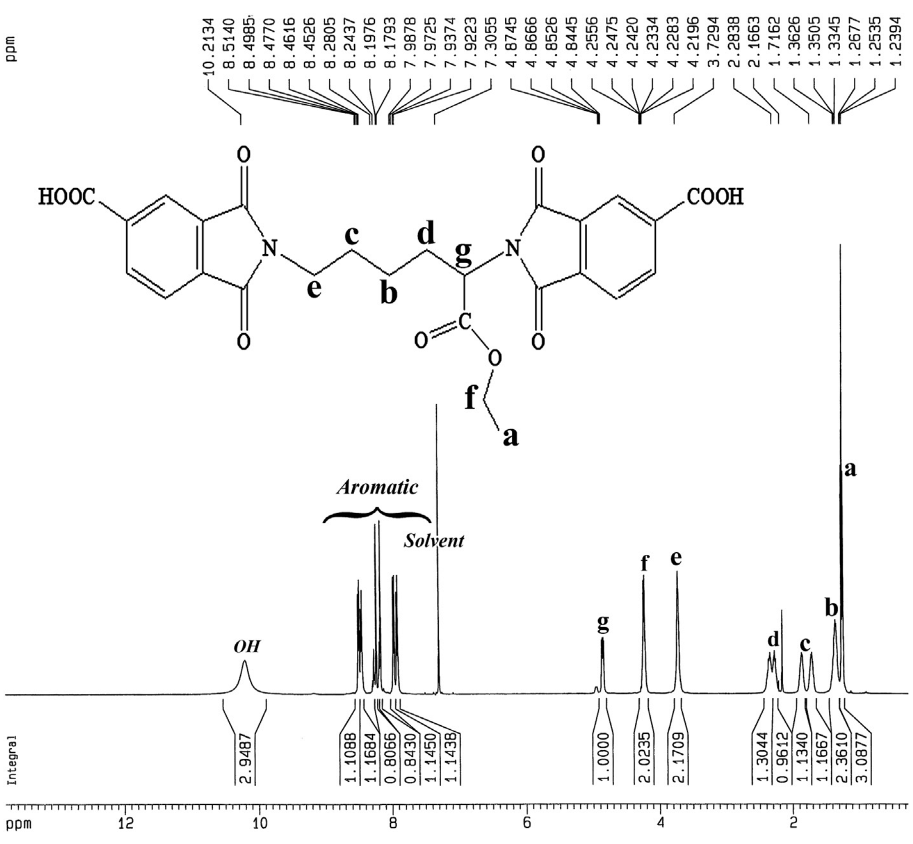


Figure 2 1H NMR spectrum of diacid 1.

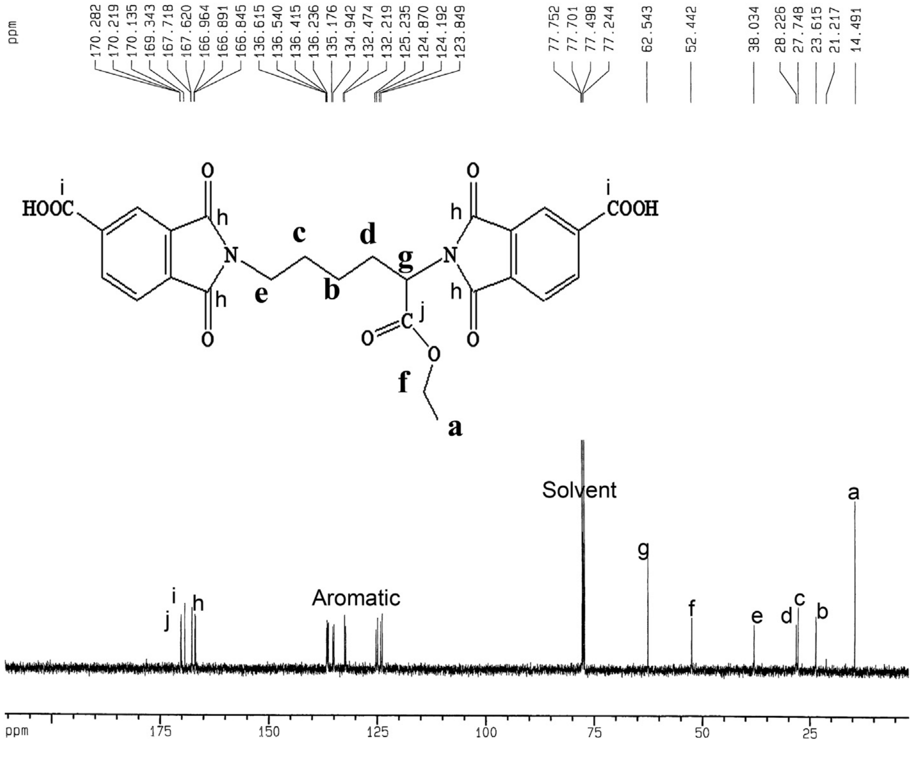
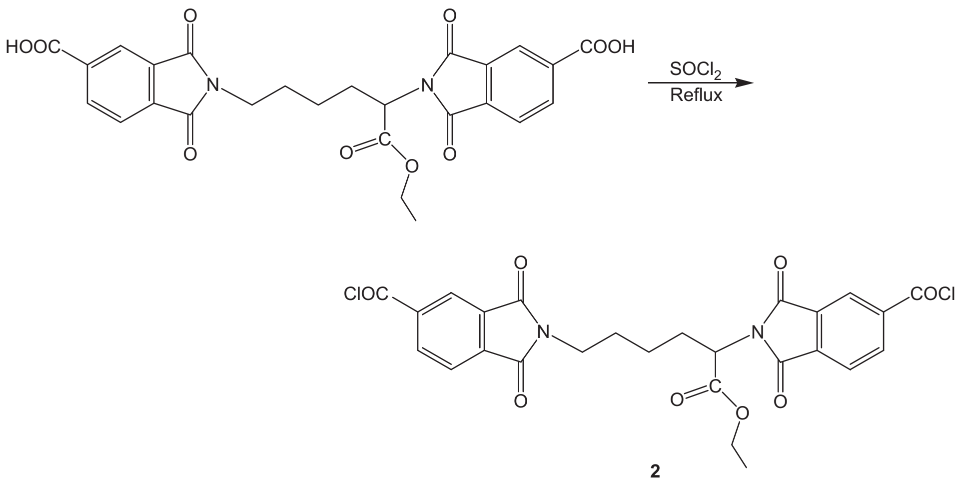
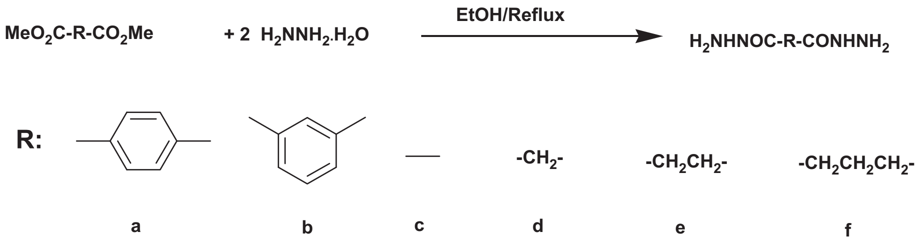


Figure 3 13C NMR spectrum of diacid 1.

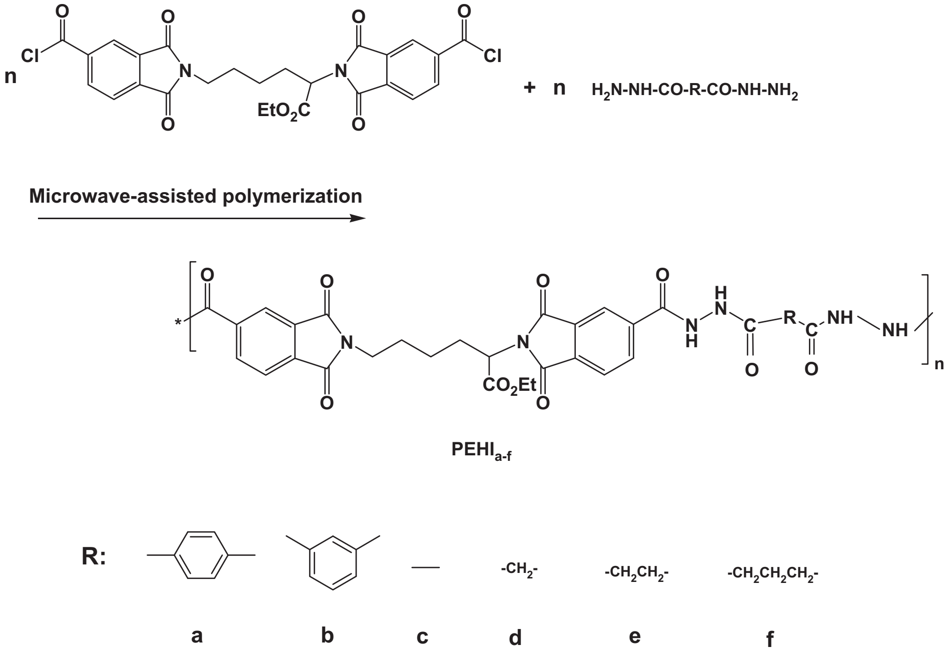
further 5 min. 0.25 ml of O-cresol as a solvent was added, and the mixture was ground for 5 min. The reaction mixture was irradiated in a microwave oven for 10 min (700 W, Interval: 10 s/min). The resulting homogenous



Scheme 3 Diacyl chloride **2** synthesis.



Scheme 4 Synthesis of dihydrazides (**3**–**8**).



Scheme 5 Microwave-assisted polymerization.

glassy compound film was dissolved in DMF and then isolated by adding methanol/H2O (50:50) and triturating, followed by filtration. It was washed several times with methanol and vacuum dried.

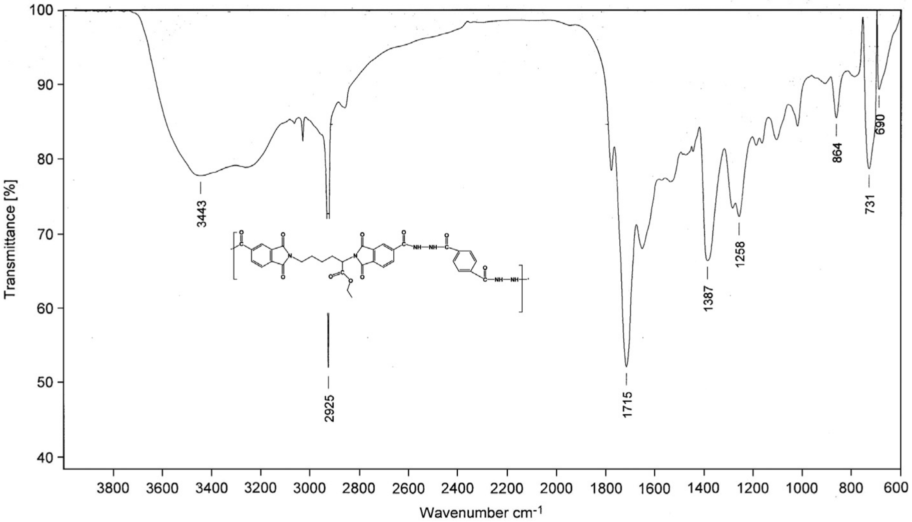


Figure 4 FT-IR spectrum of PHIa.

2.2.1.1. ***PHI$_a$***. Yellow; yield (%) = 91; $[\alpha_D^{25}] = +32.40$; UV ($\lambda_{\max}$) = 298; IR (cm^{-1}): 3640–3180, 2925, 1780, 1715, 1387, 1258, 864, 731; ^{1}H NMR (500 MHz, DMSO-d_6) δ: (ppm): 1.1 (3H), 1.2 (2H), 1.4 (2H), 1.7 (2H), 2.1 (2H), 4.1 (2H), 4.8 (1H), 7.2–8.5 (10H), 10.8 (4H).

2.2.1.2. ***PHI$_b$***. Yellow; yield (%) = 83; $[\alpha_D^{25}] = +5.20$; UV ($\lambda_{\max}$) = 268; IR (cm^{-1}): 3630–3180, 2924, 1770, 1716, 1379, 726, 689; ^{1}H NMR (500 MHz, DMSO-d_6) δ: (ppm): 1.1 (3H), 1.2 (2H), 1.4 (2H), 1.7 (2H), 3.6 (2H), 4.2 (2H), 4.9 (1H), 7.6–8.5 (10H), 10.9 (4H).

2.2.1.3. ***PHI$_c$***. White; yield (%) = 87; $[\alpha_D^{25}] = +10.30$; UV ($\lambda_{\max}$) = 260; IR (cm^{-1}): 3630–3170, 1780, 1716, 1389, 1243, 730, 689; ^{1}H NMR (500 MHz, DMSO-d_6) δ: (ppm): 1.1 (3H), 1.2 (2H), 1.4 (2H), 1.7 (2H), 2.1 (2H), 4.2 (2H), 4.8 (1H), 7.8–8.5 (6H), 11.2 (4H).

2.2.1.4. ***PHI$_d$***. White–Gray; yield (%) = 82; $[\alpha_D^{25}] = +15.50$; UV ($\lambda_{\max}$) = 262; IR (cm^{-1}): 3600–3200, 2942, 1770, 1716, 1387, 1294, 733; ^{1}H NMR (500 MHz, DMSO-d_6) δ: (ppm): 1.1 (5H), 1.6 (2H), 2.1 (2H), 3.6 (4H), 4.1 (2H), 4.8 (2H), 7.7–8.5 (6H), 10.4 (2H), 10.9 (2H).

2.2.1.5. ***PHI$_e$***. Pale yellow; yield (%) = 80; $[\alpha_D^{25}] = +8.30$; UV ($\lambda_{\max}$) = 268; IR (cm^{-1}): 3630–3130, 1790, 1716, 1388, 1251, 731, 688; ^{1}H NMR (500 MHz, DMSO-d_6) δ: (ppm): 1.1 (3H), 1.2 (2H), 1.7 (2H), 2.2 (6H), 3.6 (2H), 4.2 (2H), 4.8 (1H), 7.9–8.5 (6H), 10.9–11.2 (4H).

2.2.1.6. ***PHI$_f$***. Yellow; yield (%) = 77; $[\alpha_D^{25}] = +12.40$; UV ($\lambda_{\max}$) = 269; IR (cm^{-1}): 3630–3150, 1770, 1716, 1388, 1251, 731, 688; ^{1}H NMR (500 MHz, DMSO-d_6) δ: (ppm): 1.1 (3H), 1.2 (2H), 1.7 (4H), 2.1 (6H), 2.4 (2H), 4.2 (2H), 4.8 (1H), 7.7–8.4 (6H), 10.8 (2H).

3. 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 3350–2514 cm^{-1} corresponding to the Ammonium N–H stretchings and a strong peak at 1740 cm^{-1} corresponding to the C$\equiv$O stretching of ester moiety. ^{1}H 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 diacide (**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. 1–3). FT-IR spectroscopy shows a strong and broad peak at 3600–2700 cm^{-1} corresponding to the COOH stretchings, a strong peak at 1740 cm^{-1} corresponding to the C$\equiv$O stretching of ester moiety, a strong peak at 1702 cm^{-1} corresponding to the symmetric and unsymmetric C$\equiv$O stretching of imidic moiety and two peaks at 1411 and 750 cm^{-1} due to the cyclic imide groups. ^{1}H NMR ($CDCl_3$, ppm) spectroscopy shows 14 peaks and the corresponding peaks such as 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

Table 1 Optimization of microwave-assisted polycondensation on **PHI$_a$**.

Power	Time (min)	Interval (10 s/min)	inh (dl g^{-1})	α_D^{25}]
900	15	–	0.31	+9.9
900	15	+	0.30	+8.4
700	10	+	0.37	+18
600	15	+	0.31	+6.3
300	20	+	0.29	+7.9
300	20	+	0.21	+8.5

Table 2 Polymer properties.

Polymer code	Color	Yield (%)	$_{inh}$ (dl g^{-1})	α_D^{25}]	*Film quality*[a]
PHI_a	Yellow	80	013	+16.20	Flexible
PHI_b	Yellow	78	0.21	+6.30	Flexible
PHI_c	White	86	0.10	+8.65	Flexible
PHI_d	White–gray	78	0.37	+18.00	Flexible
PHI_e	Bright yellow	75	0.11	+7.28	Flexible
PHI_f	Yellow	53	0.17	+11.00	Flexible

[a] Films were casted by slow evaporation of polymer solution in DMAc.

Table 3 Solubility of polymers[a].

Solvents	$\mathbf{PHI_a}$	$\mathbf{PHI_b}$	$\mathbf{PHI_c}$	$\mathbf{PHI_d}$	$\mathbf{PHI_e}$	$\mathbf{PHI_f}$
NMP	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMF	+	+	+	+	+	+
H_2SO_4	+	+	+	+	+	+
CH_2Cl_2	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
MeOH	–	–	–	–	–	–
H_2O	–	–	–	–	–	–

[a] Concentration: 5 mg ml^{-1}: +, soluble at room temperature; –, insoluble at room temperature.

spectroscopy shows the corresponding carbonyl stretching of acyl chloride at 1862 cm^{-1}. Synthesis of dihydrazides (**3**–**8**) is presented in scheme 4. FT-IR spectroscopy shows the corresponding carbonyl stretching at 1663 cm^{-1} and that of NH at 3050–3289 cm^{-1}.

Microwave-assisted polymerization was applied to prepare the poly (hydrazide-imide)s (Scheme 5). The Microwave-assisted procedure provided a more satisfactory performance compared to the use of homogeneous systems since only about 10 min. of Microwave-assisted polycondensation was required for obtaining both yields and η_{inh} attained after 12 h by solution procedure. To optimize the polymerization conditions, we did six experiments on $\mathbf{PHI_a}$. The optimum condition is as follow: Power = 700 W; Time = 10 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 of the very probable atactic polymers were obtained from an inexpensive starting material in quantitative yields with moderate inherent viscosities (0.10–0.37 dl g^{-1}) and optical rotation (+6.30 to +18.00) (Table 2). In contrast to our previous papers, here there is no obvious regioselectivity between alpha and epsilon acyl chloride groups of the lysine ester containing diacid during the polymerization 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 (53–86%) and being thermally stable (*T* (10%): 248–301 °C). The color of these polymers was white to yellow. The resulting homogenous glassy compound films were

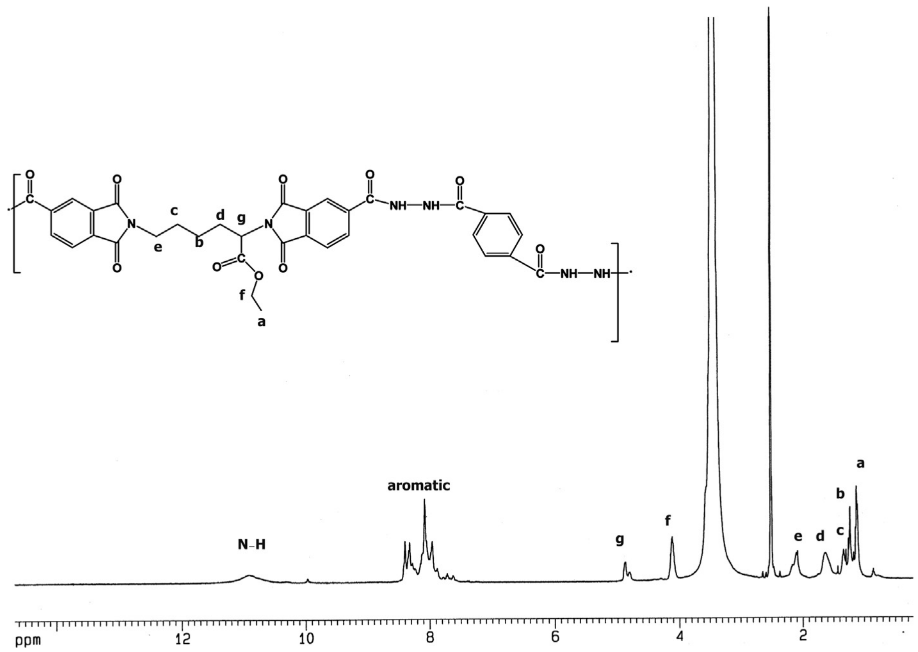


Figure 5 1H NMR spectrum of PHIa.

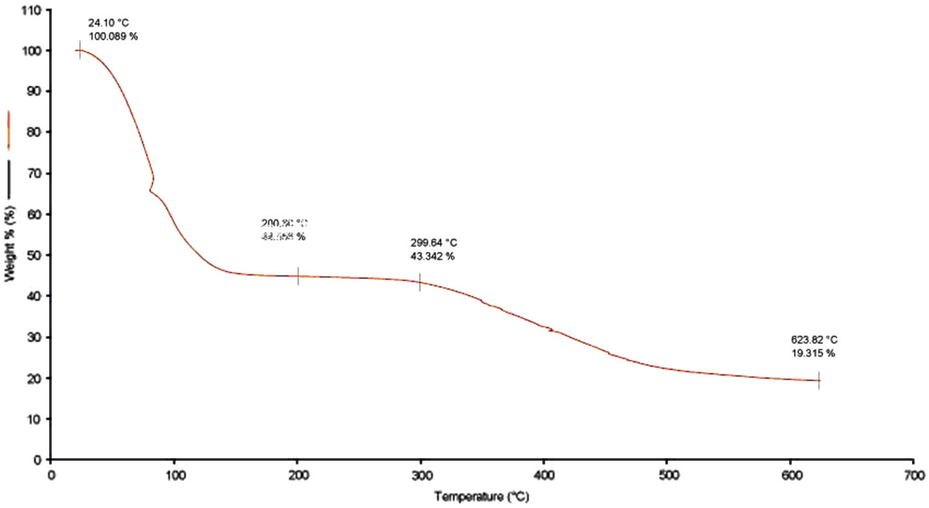


Figure 6 TGA spectrum of PHIa.

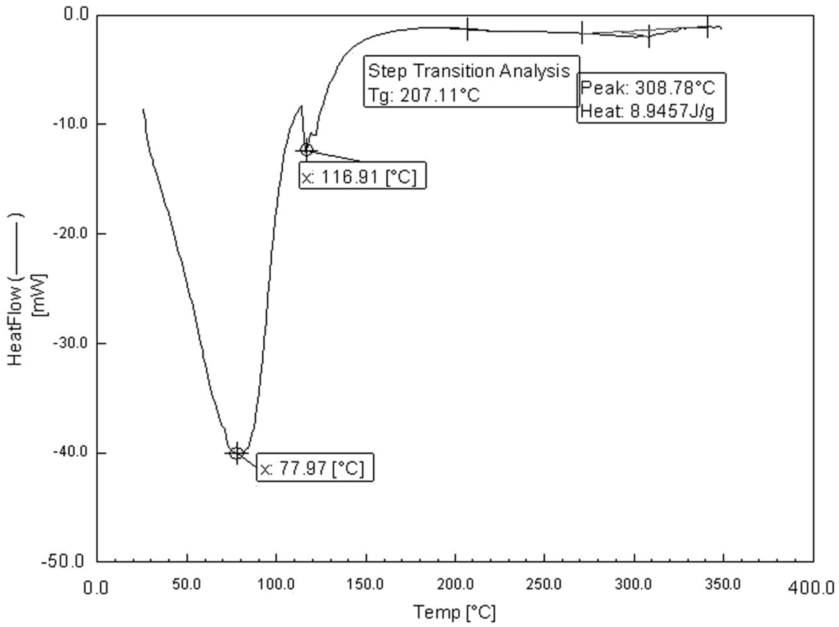


Figure 7 DSC spectrum of PHIa.

Table 4 Thermal behavior of polymers.

Polymer	Decomposition temperature (°C) $T_{10\%}$[a]	Char yield (%)[b]
PHI_a	299.6	19.3
PHI_b	292.6	21.22
PHI_c	239.5	36
PHI_d	248	40.49
PHI_e	301	13.22
PHI_f	250	32.34

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

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

isolated by adding methanol/H_2O (80:20) and triturating, followed by filtration. It was washed several times with methanol and vacuum dried. Transparent, flexile, 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 3). The novel polymers were fully characterized by spectroscopic analysis (UV, FT-IR, ^{1}H NMR), thermal analysis (TGA, DSC), viscometric measurements, optical rotation measurements and solubility tests. As an example the corresponding spectra of $\mathbf{PHI_a}$ are represented in Figs. 4–7, respectively.

Thermal properties of these polymers are investigated by TGA/DTG under air atmosphere at 6 °C/min and by DSC under nitrogen atmosphere at 10 °C/min (Table 4). In FT-IR spectra of these polymers some characteristic peaks could be seen, including the N–H stretching of hydrazide group at around 3443 cm^{-1}, C=O asymmetric and symmetric stretching of imide groups at 1716 cm^{-1}, C=O stretching of hydrazide group at 1630 cm^{-1}. All of these **PHI**s exhibited strong absorption at around 1380 and 720 cm^{-1}, which shows the presence of the heterocyclic imide groups. The ^{1}H NMR spectra of **PHI**s shows 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.

4. Conclusion

A fast and effective procedure to prepare a serious of optically active polyhydrazides 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 then random orientation of lysine moieties along the polymer backbone can be predicted.

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