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Optically active polymer: synthesis and characterization of new optically active poly (hydrazide-imide)s incorporating L- leucine

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Abstract: This paper deals with the polycondensation between a chiral diacyl chloride (*N,N′*-Pyromelliticdiimido-di-L-leucine chloride) and six different dihydrazides. The corresponding poly (hydrazide-imide)s which have been obtained in quantitative yields are moderately soluble in polar aprotic solvents, have good thermal stability and optical activity. The synthetic compounds have been characterized by IR, UV and ^{1}H NMR spectroscopy, elemental analysis and specific rotation. The thermal properties of the polymers (**10** and **15)** have been studied by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Keywords: N,N′-Pyromelliticdiimido-di-L-leucine, poly (hydrazide-imide), optically active, L-leucine, thermal stability

Introduction

Due 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. Polyimides and their copolymers are certainly one of the most useful classes of high-performance polymers, which have found many applications in industry [1, 2]. Aromatic polyimides are one of the important classes of heterocyclic polymers with remarkable thermal stability, durability, superior mechanical and electrical properties [3-5]. Poor thermoplastic fluidity and solubility are the major problems in the wide application of polyimides.

Polyhydrazides [6, 7] have been extensively studied since they enhance the dyeability of the synthetic fibers and also improve elasticity over other polymer types. They possess fair absorption characteristics when the hydrazide link is in the main chain or in the polymer backbone [8]. They have been cyclized to give polytriazoles [9, 10]. They also provide a synthetic base for the chelate polymers [11], since the hydrazide group (-CO-NH-NH-CO-) can react with metal ions to form complexes. Hydrazide groups have been incorporated into the structure of some synthetic compounds as good candidate vectors for gene delivery [12].

High-molecular weight aliphatic, aliphatic–aromatic and aromatic polyhydrazides, which have very interesting solubility behavior, were also prepared by the low temperature solution polycondensation of diacyl dichlorides with hydrazine hydrate or diacid dihydrazides in N,N-dialkylamide solvents [13, 14].

Polyhydrazides are generally synthesized by the low temperature solution polycondensation of a dihydrazide with a diacyl chloride in a solvent such as N-methyl-2-pyrrolidone (NMP) in the presence of an inorganic salt like lithium chloride [15–19]. Interfacial polycondensation of a dihydrazide with a diacid chloride in two immiscible solvents can yield high molecular weight polyhydrazides [20]. Higashi and co-workers [21, 22] demonstrated that high molecular weight polyhydrazides and poly (amide-hydrazide)s could be synthesized by the direct polycondensation reaction of an aromatic dicarboxylic acid by means of di- or tri-phenyl phosphite.

Polyhydrazides are important intermediates in the preparation of poly(1,3,4-oxadiazoles), through their cyclodehydration either by heating at elevated temperature or by use of dehydrating agents [23, 24]. Poly(1,3,4-oxadiazole)s have been the focus of considerable attention with regard to the production of high-performance materials, particularly owing to their high thermal stability and tough mechanical properties, along with a fruitful combination of optical and electronic properties determined by the specific structure of 1,3,4-oxadiazole ring [25, 26]. Some efforts have been done into the synthesis and study of new silicon-containing polyoxadiazoles [27].

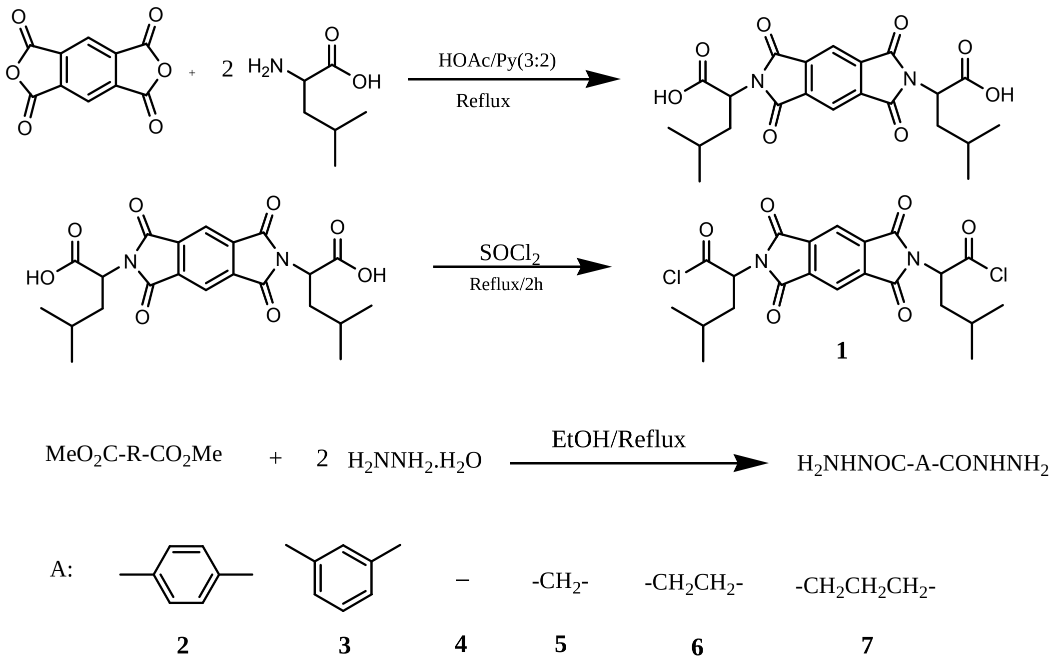
The synthesis and application of optically active polymers are new considerable topics which have been paid more attention recently [28]. Most of the natural polymers that have been made in genes, proteins and enzymes are optically active and have special chemical activities, such as catalytic properties. Some other applications are construction of chiral media for asymmetric synthesis, chiral stationary phases for resolution of enantiomers in chromatographic techniques [29-33], chiral liquid crystals in ferroelectrics and nonlinear optical devices [34-37]. These synthetic polymers can be synthesized using the commercially available optically pure L-amino acids that can induce crystallinity with their ability to form higher ordered structures that exhibit enhanced solubility characteristics [38]. These properties have caused them to be good candidate for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials and also as chiral purification media [39]. Therefore, more efforts for improving different synthetic procedures of optically active polymers have been made. Recently, we have reported the synthesis of optically active polymers by different methods [40-43].

In this research, we report the synthesis and characterization of six new heterocyclic, optically active poly (hydrazide-imide)s (PAIs) from a chiral diacyl chloride with preformed imide group (**1**) and six dihydrazides (**2**-**7**) by solution and interfacial polycondensation. We have used L-leucine to induce chirality in the corresponding polymers. We also expected that the interfacial polycondensation would improve the viscosity of the corresponding polymers, since the monomers react with the growing chains at the interface more rapidly than they diffuse through the polymer film to initiate new chains. Cyclodehydration of one polyhydrazide (**10**) to its corresponding polyoxadiazole (**15**) which might display interesting properties as materials for electronic applications has been studied. In addition, other characteristics of these polymers such as thermostability, specific rotation, and solubility are discussed.

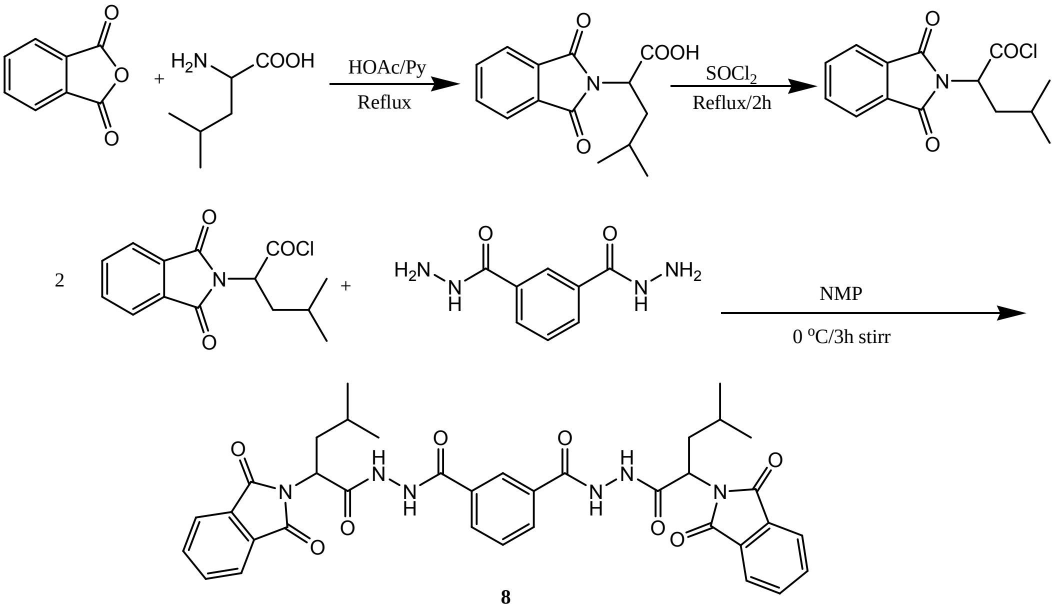
Results And Discussion

Polyhydrazides

Scheme 1 presents the synthesis of monomers used in this project. The model compound **8** was prepared to study the efficiency of polymerization method (Scheme 2).

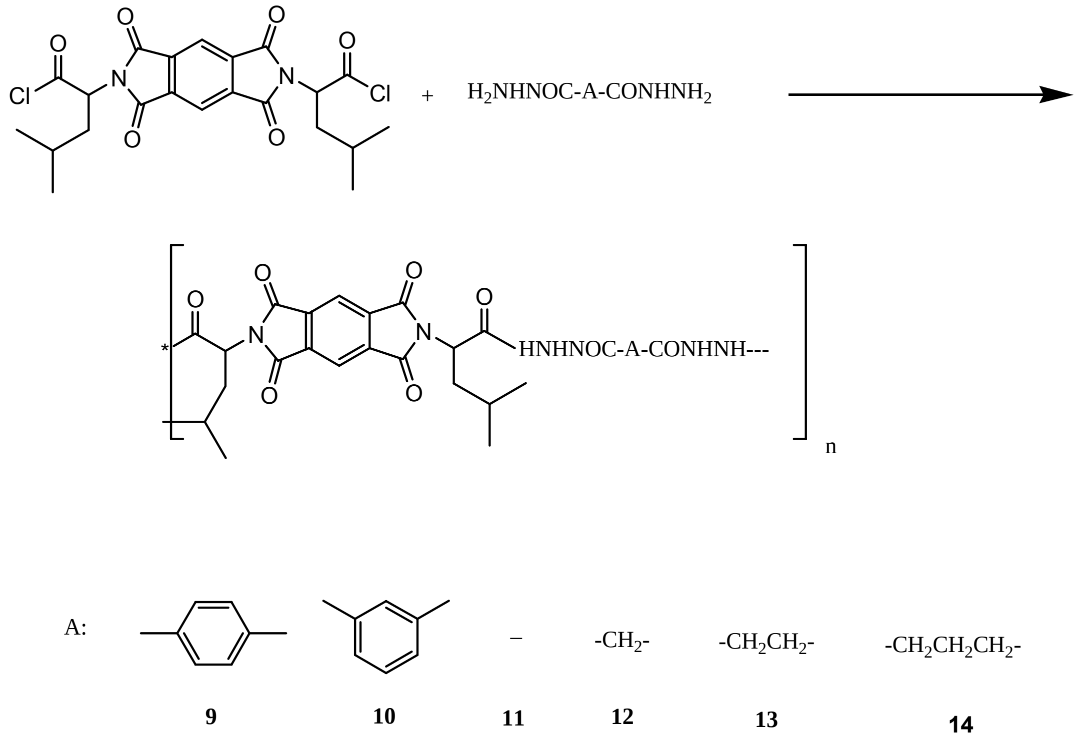


Scheme 1. Synthesis of various monomers used in this study.



Scheme 2. Polymerization of model compound (**8**).

The two polycondensation processes (solution and interfacial) related to dihydrazides (**2**–**7**) and diacid chloride (**1**), leading to the corresponding polyhydrazides are shown in Scheme 3. Table 6 gives the conditions and the results related to the two techniques of polycondensation used in this study to prepare the relevant materials. As the regularity of the pendant group at the chiral center contribute to the chemistry of the obtained polymers, the different sacial orientation, chirality and also specific rotation is seen in these two polymer series. The progress of the reaction was followed by the evolution of the inherent viscosity of samples withdrawn at regular intervals from the reaction media.



Scheme 3. The two polycondensation processes (solution and interfacial) related to dihydrazides (**2**–**7**) and diacid chloride (**1**), resulting in the corresponding polyhydrazides.

The higher molecular weight obtained by interfacial polycondensation, as suggested by the fact that polymers became insoluble in DMF and had to be characterized by dissolving them in a solution of LiCl (5%) in NMP. The polymers obtained from solution polycondensation show better solubility than those obtained from interfacial method (Tables 1 and 2).

Tab. 1. Solubility of the polymers obtained from solution polycondensation (**9-15**).[a]

Polymer	DMAc	DMF	NMP	DMSO	H_2SO_4	m-cresol
9	+	+	+	+	+	-
10	+	+	+	+	+	-
11	+	+	+	+	+	-
12	+	+	+	+	+	-
13	+	+	+	+	+	-
14	+	+	+	+	+	-
15	+	+	+	+	+	-

[a] (+: soluble at room temperature.-: insoluble at room temperature)

The FT-IR and ^{1}H NMR spectra of all these polymers confirmed their regular linear structures. Figure 1 shows the IR and ^{1}H NMR spectra of the model compound **8** as example of satisfactory structural features.

Tab. 2. Solubility of the polymers obtained from interfacial polycondensation (**9-15**).[a]

Polymer	DMAc	DMF	NMP	DMSO	H_2SO_4	NMP (3% LiCl)	NMP (5% LiCl)
9	+-	+-	+-	+-	+	++-	+
10	+-	+-	+-	+-	+	++-	+
11	+-	+-	+-	+-	+	++-	+
12	+-	+-	+-	+-	+	++-	+
13	+-	+-	+-	+-	+	++-	+
14	+-	+-	+-	+-	+	++-	+
15	+-	+-	+-	+-	+	++-	+

[a](+: soluble at room temperature. ++-: soluble on heating. +-: partially soluble on heating)

These polymers can be good candidates for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials, chiral purification media and can act as a good chelating agent to trap metal ions.

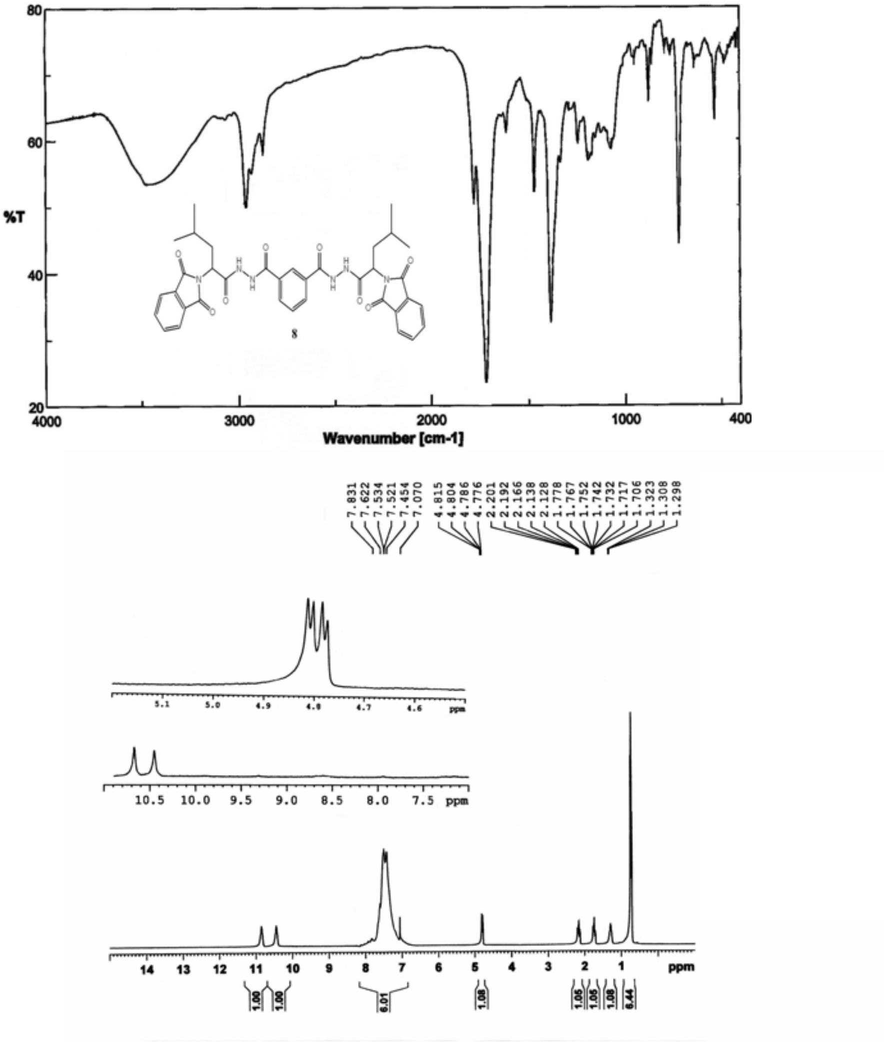
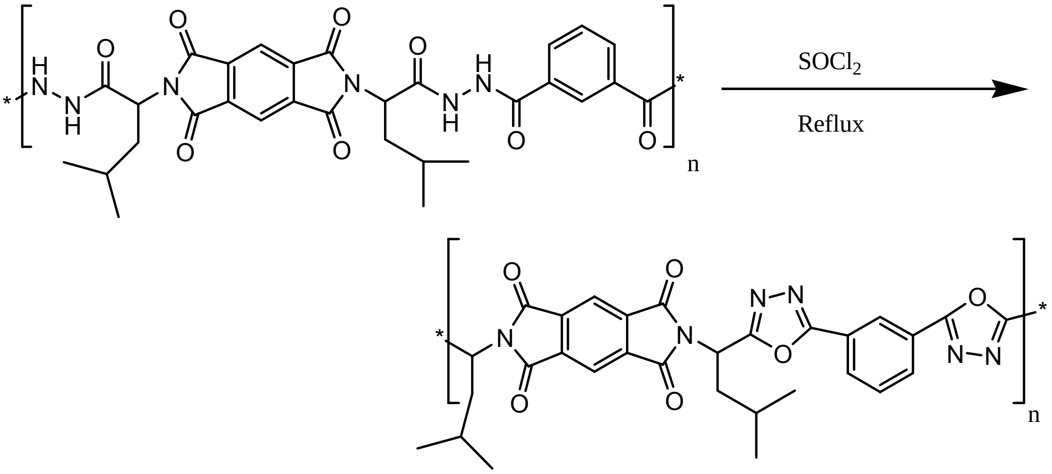


Fig. 1. IR and ^{1}H NMR spectra of the model compound **8.**

3.2. Polyoxadiazole

Aromatic polyhydrazides are known to undergo cyclodehydration either by heating in vacuum at 100–200 °C, or in solution using an appropriate dehydrating agent [10]. In order to assess the feasibility of this chemical modification on our polymers, we treated polymer **9** with thionyl chloride (Scheme 4).



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Scheme 4. Cyclodehrdation of polymer **9**.

The presence of 1,3,4-oxadiazole rings between the aromatic moieties was established by spectroscopic analysis. The FT-IR spectrum of polyoxadiazole **15** (Fig. 2) showed the presence of the characteristic peaks of the 1,3,4-oxadiazole ring at 1620 and 970 cm^{-1}.

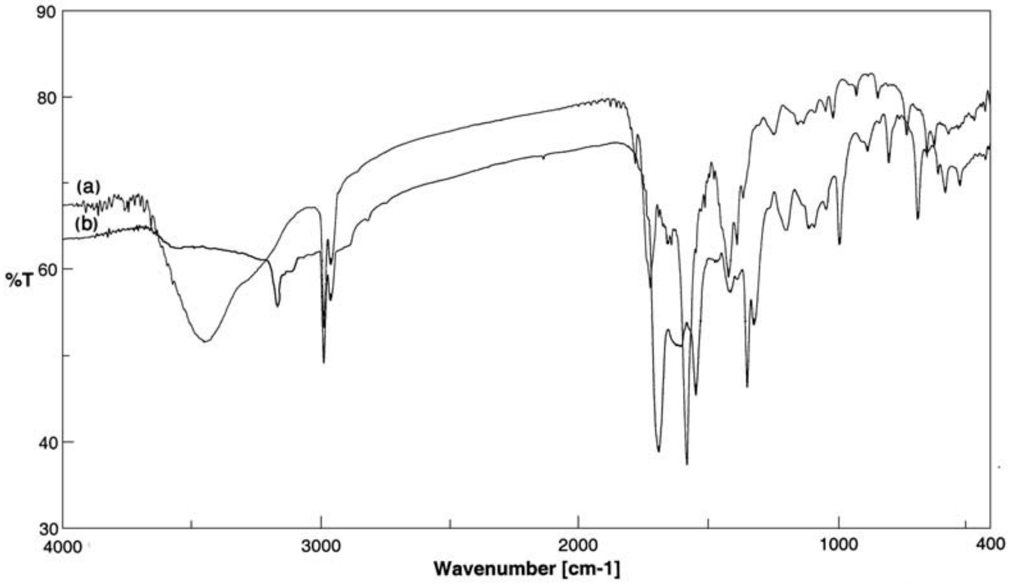

Fig. 2. FT-IR spectra of (a) Polyhydrazide **10** and (b) polyoxadiazole **15**.

Thermal Behavior

The thermal properties of polymers (**10** and **15**) were evaluated by means of TGA/DTG under air atmosphere and DSC under nitrogen atmosphere at a heating rate of 5 °Cmin^{-1} (Table 3). The residual weights for these polymers at 600°C are 9.6% and 10.4% under air atmosphere (Fig. 3).

Tab. 3. Thermal properties of polymers (**10,** and **15**).

Polymer	$T_{5\%}$ (°C)^a	$T_{10\%}$ (°C)^a	T_g^{b}	Ch.Y^c
10	**218**	**275**	**-**	**9.6**
15	**265**	**318**	**-**	**10.4**

^{a}Temperature of 5% and 10% weight loss obtained from TGA, ^{b}Glass transition temperature, obtained from DSC, ^{c}Char yield percentage at 600°C, obtained from TGA

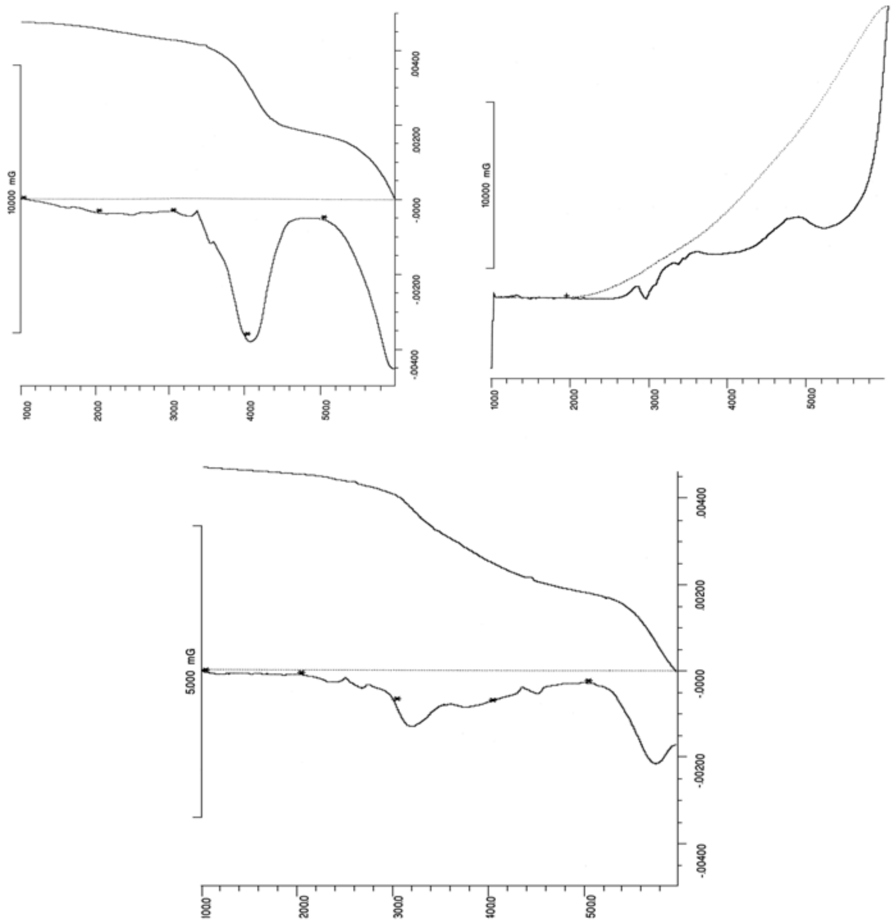

Fig. 3. (a) TGA and DSC spectra of polymer **10**; (b) TGA spectrum of polymer **15**.

Conclusions

Novel chiral polyhydrazides incorporating L-leucine have been synthesized with two different polycondensation methods which have caused polymers with different chemistry. The polymers have reasonably high molecular weights, bearing aliphatic and aromatic moieties in their backbone, and have been obtained in good yields from the reaction of the appropriate combinations of dihydrazides and diacid dichloride. These materials can undergo cyclodehydration to give the corresponding polyoxadiazoles. These polymers are chiral, show good thermal stability (polymer **10** and **15**) and can act as a good chelating agent to trap metal ions. Work is in progress to optimize these syntheses, extend the range of structures and assess the properties of all ensuing materials.

Experimental

Material and Measurements

N-Methyl-2-pyrrolidone (NMP, Merck) and pyridine (Py, Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieve. Dimethyl formamide (DMF), L-leucine (Merck), hydrazine monohydride (Merck), thionyl chloride ($SOCl_2$, Merck), dimethyl isophthalate (Merck), dimethyl terephthalate (Merck), dimethyl malonate (Merck), dimethyl oxalate (Merck), dimethyl succinate (Merck), dimethyl glutarate (Merck), tetraethyl ammonium bromide (TEAB), and dichloromethane were used as received. Pyromellitic dianhydride (Merck) was recrystallised from acetic anhydride.

^1H NMR spectra were recorded on 400 MHz Bruker instrument, using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane as shift reference (tube diameter, 5mm). IR spectra were recorded on a Shimadzu FT/IR-680 plus instrument, using KBr pellets. Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermo gravimetric analyses (TGA) were recorded on a Mettler TGA-50 with heating rate of 5 ^oC min^{-1} under air atmosphere. Differential scanning calorimetry (DSC) analyses were recorded on a Mettler DSC-30 under nitrogen atmosphere with heating rate of 5 ^oC min^{-1}. Inherent viscosities of polymers were measured by a standard procedure using a KPG Cannon Fenske routine viscometer at 30 ^oC using DMF as solvent. Melting points were measured in open capillaries with a Qallenkamp instrument. UV spectra were recorded in DMF in the region of 200-450 nm on a JASCO V-570 Spectrophotometer.

Monomer Synthesis

-Synthesis Of N,N'-(Pyromellitic Diimido)-Bis-L-Leucine Diacid Chloride (1)

Diacid chloride (**1**) was prepared according to our previous work [44]. $[\alpha]_D^{25}$ = +1.20.

-Synthesis of Dihydrazide

General procedure: A mixture of dimethyl ester (1 mol) and hydrazine mono hydrate (3 mol) was kept under stirring and refluxed in ethanol for 2 h. Corresponding dihydrazide was precipitated by cooling down the solution to room temperature. Pure dihydrazide was obtained after recrystallization from ethanol.

Synthesis Of Model Compound (8)

Frazer and Wallenberger's method [45] was adopted without any modification to prepare this model compound. This procedure involves the reaction of dihydrazide **3** with N-(phthalic imido)-L-leucine acid chloride, which is prepared as reported [44] in NMP under nitrogen atmosphere at 0 °C for 3 h.

Table 4 presents some physical properties (color, *mp*, yield (%)), Table 5 presents IR and ^{1}H NMR, and Table 8 presents CHN analyses of the monomers and the model compound.

Tab. 4. Physical property of monomers and the model compound **8**.

Monomer	Color	Mp (°C)	Yield (%)
1	Off White	128-130 (dp)	95
2	White	>300	95
3	White	244-246	98
4	Off White	240-241	75
5	Yellow	148-149	80
6	Bright White	169-170	83
7	White	176-177	87
8	Bright yellow	140 (dehydration), 160	96

Tab. 5. IR and ^{1}H NMR spectra of monomers and the model compound **8**.

Monomers	IR (cm^{-1})	^{1}H NMR δ: (ppm)
1	3330, 2948, 1850, 1775, 1720, 1619, 1382, 1295, 1162, 1094, 1020, 851, 728, 573 1380, 740	1.00 (d, 12H), 1.50 (m, 2H), 1.90 (ddd, 2H), 2.20 (ddd, 2H), 4.88 (dd, 2H), 8.50 (s, 2H)
2	3324, 3033, 1605, 1540, 1489, 1340, 1291, 1103, 1016, 927, 886, 736, 713, 638	4.51 (s, 4H), 7.90 (s, 4H), 9.90 (s, 2H)
3	3289, 3055, 1663, 1625, 1585, 1524, 1321, 1108, 996, 923, 819, 723, 687, 625	4.51 (s, 4H), 7.50 (t, 3H), 7.91 (dd, 2H), 8.30 (t, 1H), 9.80 (s, 2H)
4	3282, 3181, 3007, 1679, 1611, 1534, 1360, 1269, 1097, 998, 793, 537	4.11 (s, 4H), 9.60 (s, 2H)
5	3304, 3201, 3131, 3034, 2873, 1667, 1647, 1532, 1363, 1248, 1203, 1052, 955, 788, 694	2.90 (s, 2H), 4.20 (s, 4H), 9.11 (s, 2H)
6	3313, 3291, 3200, 3181, 3042, 2874, 2779, 1627, 1531, 1353, 1241, 1012, 949, 752, 664	2.30 (s, 4H), 4.11 (s, 4H), 8.90 (s, 2H)
7	3315, 3180, 3046, 2965, 2927, 1636, 1532, 1379, 1330, 1157, 1016, 1001, 954, 711, 618	1.75 (quin, 2H), 2.00 (t, 4H), 3.51 (s, 4H), 8.90 (s, 2H)
8	3470, 2959, 2872, 1777, 1717, 1611, 1468, 1384, 1287-1073, 875, 718, 530	0.82 (d, 12H), 1.31 (m, 2H), 1.75 (ddd, 2H), 2.16 (ddd, 2H), 4.80 (dd, 2H), 7.45-7.83 (m, 12H), 10.51 (s, 2H), 10.86 (s, 2H)

Synthesis of Polyhydrazide

The polycondensation of the dihydrazides (**2**-**7**) with diacyl chloride **1** were preformed following two alternative techniques, namely:

(i) Frazer and Wallenberger's method [45] was adopted without any modification for solution polycondensation. This procedure involved the polycondensation of dihydrazides (**2-7**) with the dicarboxylic acid dichloride (**1**) in NMP under nitrogen atmosphere at 0 °C for 12 h.

(ii) Interfacial polycondensation were carried out at room temperature using a 0.2 M NaOH aqueous solution containing TEAB coupled with a methylene chloride organic phase. Equal molar amounts of the complementary monomers were introduced in each phase to give a 0.1 M concentration of the dicarboxylic acid dichloride in CH_2Cl_2 and a 0.1 M concentration of the dihyrazide in the aqueous phase. The resulting biphasic reaction mixture was then stirred for 3 h at room temperature. The ensuing white powder was isolated by filtration, washed with methanol and vacuum dried at 90 °C to constant weight.

Cyclodehydration Reaction

Polymer **10** was dehydrated with an excess of thionyl chloride under reflux for 50 min to yield the corresponding 1,3,4-oxadiazole polymer (**15**).

Structural and Size Characterization

The structures of all products were assessed by FT-IR, ^{1}H NMR spectroscopy, elemental analyses and specific rotation. Inherent viscosities were determined at 30 °C from DMF solution. Table 6 presents yields and viscosities of polymers with two different methods. Table 7 presents IR, UV, and ^{1}H NMR of polymers. Table 8 presents CHN analyses of polymers.

Tab. 6. Yields, inherent viscosities (0.5 g/dl in DMF at 30 °C), and specific rotation (at 25 °C with Hg (365 nm) lamp) of polyhydrazides.

	Polymer	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Solution	Yield (%)	85	85	70	70	60	50	80
	$\acute{\eta}_{inh}$ (dl g^{-1})	0.14	0.22	0.10	0.11	0.17	0.19	0.16
	Specific rotation	+115.5	+27.7	+97.8	+134.8	+32.6	+112.5	+60.5
Interfacial Polycondensation	Yield (%)	95	97	88	85	85	90	90
	$\acute{\eta}_{inh}$ (dl g^{-1})	0.19	0.29	0.18	0.17	0.22	0.30	0.25
	Specific rotation	+200.6	+13.2	+112.6	+124.2	+20.0	+114.7	+76.4

Tab. 7. IR (characteristic bonds), UV, and ^{1}H NMR spectra of polymers.

Polymers	UV (λ_{max})	IR (cm^{-1})	^{1}H NMR δ: (ppm)
9	265, 323	3660-3150, 2959, 1776, 1724, 1650, 1575, 1384, 726	0.95 (d, 12H), 1.50 (m, 2H), 1.93 (m, 2H), 2.25 (m, 2H), 4.98 (br, 2H), 8.21 (s, 4H), 8.36 (s, 2H), 10.2 (s, 4H),

10	265, 324	3640-3200, 2960, 1778, 1726, 1625, 1577, 1383, 724	0.90 (d, 12H), 1.50 (m, 2H), 1.95 (m, 2H), 2.25 (m, 2H), 5.05 (br, 2H), 8.10-8.53 (m, 6H), 10.11 (s, 2H), 10.25 (s, 2H)
11	265, 320	3635-3220, 2961, 1779, 1723-1646, 1570, 1383, 726	0.96 (d, 12H), 1.50 (m, 2H), 1.90 (m, 2H), 2.22 (m, 2H), 5.00 (br, 2H), 8.35 (s, 2H), 11.1 (s, 2H), 11.5 (s, 2H)
12	265, 321	3641-3200, 2960, 2876, 1776, 1723, 1623, 1577, 1384, 726	1.00 (d, 12H), 1.50 (m, 2H), 1.93 (m, 2H), 2.23 (m, 2H), 3.10 (s, 2H), 4.97 (br, 2H), 8.35 (s, 2H), 10.1 (s, 2H), 10.2 (s, 2H)
13	265, 321	3652-3205, 2960, 2873, 1777, 1724, 1641, 1578, 1383, 727	0.94 (d, 12H), 1.50 (m, 2H), 1.95 (m, 2H), 2.25 (m, 2H), 2.90 (s, 4H), 4.98 (br, 2H), 8.35 (s, 2H), 10.1 (s, 2H), 10.2 (s, 2H)
14	265, 321	3658-3190, 2960, 2873, 1777, 1724, 1631, 1574, 1383, 726	1.00 (d, 12H), 1.50 (m, 2H),1.81-1.90 (m, 4H), 2.20 (m, 6H), 4.95 (br, 2H), 8.35 (s, 2H), 10.2 (s, 4H)
15	267	3008, 2959, 2872, 1778, 1726, 1625, 1619, 1577, 1383, 970, 724	-

Tab. 8. Elemental analyses of monomers, model compound **8** and polymers.

Compound		C (%)	H (%)	N (%)
1 ($C_{22}H_{22}N_2O_6Cl_2$: 397.166)	Calculated	54.90	4.61	5.82
	Found	55.12	4.67	5.97
2 ($C_8H_{10}N_4O_2$: 194.194)	Calculated	49.48	5.19	28.85
	Found	49.39	5.22	28.76
3 ($C_8H_{10}N_4O_2$: 194.194)	Calculated	49.48	5.19	28.85
	Found	49.45	5.21	28.77
4 ($C_2H_6N_4O_2$: 118.096)	Calculated	20.34	5.12	47.44
	Found	20.27	5.16	47.40
5 ($C_3H_8N_4O_2$: 132.123)	Calculated	27.27	6.10	42.41
	Found	27.18	6.17	42.37

6 ($C_4H_{10}N_4O_2$: 146.15)	Calculated	32.87	6.90	38.33
	Found	32.79	6.98	38.28
7 ($C_5H_{12}N_4O_2$: 160.177)	Calculated	37.49	7.55	34.98
	Found	37.41	7.61	34.87
8 ($C_{36}H_{36}N_6O_8$: 680.69)	Calculated	63.52	5.33	12.35
	Found	63.48	5.39	12.31
9 ($C_{30}H_{35}N_6O_8$: 602.61)	Calculated	59.79	5.02	13.95
	Found	59.69	5.09	13.90
10 ($C_{30}H_{35}N_6O_8$: 602.61)	Calculated	59.79	5.02	13.95
	Found	59.67	5.12	13.88
11 ($C_{24}H_{26}N_6O_8$: 526.51)	Calculated	54.75	4.98	15.96
	Found	54.66	5.03	15.89
12 ($C_{25}H_{28}N_6O_8$: 540.54)	Calculated	55.55	5.22	15.55
	Found	55.42	5.27	15.58
13 ($C_{26}H_{30}N_6O_8$: 554.57)	Calculated	56.31	5.45	15.15
	Found	56.26	5.54	15.01
14 ($C_{27}H_{32}N_6O_8$: 568.60)	Calculated	57.03	5.67	14.78
	Found	56.95	5.72	14.66

Acknowledgements

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