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New chiral poly(urethane-imide)s. Synthesis, characterization and optical properties

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New poly(urethane-imide)s have been prepared by the classical polyaddition reaction of two imide-containing diols with hexamethylene diisocyanate. The chirality was provided by the diols whose design was performed in two synthesis steps. The structure of the polymers were confirmed by elemental analysis and IR, ^{1}H NMR spectroscopy techniques. The polymers have been also characterized by WAXD, DSC, TGA and solubility measurements. The specific rotatory power $[\alpha]_{546}$ was measured and the mean residue rotations $[m]_{546}$ values were calculated. The refractive index of each polymer was determined by succesive dilution measurements. The transparency (τ) and stress optical coefficient (SOC) were also determined.

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1. Introduction

Optically active compounds have attracted great attention because living systems are chiral. Proteins and nucleic acids possess chiral characteristic structures that are related closely to their functions. Because of the chirality, living organisms usually show different biological responses to one or the other of a pair of enantiomers or optical isomers whether they are drugs, pesticides or wastes. Although the synthesis and application of optically active polymers were first studied a long time ago, more attention has been paid to this topic recently because polymers with chiral structures are biologically very important compounds and the recognized need to create new, more versatile polymeric reagents, catalysts and enetioselective supports is likely to be a dominant driving force behind the synthesis of novel optically active monomers and polymers [1-4]. Optically active polymers can be used mainly as catalysts for asymmetric synthesis [5,6] and as chiral stationary phases for the direct optical resolution of enantiomers [7-9]. Among optically active polymers, polyimides are of great interest because the introduction of chirality into the polymer chains provides new physical properties [10-13]. Optically active binaphtyl-containing polyimides show an excellent stability of optical rotatory power at high temperature [10]. Chiral thermotropic polyimides containing imide rings as mesogenes and aliphatic or semialiphatic spacers can form enantiotropic melt which show selective transmission and reflection of circularly polarized light if macroscopic orientation of the entire domain is feasible [14]. These properties make them useful for applications in optoelectronics. However, this family of polymers lack melting processability and require machining operations similar to metal fabrication. Being very important for the technical interests [15,16], incorporation of ether, carbonate, ester or urethane linkages into polyimide backbone generally provides sufficient flexibility and processability without sacrificing the imide characteristics [17].

Meanwhile polyurethanes (PUs) belong to a class of versatile materials that can easily be prepared by polyaddition of diols with diisocyanates. Their tailor-made properties extend from super soft flexible foam to tough elastomers and to longwear coatings, and have resulted in many end uses. [18]. Optically active PUs were synthesized and applied to chiral stationary phase [8, 19, 20] proving higher chiral recognition abilities for liquid chromatography technique then polyamides with similar structure [8].

A significant drawback of PUs is their poor thermal stability. Their acceptable mechanical properties (strength, module) vanish above 80^0C, and thermal degradation occurs above 200^0C, which has limited its application. Attempts to improve thermal stability of polyurethanes have been made over long period. Particular attention has paid to modifications of these polymers by heterocyclic groups. This can be achieved by incorporation of an imide moiety into the polyurethane chain [21]. So, it is expected that the new type of polymers, such as poly(urethane-imide)s, can combine the useful properties of both class of polymers, namely polyimides and polyurethanes classes.

Various attempts to incorporate polyimide units into polyuretanes can be classified as (a) reaction of isocyante terminated PUs prepolymers with acid anhydride [22-25], (b) reaction of amine-blocked polyurethane prepolymers with acid anhydrides [26,27], (c) reaction of isocyanate terminated PUs prepolymers with diols containing build-in imide groups [28, 29], (d) intermolecular Diels-Alder reaction of molecules containing bis(2-furyl-carbamate) units [30-33], (e) thermal crosslinking of PUs prepolymers containing maleimide functions [34, 35], (f) reaction of diisocyantes containing preformed imide groups with different polyols [36-38] or reaction of various

diisocyantes with diols containing preformed imide rings [17,21,39], (g) reaction of epoxy resins containing imide structure [40], of hydroxyl-containing polyimides [41,42] or of polyimides precursor (polyamic acid) [43, 44] with blocked PUs prepolymers. All of these synthesized poly(urethane-imide)s were studied especially in terms of solubility and thermal stability, some of them being reported as liquid crystalline materials based on aromatic imides as mesogene moieties [29]. To the best of our knowledge the informations about synthesis and characterization of optically active poly(urethane-imide)s come only from one source [45]. They were synthesized starting from optically active diisocyanate containig build-in imide groups and various aromatic diols.

The goal of this paper is to present the synthesis and characterization of new optically active poly(urethane-imide)s using two chiral imide containing diols, prepared by us [2] in view to investigate their optical properties.

2. Experimental

2.1 Materials

Pyrromellitic dianhydride (PMDA), *p*-toluenesulfonic acid (PTSA), acetic anhydride, N,N-dimethylformamide (DMF, all from Fluka), (R)-(-)-2-aminobutane-1-ol ([(R)-2-AMB] , Merck) were used as received. Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA, Fluka) was recrystallized from acetic anhydride (mp 225 – 226 ^{o}C). Hexamethylene diisocyanate (HMDI), dibutyltin dilaurate (DBTDL, both from Aldrich) were used as received. Pyridine was purified by vacuum distillation (bp 36-40 ^{o}C / 20 Torr).

2.2 Measurements

The IR spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrophotometer, using KBr pellets. ^{1}H NMR spectra were registered on a Jeol 60 MHz spectrometer using as solvents $CDCl_3$ for the analysis of diols or DMSO-d_6 for polymers, and TMS as internal reference. The differential scanning calorimetry (DSC) measurements were taken using a Mettler TA Instrument DSC 12E at a heating / cooling rate of 10 ^{o}C/min in nitrogen atmosphere. Indium was used as calibration standard. The thermal stability of polymers was determined dynamically by thermogravimetric analysis (TGA), in air, at a heating rate of 12 ^{o}C / min, using an F. Paulik Derivatograph (Hungary). Gel permeation chromatographic analyses (GPC) were carried out on a PL-EMD 950 evaporative mass detector instrument by using DMF as eluent after calibration with standard polystyrene samples. X-ray measurements were performed with a TUR M62 diffractometer using Ni – filtered CuK_{α} radiation (36 kV, 25 mA). Refraction index of polymers was measured with an Abbe refractometer, at 25 $\pm$ 0.01 ^{o}C, using a solution of samples in DMF (10 % wt.). Successive measurements were performed on aliquots obtained by dilution. Optical rotation measurements were performed using a Carl Zeiss Jena Polamat A– Spectropolarimeter with a sensitivity of ± 0.01^{o} and l =2dm. Specific rotatory powers $[\alpha]^{20}_{546}$ are expressed as deg·dm^{-1}·g^{-1}·dL and mean residue rotations $[m]_{546}$ in deg cm^{2} dmol^{-1}. Hyperchem program, Version 4 (Ontario) was used to visualize the structures obtained after energy minimization. The calculations were performed with full geometry optimisation (bond lengths, bond angles and dihedral angles).

2.3 Synthesis of optically active monomers

2.3.1. Synthesis of acetylated compounds DA1 and DA2

N,N'-Bis(1-ethyl-2-acetoxyethyl)-pyrromellit diimide (DA 1)
N,N'-Bis(1-ethyl-2-acetoxyethyl)-benzophenonetetracarboxylic diimide (DA 2)

4.36 g (0.02 mol) of PMDA or 6.44 g (0.02 mol) of BTDA, 3.74 g (0.042 mol) of (R)-2-AMB were stirred in 15 mL DMF at room temperature. After 24 h, 20 mL acetic anhydride and 4 mL pyridine were added to the reaction mixture while stirred at r.t. for 48 h. Then the solution resulted was poured into an ice-water mixture and brown (**DA 1**) or orange (**DA 2**) gum was obtained and dried at 40 ^{o}C under vacuum overnight. Using diethyl ether as eluent, the products were separated by column chromatography packing of FLORISIL [2]. Yield (**DA 1**) 50%, mp 81-83 ^{o}C, (**DA 2**) 80%, mp. 110-114 ^{o}C. Elemental analysis: (**DA 1**) C_{22} H_{24} N_2 O_8 (444.45); calcd: C 59.46%, H 5.44%, N 6.30 %; found: C 60.01%, H 5.45%, N 6.55%. IR (KBr, cm^{-1}): 2945, 2895 (C-H, aliphatic), 1785, 1723 (C=O, imide I), 1747 (C=O of COO), 1380 (imide II), 1255, 1233 (C-O-C asym.), 825 (aromatic); (**DA 2**) C_{29} H_{28} N_2 O_9 (548.55); calcd: C 63.50%, H 5.15%, N 5.11 %; found: C 63.80%, H 5.70%, N 4.83%. IR (KBr, cm^{-1}): 2950, 2890 (C-H, aliphatic), 1780, 1730 (C=O, imide I), 1750 (C=O of COO), 1380 (imide II), 1260 (C-O-C asym.), 731 (imide IV).

2.3.2. Synthesis of diols D1 and D2

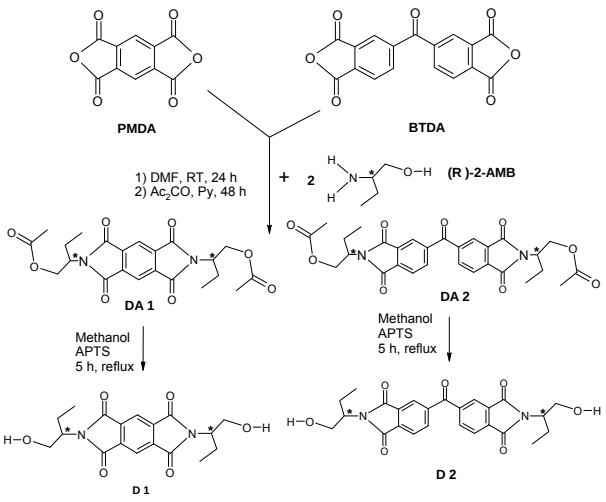
N,N'-Bis(1-ethyl-2-hydroxyethyl)-pyrromellit diimide (D 1)
N,N'-Bis(1-ethyl-2-hydroxyethyl)-benzophenonetetracarboxylic diimide (D 2)

In a solution of 4.44 g (0.01 mol) of **DA 1** (or **DA 2**) in 100 mL methanol, 0.05 g of p-toluenesulfonic acid were added and the reaction mixture was heated at the reflux for 5 h. After cooling, the diols (**D 1**) or (**D 2**) were filtered off and purified by reprecipitation three times from the chloroformic solution with methanol. Yields (**D 1**) 76 %, mp 171 – 173 ^{o}C; (**D 2**) 68 %, mp 162 – 165 ^{o}C.Elemental analysis: (**D 1**) Calcd. for C_{18} H_{20} N_2 O_5 (360); Calcd: C 59.98 %, H 5.61 %, N 7.77 %; Found: C 59.89%, H 5.91%, N 7.67%. IR (KBr, cm^{-1}) 3500-3400 (-O-H), 2900 (C-H aliphatic), 1775, 1710 (imide I), 1475 (aliphatic), 1380 (imide II), 820 (aromatic), 731 (imide IV). ^{1}H-NMR ($CDCl_3$, ppm, TMS) δ = 8.2-7.8 (m, 2H, aromatic), 4.5-3.4

(m, 6H, –C<u>H</u><, -C<u>H</u>$_2$OH), 2.8 (s, 2H, OH), 2.2-1.4 (m, 4H, C<u>H</u>$_2$-CH$_3$), 1.3-0.7 (t, 6H, C<u>H</u>$_3$-). $[\alpha]^{20}_{546}$ = - 12.5 deg·dm^{-1}·g^{-1}·dL.Elemetal analysis (**D 2**) Calcd. for C_{25} H_{24} N_2 O_7 (464); Calcd: C 64.65 %, H 5.17 %, N 6.03 %; Found: C 64.59%, H 5.40%, N 6.10%. IR (KBr, cm^{-1}) 3600, 3460 (-O-H), 2900, 2850 (C-H aliphatic), 1720 (imide I), 1475 (aliphatic), 1380 (imide II), 731 (imide IV). ^{1}H NMR (CDCl$_3$, ppm, TMS) δ = 8.2-7.5 (m, 6H, aromatic), 4.6-3.7 (m, 6H, –C<u>H</u><, -C<u>H</u>$_2$OH), 2.5 (s, 2H, OH), 2.1-1.8 (m, 4H, C<u>H</u>$_2$-CH$_3$), 0.98 (t, 6H, C<u>H</u>$_3$-). $[\alpha]^{20}_{546}$ = - 10.5 deg·dm^{-1}·g^{-1}·dL.

2.3.3 Polymer Synthesis (PUI 1, PUI 2).

To a solution of 6.02 mmol of diol **D 1** or **D 2** in 30 mL anhydrous chloroform 6.93 mmol HMDI were dropped under stirring in argon atmosphere. Three drops of dibutyltin dilaurate, as a Lewis acid catalyst, were added to the solution and the reaction mixture was maintained under stirring at the reflux for 20 h. After this time, the solvent was evaporated out and the resulted polymers were dissolved in DMF and reprecipitated for three times with distilled water and than filtered and dried under vacuum at 40 °C for 24 h. The polymers presented as white powders, yield 72% **PUI 1** and 75% **PUI 2**. Their physico-chemical characteristics are described in Table 1.



Scheme 1. Synthesis of optically active diols

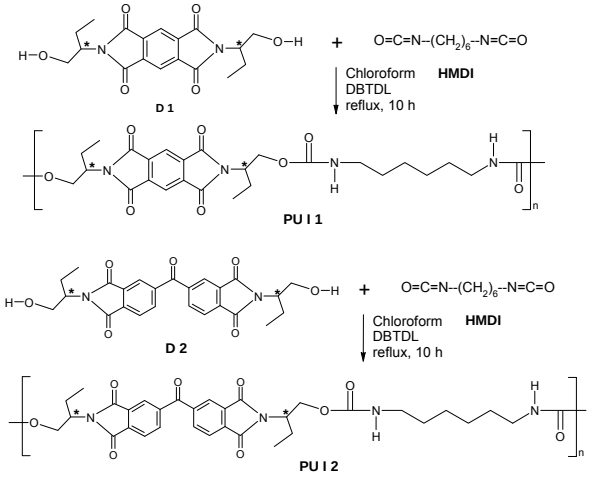
3. Results and discussion

3.1. Synthesis and structural characterization of chiral polymers

Optics plays an important role in applications as diverse as telecommunications, sensing, and displays. Although polymers have not been the traditional materials of choice in optics because of their higher attenuation compared to glasses, they have significant advantages in terms of cost, weight, and flexibility. Materials that rotate the electric field vector of an incident linear plane wave are known as optically active or circularly birefringent. So, chirality has important optical implications relating to the polarization state of the light. This means that some useful optical elements could be conveniently made using films or fibers of chiral polymers [46]. It was suggested that such kind of polymers can be used in guided-wave structures to produce chiral waveguides for integrated optical devices, telecommunication electronic systems, printed circuit elements, information storage materials or optical modular devices [46].

In the design of our syntesized materials was taken in account the fact that thermal stability is enhanced by an increase in the glass-transition temperatures, so our interest was driven to the synthesis of high glass transition temperature chiral polymers, by introducing the aromatic imide moieties in their main chain. In a previous work [2] we reported the synthesis and optical properties of chiral diols with aromatic imide (pyrromelitic and benzophenonetetracarboxylic) moieties **D1** and **D2** (Scheme 1). These imide-containing diols are interesting because their stereogenic centers are placed far from each other, so that the possibility of one center to influence the stereochemical environment of the other is minimized. Moreover, an optically active β-amino-alcohol was used for their synthesis that is useful building block for optically active biocompatible polymers [4].

The poly(urethane-imide)s **PUI 1, PUI 2** were prepared by the reaction of stoichiometric amounts of HMDI with the corresponding imide diols (**D 1, D 2**) as illustrated in Scheme 2. The reactions were performed in chloroform as good solvent for both semi-aromatic diols and HMDI, too. During the reaction's time a part of the new-formed polymers were deposited on the walls of the flask as sticky materials due to their insolubility in the used chlorinated solvent. They were recovered by dissolving them in DMF as a good solvent and reprecipitation in distilled water. The crude polymers **PUI 1** and **PUI 2** were dried at low temperature (40 °C) to avoid probable thermal dissociation of the carbamic ester linkage [47]. This procedure used for recovering the polymers had an influence on their morphology as will be emphasized in the further explanations.



Scheme 2. Synthesis of optically active polymers

Elemental analysis data of the polymers are presented in Table 1. A good concordance between the calculated and found values was observed.

As can be seen from Table 1, the absence of both the absorption bands from 2271 cm $^{-1}$ (-N=C=O) and from 3500 cm $^{-1}$ (-O-H) in the IR spectra of polymers confirms the complete consumption of the reacting

–NCO and –OH functional groups during the polyaddition reactions, with the formation of the new urethane functions. The IR survey of synthesized polymers revealed that the spectra contain prominent characteristic bands of the imide and urethane groups as is presented in Table 1. The characteristic absorptions of aromatic imide ring are present at 1755 and 1725 cm^{-1} in **PUI 1** and at 1780 cm^{-1} and 1750 cm^{-1} in **PUI 2** for C=O stretch, at 1380 cm^{-1} (C-N-C stretch) and 740 cm^{-1} (ring deformation). The peaks near 3400 cm^{-1} (urethane N-H), 1710 cm^{-1}-1703 cm^{-1} (C=O bond stretch) and 1260 cm^{-1} or 1250 cm^{-1} (C-O-C stretch), showed the formation of the urethane linkage. For the polymer **PUI 2** the band at 1670 cm^{-1} was attributed to carbonyl originating from benzophenone-3,3',4,4'-tetracarboxylic dianhydride. In Table1 are also collected the ^{1}H NMR spectral data of **PUI 1** and **PUI 2**. By comparing these data it can be emphasized that characteristic peak for the proton of the asymmetrical substituted carbon atoms in the structures of the polymer **PUI 2** was shifted to the lower field may be due to the structural differences of the used dianhydride. Moreover, if in the case of **PUI 1** the peak attributable to the proton in the NH-CO-O linkage appeared as a sharp singlet at 8.1 ppm, in the case of **PUI-2** this proton appeared together with the aromatic protons in the range 8.09-8.25 ppm.

Table 1. Physico-chemical characteristics of optically active poly(urethane-imide)s.

Polymer Code		**PUI-1**	**PUI-2**
Yiled, %		75	72
Elemental Formula (Molecular weight of structural units)		$C_{26}H_{32}N_4O_8$ (528.562)	$C_{33}H_{36}N_4O_9$ (572.616)
Elemenatal analysis	C%	59.08 (58,92)	69.22 (68.94)
Calcd.	H%	6.1 (6.15)	6.33 (6.29)
(Found)	N%	10.6 (10.22)	9.78 (9.55)
FT-IR (cm^{-1}) KBr		3425;1755;1725 1703;1530; 1380;1260; 740	3410;1780;1730; 1710;1670;1520; 1380;1250;740
^{1}H-NMR (ppm)		0.7(t,6H); 0.9-2(m,12H); 2.7-3(d,4H); 3.85-4.1(m,4H); 4.2-4.6(m,2H); 7.9(s,2H); 8.1(s,2H)	1.07(t,6H); 1.34-1.5(m,8H); 2.05-2.16(m,4H); 3.16-3.27(m,4H); 4-4.2(m,4H); 4.6-4.8(m, 2H); 8.09-8.25(m, 8H)
M_n (PI)		3915 (1.09)	4302 (1.1)

As a result of the comparison between these three sets of data measurements it was concluded that the obtained polymers had the proposed chemical structures. Numerical average molecular weights (M_n) were determined by GPC in DMF solution of samples, their values being around 4000, which means that mainly oligomers were obtained. The polydispersity index values were found to be almost 1.1 for both polymers.

The crystallinity of the crude polymers was examined by wide-angle X-ray diffraction diagrams obtained by the powder method with the use of nickel-filtered CuK_α radiation. The results are presented in Figure 1. It was reported that PUI could be crystallisable materials [29] because the soft segments are subjected to form crystals and also urethanes groups can be involved in strong ordered hydrogen bonds [29]. The peaks of the strongest diffraction intensity were observed for such polymers at $2\theta = 19.5\text{-}20^o$ [22, 29]. Also very weak XRD peaks were reported for some poly(imide-urethane)s containing pyromellitimide units [17]. It is well known that a small amount of water to a hydrophilic polymer may disrupt the intermolecular bonds. Moreover, even if the **PUI 1** and **PUI 2** polymers containing in the main chains the imide and urethane polar groups, the probability of the intermolecular interactions could be diminished by the possible shielding effect due to the presence of the hydrophobic pendant ethyl groups in the proximity of imide bonds. Both of these effects can be responsible for the very week peaks in the X-ray diagrams of our synthesized polymers that are centred at around $2\theta = 19^o$.

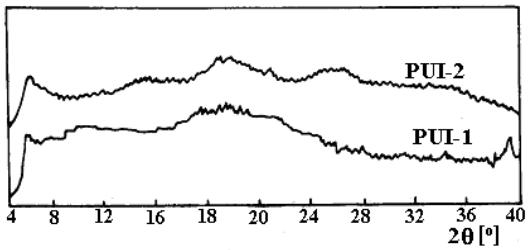


Fig. 1. The X-ray diffractograms of the synthesized polymers

These assumptions are also sustained by the results of the IR measurements (see Table 1). It was claimed that the IR peaks of the carbonyl in the urethane functions are present at different positions, depending of their association or not in hydrogen bonds. So it was reported that the peak in the range 1720 cm^{-1} - 1730 $cm^{-1}$are characteristic to the carbonyl group remaining free while the peak at 1703 cm^{-1} was assigned to the absorption of urethane groups involved in the strongest ordered hydrogen bonds [48]. As can be seen from Table 1, for **PUI 1** and **PUI 2** only the peaks characteristic to the free carbonyls are present, a small shoulder at 1703 cm^{-1} being present in the IR spectrum of **PUI-1**.

3.2. Thermal behaviour of chiral polymers

The thermal behaviour of the polymers were followed by combining the results of the thermogravimetrical analysis (TGA) with that ones of the differential scanning calorimetry (DSC).

Table 2. Thermal properties of polymers

Polymer	IDT (°C)[b]	T_{dmax} (°C)[c]	Y_c^{600} (%)[d]
PUI 1	210	320	18
PUI 2	235	347	27

IDT-initial degradation temperature at a heating rate of 10°C/min in air;
T_{dmax}-temperature for which the weight loss was maximum;
Y_c^{600}- residual weight percentage at 600 °C in air

The results of the thermogravimetrical analysis of the polymers at the heating rate of 12°C/min in air are presented in Table 2. It can be observed that the initial degradation temperatures are above 200°C and the values of the residual weight percentage are decent taking in account the oligomeric nature of the synthesized materials. Also in the range 50°C - 100°C a weight loss ranging between 7% and 9% was observed for both **PUI 1** and **PUI 2** that could be attributed to the loss of retained water. This phenomenon was also emphasized by DSC measurements. So, the Figure 2 shows a first set of DSC measurements results for **PUI-1**. For the above -mentioned phenomenon a broad endotherm can be seen in the trace I that represents the first run in the temerature range 20°C - 150°C.

Generally, for the polyurethanes containing hard segments and soft segments the glass transition temperature and melting temperature for both kind of segments can be evidenced in DSC experiments [22].

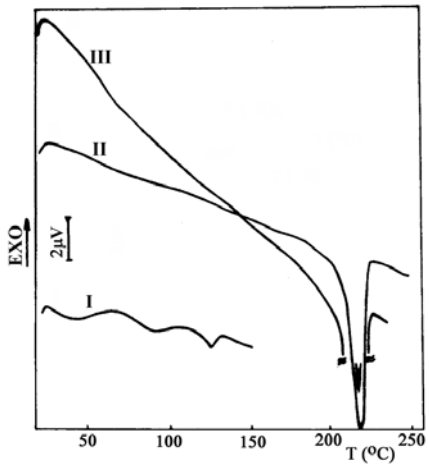


Fig. 2. The DSC traces of PUI-1: I-first run in the range 20-150°C; II-the second run; III-the third run.

In the case of **PUI 1** the glass transition temperature of the soft segments (T_gs) was observed at 34°C that is followed by the broad endotherm due to the water elimination and also by the one sharp endotherm centred at 128°C (T_k) and one exotherm centred at 135°C (T_c). The endotherm could be attributed to a solid-solid transition and the exotherm to a crystallization phenomenon [49]. This crystallization can't be observed directly to the crude polymers in the X-ray diagrams due to their relative disordered morphology during precipitation [50]. In the second run of **PUI 1** performed between 20°C -250°C only the endotherm centred at 218°C attributable to the melting of the polymer can be observed. The absence of the T_gs in the second run II it is supposed to be due to the crystallization that implied a more ordered structure by intermolecular interaction that hinder the free motion of the soft segments. Also the initial degaradation temperature of the **PUI 1** it is changed after the presented thermal treatment being at least 20°C highest when comparing with that one of the crude polymer (Figure 2(III)).

The third run III in Figure 2 was performed after the cooling, in the aim to evidence a liquid-crystalline mesophase, if exist, taking in account the reported results on a such behaviour for the polymers synthesized from aromatic imidic diols [14]. As was also showed by hot-stage optical polarized microscopy no thermotropic behaviour was found for our synthesized polymers as confirmed by DSC analysis. This could be due to the fact that aromatic imide groups are planar, rigid and polar but they proved to be rather poor mesogens (especially pyromellitimide) [17]. This indicates that the thermotropic LC polymers need the adequate content of flexible spacer and mesogenic units to give LC behaviour. For confirming the veracity of the crystallization phenomenon and the correctness of the attribution of the exotherm centred at 135°C in the first run in Figure 2 an additional DSC experiment was performed, the results of which are presented in Figure 3. So, the first run I of **PUI 1** was performed in a shorter range (20°C -125°C) and only solid-solid transition took place.

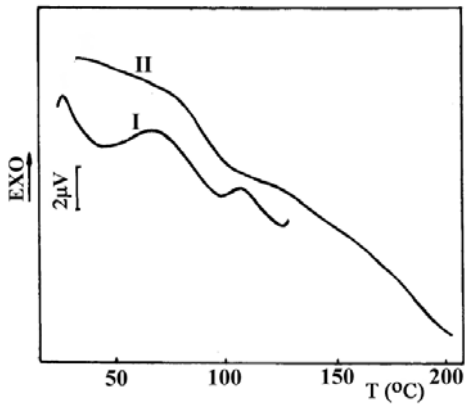


Fig. 3. The DSC traces of PUI-1: I-first run in the range 20-125 °C; II-the second run.

The trace of the second run in Fig. 3 differs substantially from that one in Fig. 2. In the absence of crystallization, in the second run II in Figure 3 the endotherm of melting is missing and only the glass transition temperature of the hard segments at 88°C in **PUI 1** it is present.

Model molecules for polymer **PUI 1** containing eight structural units (as results from GPC data) were obtained by molecular mechanics (MM+) in the aim to explain the most probable conformations of the chains and to gain insight into the behaviour observed in the above DSC experiments when **PUI 1** was thermally treated. A regular flat structure was obtained in the case if isolated chain (Figure 4 (a)).

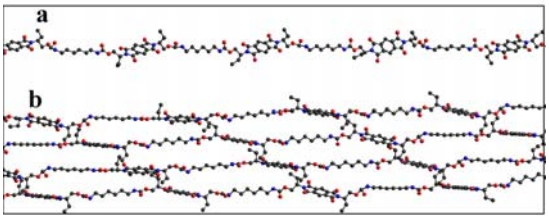


Fig. 4. (a)Representation of a single polymer chain of PUI 1 in a flat conformation; (b) Representation of the four intercalated flat chains of polymer PUI 1 (the hydrogen atoms were omitted for clarity)

It's seem that for these polymers a disordered conformation is energetically favoured, fact revealed also by the X-ray difractograms on the crude polymers in Figure 1. After the thermal treatment of **PUI 1** performed in the first set of DSC experiments it can be supposed that a tightly packing between the chains take place. The first endotherm centred at 128°C (T_k) can be attributed to the transition from the disordered conformation of the chains to the flat conformations. It is known that the packing of the chains causes a decrease in energy related to that of the isolated chains, a lowering that is proportional to the regularity of the packing [50]. To this phenomenon could be attributed the exotherm in the range 130°C-150°C, centred at 135°C (Figure 2(I)). Two possibilities of the chains' close packing can be considered: one by superimposing the main and the side chains in parallel layers and another one by intercalation of the side chains as seen in Fig. 4 (b). In the case of the second DSC experiment, in the first run performed in the range 20-125°C (Fig. 3(I)) only the rearrangement of the disordered conformations of the chains to the flat ones took place and not packing This has as a results the missing of the melting and a more free motion of the chains resulted in the presence of the glass tramsition (Fig. 3(II)).

3.3. Optical properties of chiral polymers

The synthesized poly(urethane-imide)s are optically active polymers, their specific rotatory powers$[\alpha]^{20}_{546}$ being showed in Table 3. They have the same sign as the starting chiral monomers. There is a small difference between the obtained values as a consequence of their structural differences. We have calculated some molecular parameters in view to find supplementary arguments for this fact: mean residue rotation $[m]^{20}_{546}$ (which counts for the molecular weight of the structural units), refraction index, transparency (τ) and stress optical coefficient (SOC). All these data are collected in Table 3. The last three parameters were also calculated for a commercial thermoplastic polymer polysulfone Udel. We have chosen this polymer because it's polarity features makes it similar with our polymers and also due to it's well known ability to give transparent flexible films.

Table 3. Optical properties of polymers.

Polymer code	**PUI 1**	**PUI 2**	**Udel PSF**
Specific rotation $[\alpha]^a$	-30	-24	-
Molecular rotation $[m]^b$	158.6	-151.8	-
Refraction index Calc^c. (Exp)^d	1.539 (1.535)	1.588 (1.582)	1.625 (1633)
Transparency^e τ	0.925	0.948	0.942
Stress optical coefficient^f SOC (B)	136.46	117.28	108.20

a- measured in N,N-dimethylformamide , c= 0.5 g/dL, l=10 mm; **b**- Calculated with the formula: $[m]^{20}_{546} = [\alpha]_{546}{}^{20}\cdot M/100$, where M is the molecular weight of the structural unit;**c**- Calculated using the Bicerano's method [51];**d**- Measured in DMF solution; **e**- Calculated by using the Fresnel's formula: $\tau = 1 - R_o$ where $R_o = 1 - [(n-1)^2/(n+1)^2]$ is the reflectivity of the system and **n** is the calculated refraction index; **f**- Calculated by the Askadskii method [52]; **g**- Comercial engineering thermoplastic polymer

The refraction index was determined experimentally for **PUI 1** and **PUI 2**, by successive dilution measurements of a 10 wt. % solution of polymer in DMF. By extrapolation to 100 % concentration we obtain the values of refraction index of the polymers. The experimental values agree with the calculated ones. The calculated values of the transparency (τ) showed values even higher than that of the polysulfone, which could be an indication of potential optical applicability for these polymers.

The stress optical coefficient (SOC) of **PUI 1** and **PUI 2**, which is correlated with the anisotropy of polarizability, had higher values than polysulfone, probably due to the great amount of highly polarizable groups contained in their structures.

4. Conclusions

Two new optically active diols containing aromatic imide groups were used for synthesis of chiral poly(urethane-mide)s in conjuction with HMDI. These

polymers were designed to be optically active materials with enhanced phase separation of the hard and soft segments due to the strong intermolecular interaction of the imide groups, with appropriate processing temperature and good thermal stability while having liquid-crystalline behaviour. By applying different investigation methods, near to the confirming the proposed structure it was demonstrate that the synthesized materials are optically active and transparent with a good thermal stability by comparing with both class of elastomeric polyuretanes and with aromatic polyimides. It was also emphasized that the thermal treatment is very important factor influencing the morphology and supramolecular structure of the polymers and consequently their processability and area of application. So, depending of the temperature range of the thermal treatment it is possible to have a material with a reasonable galss transition temperature (88°C) or a material that melt at around 218°C with an enhanced intial degaradation temperature. Unfortunately no thermotropic behaviour was found for our polymers. New efforts are currently devoted to enlarging the family of poly(urethane-mide)s by employing in synthesis different diisocyanates or PU prepolymers in the aim to improve the processability adequate for opto-electronic applications.

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