

Note

SYNTHESIS, CHARACTERIZATION OF CHIRAL POLY(ESTER AMIDE)S DERIVED FROM L-ISOLEUCINE*

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Abstract A series of new optically active aromatic poly(ester amide)s containing a chiral group in the side chain prepared from the *p*-toluenesulfonic acid salt of *o,o'*-bis(leucyl)-hexanediol ($\text{TS}^-\text{LHD}^+\text{TS}^-$) and *p*-phthaloyl chloride and styrene-2,5-dicarbonyl chloride styrene have been synthesized by interfacial polymerization. The structure of the monomer is elucidated by FT-IR and elemental analysis. The thermal properties of the polymers were studied by DSC and TGA. The chiroptical properties of the above polymer have also been studied by circular dichroism (CD) spectroscopy. Results indicated that these polymers form helical structures.

Keywords Poly(ester amide), 1,6-Hexanediol, L-Isoleucine, *p*-Phthaloyl chloride

INTRODUCTION

Proteins and nucleic acids are unique in being able to adopt well-defined folding patterns, and in consequence, to perform highly selective functions^[1–4]. Among synthetics, poly(ester amide)s derived from amino acids have been traditionally considered as the only polymers able to form stable secondary structures with features similar to those found in proteins^[5, 6]. The design of new polymers with predictable folding properties but composed of building blocks other than natural amino acids is an emerging field to which great efforts are being devoted^[7]. However, studies on the poly(ester amide)s are nowadays relatively scarce. Recently, Saotome^[8] *et al.* have reported the enzymatic degradation of polymers derived from 1,2-ethanediol, adipic acid, and different amino acids. More recently^[9, 10], a detailed study on the biodegradation and biocompatibility of polymers formed by L-alanine, dodecanediol, and sebacic acid was performed, since additional interesting characteristics such as solubility in organic solvents and film-forming properties were found. On the other hand, we have noted that poly(ester amide)s containing chiral group in the side chain could be used as a potential family of polymers for non-linear optical applications^[11]. These poly(ester amide)s were selected because they are easily obtainable and, in principle, biocompatible. However, little is known about poly(ester amide)s obtained from L-isoleucine. In order to develop novel functional polymers and exploit their properties, this paper deals with the synthesis and structural characterization of aromatic poly(ester amide)s containing a chiral group in the side chain. They are abbreviated as PLHDP and PLHDV, and were prepared by interfacial polymerization using L-isoleucine following the procedure outlined in Scheme 1. Then, the characteristics of the polymers, as well as their photochromic behavior were investigated.

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A three-necked round-bottom flask equipped with a CaSO₄ drying tube, magnetic stirrer, and a Dean-Stark apparatus was charged with *L*-isoleucine (272 mmol), *p*-toluenesulfonic acid monohydrate (272 mmol), 1,6-hexanediol (123 mmol) and toluene (750 mL). Then, the reaction mixture was refluxed until no more water was released (20 h). The mixture was cooled at room temperature and then viscous oil separated from the toluene solution. After drying under vacuum, the recovered hard solid was recrystallized twice from isopropanol/acetone (10/1 *V/V*) to yield 64 g of a white solid TS⁺LHD⁺TS⁻. MS: *m/z* 689. FT-IR (KBr, cm⁻¹) 2922 and 2850 (CH₂), 1738 (C=O); Elementary analysis: Calcd. for C₃₂H₅₂N₂O₁₀S₂ (%): C 55.73; H 7.55; N 4.06. Found (%): C 55.80, H 7.46, N 4.02.

Polymer Synthesis

The aromatic poly(ester amide) containing chiral group in the side chain, PLHDP, was synthesized by interfacial polymerization following the procedure outlined in Scheme 1. A typical preparation of PLHDP was as follows. To an aqueous solution (70 mL) of $\text{TS}^-\text{LHD}^+\text{TS}^-$ (7 mmol) and sodium carbonate (24 mmol) was carefully added a solution of *p*-phthaloyl chloride (7 mmol) in carbon tetrachloride (240 mL). Then, the two phases were stirred for 50 min. The polymer which precipitated was isolated by filtration and successively washed with ethanol, water, ethanol, carbon tetrachloride and ethyl ether before drying in a vacuum desiccator at 60°C. The polymer was purified by precipitation from formic acid or trifluoroacetic acid solution with a mixture of water/acetone (1/1 *V/V*). FT-IR spectra of the polymer show the characteristic absorption bands of methylene, amide and ester groups at 3301 cm^{-1} and 3066 cm^{-1} (amide), 2920 cm^{-1} and 2850 cm^{-1} (CH_2) and 1734 cm^{-1} ($\text{C}=\text{O}$, ester).

The poly(ester amide) containing a chiral group in the side chain, PLHDV, from styrene-2,5-dicarbonyl chloride styrene was synthesized by the method described above.

RESULTS AND DISCUSSION

Synthesis

The chemical structures of the monomer and polymers as well as their abbreviated names are presented in Scheme 1. The conversion of amino acids containing a chiral group in the side chain and aliphatic glycol yields a wide variety of diamine salt compounds, which can be used as potential monomers, and can be polymerized at room temperature. Both aliphatic and aromatic chlorides can be utilized in interfacial polymerization. Water/carbon tetrachloride is the most used system. The disadvantage of this system is the precipitation of the resulting polymer from carbon tetrachloride, which leads to polymers with a broad molecular weight distribution. Experimental results can be improved by reducing the monomer concentration (0.04–0.05 mol/L) in the organic phase and increasing the stirring speed considerably at the beginning of the polymerization process. The polymers obtained were soluble in strong acids (formic, dichloroacetic and trifluoroacetic acid) and chlorinated polar solvents such as chloroform and dichloromethane. The polymers are partially soluble in THF, therefore only the molecular weight of THF-soluble portion of the polymer was measured by means of GPC with THF as eluent. The actual molecular weight of the original polymer should be higher than the measured value due to the exclusion of the value for the insoluble portion with a higher molecular weight.

Polymer Characterization

Thermal properties of these aromatic poly(ester amide)s containing a chiral group in the side chain were examined by DSC and TGA measurements. Figure 1 shows that two distinct thermal transition temperatures are observed in aromatic poly(ester amide)s, one of which is the glass transition temperatures for PLHDV at 113.5°C and for PLHDP at 128.2°C, respectively, while the other one is phase transition point at 137.1°C and 158.2°C, respectively. These thermal properties demonstrate that poly(ester amide)s could exist in liquid crystalline phase. On the other hand, a dual melting peak (about 105.7°C and 119.5°C, respectively) was found for poly(ester amide)s, a very common result in thermal studies of polyamides. This fact may suggest that segments constituted by amide groups are predominant in the amorphous material of samples recovered from polycondensation.

Thermogravimetric analysis is usually used to demonstrate the thermal stability of the studied polymers. Figure 2 shows that TGA curve of PLHDP, in principle, coincides with that of PLHDV, and 5% weight loss appears at 290–304°C.

The quantities used to express the chirality of aromatic poly(ester amide)s containing a chiral group in the side chain are chiroptical properties like specific optical rotation $[\alpha]$ and molar ellipticity $[\theta]$ in circular dichroism (CD) measurements in solution. $[\alpha]_\lambda$ is often only measured at one wavelength λ , because it depends strongly on wavelength. The polymers displayed in DMF solution a positive value at the mercury Hg-line. The specific optical rotations $[\alpha]_{365}^{20}$ (in DMF, $c = 2.0 \text{ g L}^{-1}$) of PLHDP and PLHDV are +97.4° and +98.2°, respectively.

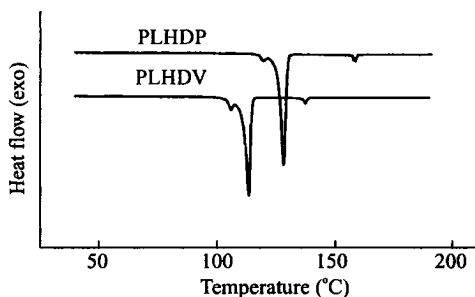


Fig. 1 Second heating DSC scans corresponding to PLHDP and PLHDV

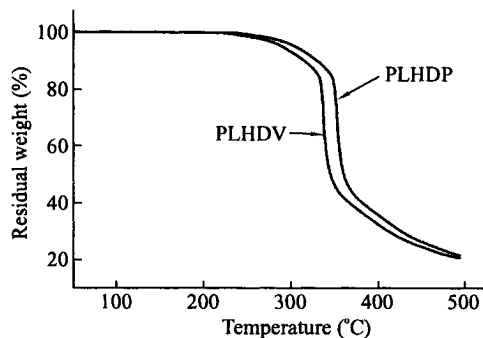


Fig. 2 TGA curves of aromatic poly(ester amide)s

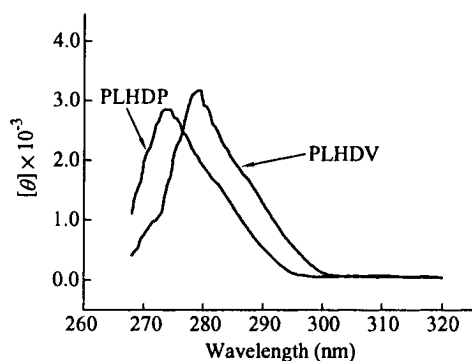


Fig. 3 CD spectra of PLHDP and PLHDV (recorded at 25°C in DMF)
 $[\theta]$ = molar ellipticity with repeating unit: $\text{deg cm}^2 \text{dmol}^{-1}$

CD spectroscopy determines the Cotton effects of each chromophore directly, as it measures the difference in the absorption of right and left handed circularly polarized light. The result of CD characterization of PLHDP and PLHDV are shown in Fig. 3. It can be seen that the CD curves of PLHDP and PLHDV are characterized by a strong positive band at 274 nm and at 280 nm, respectively. This proves that the obtained aromatic poly(ester amide)s containing chiral group in the side chain are right-handed helices in pure DMF. By contrast, it can be seen that the secondary structures of PLHDP and PLHDV are not obviously different.

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