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Synthesis, characterization and infrared emissivity property of optically active polyurethane derived from tyrosine

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Optically active polyurethanes (LPU and DPU) and racemic polyurethane (RPU) were synthesized by the self-polyaddition of the isocyanate-phenols which derived from the chiral and racemic tyrosine. All of the polymers were characterized by FT-IR, ^{1}H NMR, GPC, UV–Vis spectroscopy, circular dichroism (CD) spectroscopy, TGA and X-ray diffraction (XRD), and the infrared emissivity values were investigated in addition. LPU and DPU were two enantimorphs, they possessed helical configurations and higher degree of hydrogen bondings compared to the RPU which presented random coiled molecular chain. The crystallinity and thermal decomposition temperature of LPU and DPU were higher than that of the RPU due to the more regular secondary structure which facilitate the formation of a large number of inter-chain hydrogen bonds. Consequently, the LPU and DPU exhibited lower infrared emissivity values (8–14 μm), which came down to 0.611 and 0.625.

1. Introduction

With the development of infrared technologies, emissivity control has attracted more and more attention both in civil and military field [1,2]. Various new materials with low infrared emissivity have been reported so far, such as nanosized semiconduor particles, metallic thin films, strongly magnetic materials, and inorganic/organic composite coatings [3–8]. Moreover, the materials are supposed to meet a wide range of requirements for application besides having low infrared emissivity [9,10]. Organic polymers possess unique properties including light weight, corrosion-resistant, tractability, and the most important, the adjustable structures which can provide the possibility of tuning the infrared emissivity according to our need [11].

Special interest in the properties of polymers possessing optical activity arises from the realization that the helices are significant for organisms in maintaining their usual functions [12]. Macromolecules with optical activity possess not only the advantages of any other polymers but also some unique characteristics, such as ordered secondary structure, adjustable chiral parameter, and abundant inter-chain interaction as well [13–16]. Many naturally and synthetic optically active polymers have been used as the chiral stationary phase(CSP) in high-performance liquid chromatography(HPLC), liquid crystals for display, catalysts for asymmetric synthesis and so on [17–19]. Especially, conformational changes of polymers induced by the external stimuli lead to the changes of physical and chemical properties including viscosity, conductivity, solubility, wettability, morphology, etc., many appealing researches aimed at changing and switching the secondary structure of optically active polymers to develop smart and intelligent macromolecules have been reported [20–22]. Amino acids are the most common chiral resources that have been widely used in the synthesis of optically active materials [23–26]. Moreover, amino acid-based chiral polymers could have induced crystallinity with the ability to form higher ordered structures that exhibit enhanced properties. Poly(c-alkyl a-glutamic acid)s are used as surface treatment reagents of artificial leathers, and examined as liquid crystalline materials, piezoelectric materials, and LB films [27,28]. Polymethionine shows high biocompatibility and is expected as medical materials [29–32] (e.g., contact lenses, artificial skins, internal organs, and blood vessels). Polyleucine catalyzes the asymmetric epoxidation of chalcone with approximately quantitative optical purity [33]. However, to the best of our knowledge, there is no work referred to the investigation of infrared emissivity properties of optically active polymers which derived from amino acids.

Polyurethanes (PUs) [34,35] are types of high-performance polymeric materials that have been widely used in adhesives and coatings of various materials because of their outstanding thermal

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and chemical stabilities, mechanical properties and electrical properties. Because of the reactivity of hydroxyl and isocyanate group, there were no linear polyurethanes with head-to-tail structures until Versteegen [36] and Nagai [37−39] with their co-workers synthesized α, ω-isocyanato alcohols, isocyanate-phenols and the corresponding polyurethanes respectively. The key reagent for the preparation of the monomers was di-tert-butyltricarbonate which demanded a large volume of pentane for crystallization and low temperature to preserve [40−42]. Furthermore, amine salts needed to be converted to the corresponding free bases beforehand. In the present study, we used the solution of phosgene in the synthesis of the monomer containing phenolic hydroxyl and isocyanate group coexisting in the same molecule under a mild condition. In consideration of the solubility of esters in methylene dichloride, tyrosine hexyl ester hydrochloride was used and the corresponding isocyanate was polymerized with triethylamine as the catalyst. The optically active polyurethanes LPU and DPU possessed lower infrared emissivity values than the racemic one. The incorporation of the chirality in the resulting polymers provided a great promise in the development of macromolecules with low infrared emissivity and the adjustment between them is in progress.

2. Experimental part

2.1. Materials

L-tyrosine, DL-tyrosine and triethylamine were purchased from Shanghai Chemical Reagent Company and used as received without further purification. D-tyrosine was the product of Aladdin. Triphosgene was obtained from Aldrich. Methyltrioctylammonium chloride (Aliquat®336) was produced by Acros Organics. Thionyl chloride, 1-hexanol and other solvents were all obtained from Shanghai Chemical Reagent Company and distilled by the standard methods.

2.2. Measurements

Melting point (mp) was measured by an X-4 micro-melting point apparatus. FT-IR spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer at room temperature using KBr pellets and liquid cell with the chloroform as the solvent. The spectra were obtained at a 4 cm^{-1} resolution and recorded in the region of 4000−400 cm^{-1} ^{1}H and ^{13}C NMR spectra measurements were recorded on a Bruker AVANCE 300 NMR spectrometer. Chemical shifts were reported in ppm. The molecular weights and molecular weight polydispersities were determined by GPC (Shodex KF-850 column) calibrated by using polystyrenes with THF as the eluent. UV−vis spectra in solution were measured on a Shimadzu UV 3600 spectrometer. CD spectra were determined with a Jasco J-810 spectropolarimeter using a 10 mm quartz cell at room temperature. The optical rotation of all samples was measured in a WZZ-2S (2SS) digital automatic polarimeter at room temperature. The wavelength of sodium lamp was 589.44 nm. Thermal analysis experiments were performed using a TGA apparatus operated in the conventional TGA mode (TA Q-600, TA Instruments) at the heating rate of 10 K/min in a nitrogen atmosphere, and the sample size was about 50 mg. X-ray diffraction (XRD) measurements were recorded using a Rigaku D/MAX-R with a copper target at 40 kV and 30 mA. The powder samples were spread on a sample holder, and the diffractograms were recorded in the range 5 °−80 ° at the speed of 5 °/min. Infrared emissivity values of the samples were investigated on the IRE-I Infrared Emissometer of Shanghai Institute of Technology and Physics, China.

2.3. Monomer synthesis

2.3.1. Synthesis of L, D and DL-Tyrosine hexyl ester hydrochloride

To 1-hexanol (75 mL) at −5 °C, thionyl chloride (6.55 g, 0.055 mol) was dropped slowly in order to maintain the temperature under 0 °C. Then L-tyrosine (9.05 g, 0.05 mol) was added. The resulting mixture was stirred at 95 °C for 12 h. As the mixture cooled, the product was precipitated by the addition of diethyl ether (200 mL). The precipitate was collected, washed with ether (2 × 50 mL) and dried to give the white powdery L-tyrosine hexyl ester hydrochloride. D and DL-tyrosine hexyl ester hydrochlorides were prepared in the similar way using D and DL-tyrosine instead of L-tyrosine.

L-Tyrosine Hexyl Ester Hydrochloride: yield 89%, a white solid, mp 162−164 °C; $[\alpha]_D^{25} = +7.6$ ° ($C = 1$ g/dL, methanol). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.82−0.8 (t, $J = 6.48$ Hz, 3H, $-CH_3$), 1.20−1.25 (m, 6H, $-CH_2$-), 1.43−1.47 (m, 2H, $-CH_2$-), 2.89−3.10 (m, 2H, -$PhCH_2$-), 4.00−4.05 (t, $J = 6.42$ Hz, 2H, $-OCH_2$-), 4.10−4.14 (t, $J = 6.99$ Hz, 1H, >CH-), 6.68−7.01 (m, 4H, $-C_6H_4$-), 8.55 (s, 3H, $-N^+H_3Cl^-$), 9.41 (s, 1H, −OH). FT-IR (ν/cm^{-1}): 3297 (O−H), 2953, 2869, 1738 (C=O), 1516, 1230, 843.

D-Tyrosine Hexyl Ester Hydrochloride: yield 90%, a white solid, mp 157−159 °C; $[\alpha]_D^{25} = -7.2$° ($C = 1$ g/dL, methanol). Its ^{1}H NMR, IR data are similar to L-tyrosine hexyl ester hydrochloride and thus omitted.

DL-Tyrosine Hexyl Ester Hydrochloride: yield 95%, a white solid, mp 176−179 °C; $[\alpha]_D^{25} = 0$ ° ($C = 1$ g/dL, methanol). Its ^{1}H NMR, IR data are similar to L-tyrosine hexyl ester hydrochloride and thus omitted.

2.3.2. Isocyanate-phenols

Phosgene was obtained by decomposition of triphosgene with Aliquat 336 according to the literature [43]. The phosgene that developed during the reaction was collected in CH_2Cl_2 and preserved below 0 °C. 1.51 g L-tyrosine hexyl ester hydrochloride was added to the stirred solution of phosgene (5−10 g, 0.05−0.1 mol) in 50 mL CH_2Cl_2 which was kept at −5 °C. Then 50 mL of saturated aqueous sodium bicarbonate was dropped slowly within 10 min. The resultant mixture was stirred at 0−5 °C for an hour and then bubbled with nitrogen in order to remove the residual phosgene. The organic layer was collected, and the aqueous layer was extracted with three 5-mL portions of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), vacuum filtered, and concentrated to 20 ml to afford the colorless isocyanate of L-tyrosine hexyl ester solution. The solution was used in the polymerization without further isolation. The isocyanate of D and DL-tyrosine hexyl ester was prepared in the similar way using D and DL-tyrosine instead of L-tyrosine.

The spectroscopic data of isocyanate-phenol are as follows (take isocyanate of L-tyrosine hexyl ester for example). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84−0.88 (t, $J = 6.15$ Hz, 3H, $-CH_3$), 1.27 (m, 6H, $-CH_2$-), 1.58−1.60 (m, 2H, $-CH_2$-), 2.91−2.93 (m, 2H, $-PhCH_2$-), 4.09−4.13 (t, $J = 6.54$ Hz, 2H, $-OCH_2$-), 4.38 (m, 1H, >CH-), 6.67−6.96 (m, 4H, $-C_6H_4$-). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.5, 25.4, 28.4, 31.3, 39.1, 58.8, 66.7, 115.5, 127.5 (N=C=O), 130.6, 154.9 (C−OH), 170.8 (C=O). FT-IR (ν/cm^{-1}): 3419 (O−H), 2957, 2932, 2259 (−N=C=O), 1738 (C=O), 1516, 1004, 834.

2.4. Polymerizations

The polyaddition of isocyanate-phenols was carried out in situ with magnetic stirring under nitrogen at room temperature for 24 h by addition of triethylamine (3 mol%) as the catalyst. The reaction mixture was poured into a large amount of diethyl ether, filtered and dried under reduced pressure to give the off-white polymer. The polyurethanes prepared were record as LPU, DPU, RPU which represented the polymerization of isocyanate of L-tyrosine hexyl ester, isocyanate of D-tyrosine hexyl ester and isocyanate of DL-tyrosine hexyl ester.

The spectroscopic data of PU are as follows (take LPU for example). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (3H, $-CH_3$), 1.31 (6H, $-CH_2$-), 1.63 (2H, $-CH_2$-), 3.16 (2H, -$PhCH_2$-), 4.14 (2H, $-OCH_2$-), 4.67 (1H, >CH−), 5.61 (1H, −NH), 7.08−7.16 (4H, $-C_6H_4$-). FT-IR (ν/cm^{-1}): 3330 (N−H), 2956, 2930, 1736 ($-CO_2C_6H_{13}$), 1711 (−C(O)NH−), 1507, 1217, 1035, 898.

3. Results and discussion

3.1. Monomer synthesis

Phosgene, diphosgene and triphosgene were widely used in the synthesis of isocyanates. The reaction usually required refluxing at high temperature in order to decompose the intermediate of carbamyl chloride into isocyanate. It is not suitable for preparing unstable isocyanates. Nowick et al. [44,45] reported that amino acid ester hydrochlorides and peptide hydrochlorides could readily be converted to isocyanates by treatment with a solution of phosgene in toluene and methylene chloride under the catalyzing of pyridine or saturated aqueous sodium bicarbonate solution at 0 °C. Based on the research of them, we successfully synthesized the monomers of isocyanate-phenol using the solution of phosgene in a facile way. The length of ester chain was selected based on the solubility of the esters of tyrosine in CH_2Cl_2 in which the preparations of monomer and polyurethane were conducted. Tyrosine hexyl ester had good solubility in CH_2Cl_2 while the esters became poorly soluble below hexyl chain length [46]. The synthesis of monomers was carried out according to Scheme 1. Tyrosine hexyl ester hydrochlorides were prepared by reacting tyrosine with 1-hexanol in the presence of thionyl chloride. The methylene chloride solutions of tyrosine hexyl esters were also prepared by the same method without the use of phosgene in order to compare and confirm the formation of isocyanate-phenols. The structure of isocyanate-phenols was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. Fig. 1a illustrates the ^{1}H NMR spectra of L-tyrosine hexyl ester and the corresponding isocyanate in CH_2Cl_2. The signal assignable to the protons of primary amine ($-NH_2$) around 3.5 ppm was completely disappeared after the reaction with phosgene, from which the formation of the isocyanate group was supposed. Fig. 1b shows strong IR absorptions assignable to the isocyanate and hydroxyl groups at 2259 and 3419 cm^{-1} of the monomer, thus confirmed the synthesis of isocyanate-phenol. The ^{13}C NMR spectrum in Fig. 2 also supports the structure of the monomer. The isocyanate of L-tyrosine hexyl ester was stable in solution and could not be isolated which probably led to spontaneous polymerization. The same results were obtained in the preparation of isocyanates of D and DL-tyrosine hexyl ester.

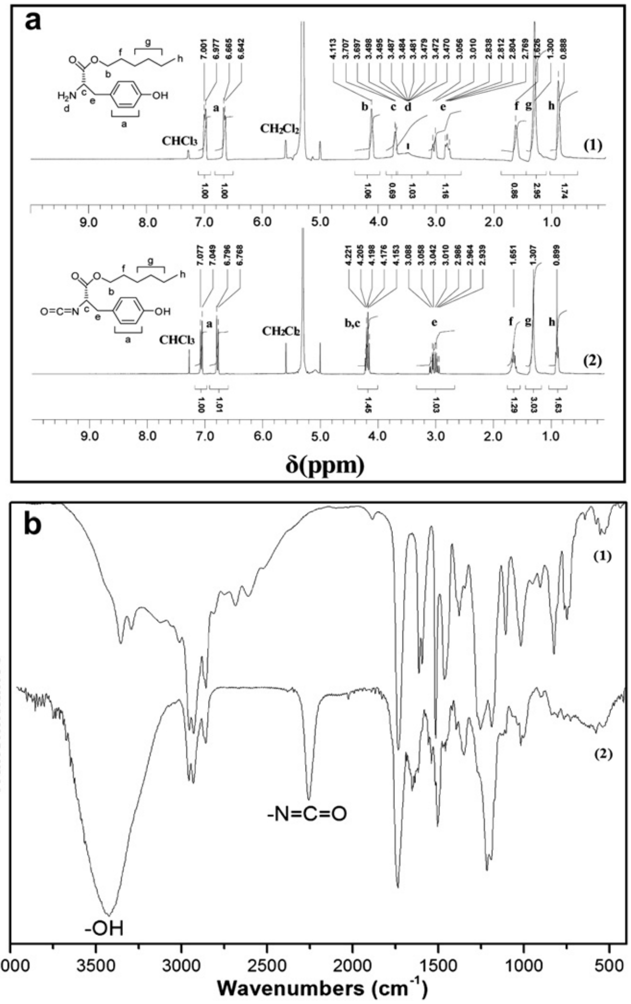
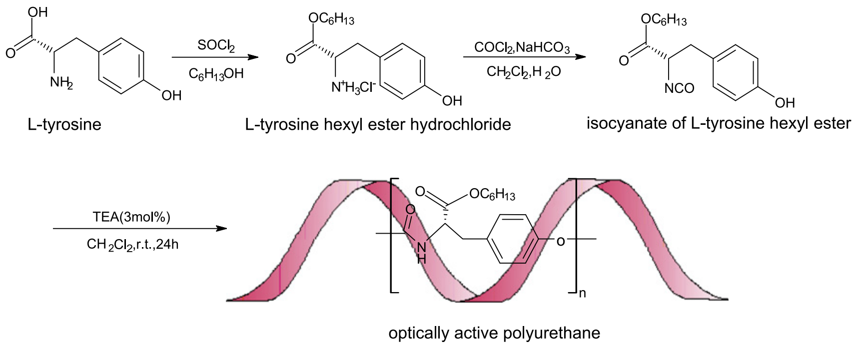


Fig. 1. (a) ^{1}H NMR in $CDCl_3$ and (b) IR spectra of (1) L-tyrosine hexyl ester and (2) isocyanate of L-tyrosine hexyl ester in the reaction.

3.2. Polymer synthesis

Zirconium acetylacetonate, dibutyltin dilaurate and tertiary amines are commonly used as the catalysts in the synthesis of polyurethane. In order to get the pure linear polyurethanes excluding the nylons, the polymerization here were performed by addition of triethylamine but not others [37]. Fig. 3a shows the FT-IR spectrum of LPU, the strong absorptions at 1736 cm^{-1} and 1711 cm^{-1} are assigned to the C=O groups of the hexyl ester and carbamate, respectively. The bands between 2980 cm^{-1} and



Scheme 1. Synthetic procedure of isocyanate-phenol and polyurethane.

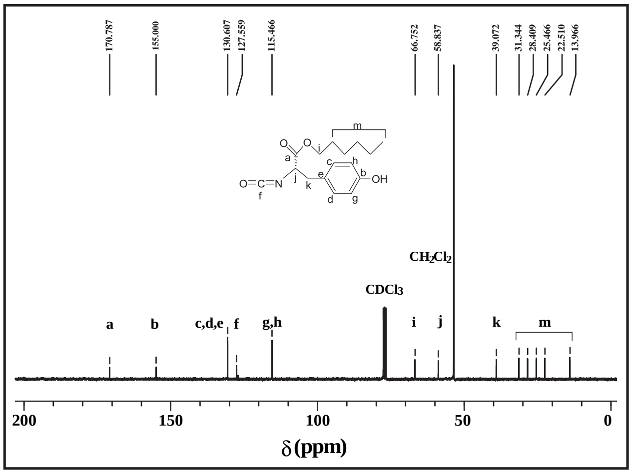


Fig. 2. ^{13}C NMR of isocyanate of L-tyrosine hexyl ester in CDCl$_3$ in the reaction.

2900 cm^{-1}, in the spectrum, are associated with asymmetric and symmetric $-CH_2$ groups. Absorption of amide N–H group appears around 3300–3500 cm^{-1}. Moreover, the characteristic band at 2259 cm^{-1} belonging to N=C=O group has disappeared. The ^{1}H NMR spectrum of LPU is shown in Fig. 3b. The signal assignable to the N–H proton of amide group at 5.6 ppm is observed, confirming the formation of linear polyurethane. These results indicate that the reaction has taken place as expected. Table 1 summarizes the results of the polymerization. Polyurethanes with moderate molecular weights and narrow molecular weight distributions were obtained in good yields. These polymeric materials are soluble in common organic solvents including chloroform, acetone, and THF, and show good film forming ability that would be of great importance for some applications.

Table 1
Polymerization results and characterization of PUs.

Polymer	Yield[a](%)	M_n[b]	M_w/M_n[b]	$[\alpha]_D^{25}$[c]
LPU	93	21,243	1.58	+126 ± 5
DPU	91	24,094	1.54	−120 ± 5
RPU	86	21,235	1.68	0

[a] Ether-insoluble part.
[b] Determined by GPC eluted with THF based on polystyrene standards.
[c] Measured by polarimetry at room temperature, $c = 0.50$ g/dL in CH$_2$Cl$_2$.

3.3. Hydrogen bond analysis

The IR spectrum is not only for the structure confirmation, it is also useful in the study of hydrogen bond effect. Participation in

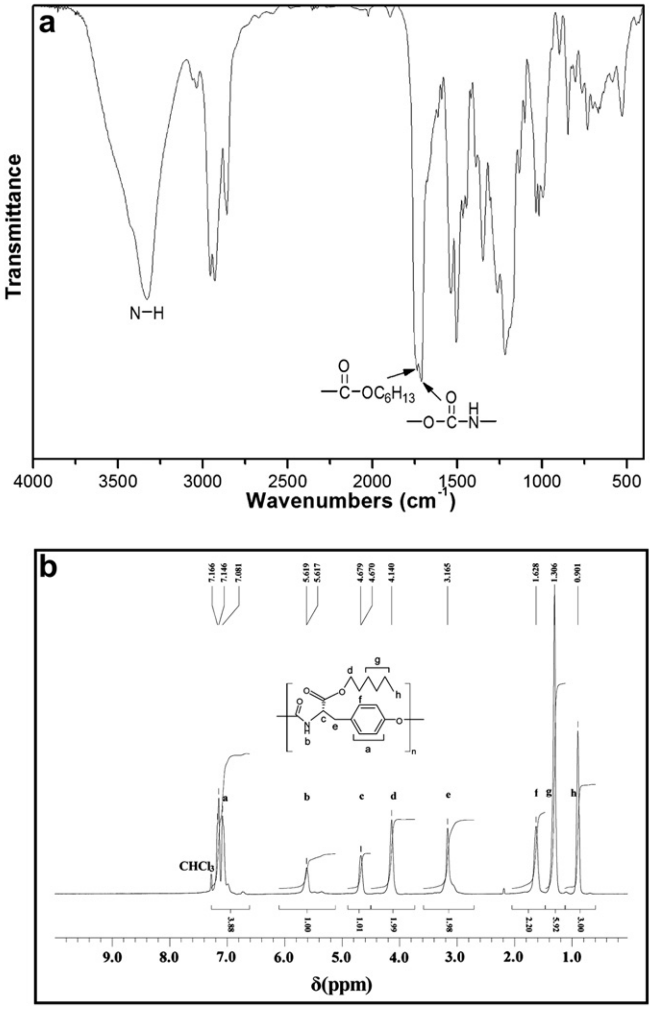


Fig. 3. (a) IR and (b) ^{1}H NMR spectra of LPU in CDCl$_3$.

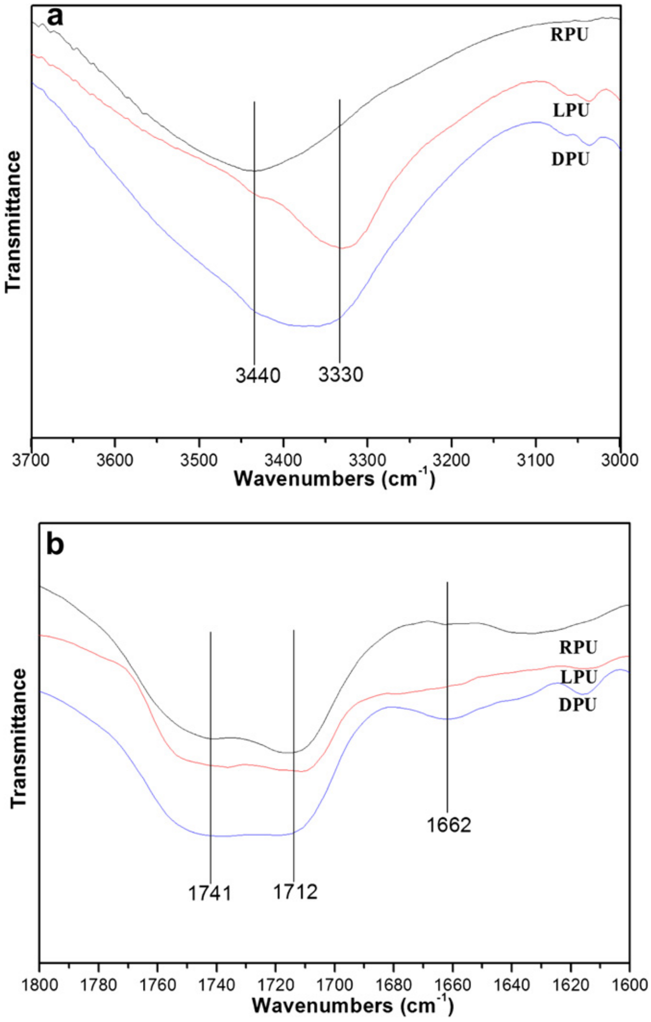


Fig. 4. IR spectra of PUs at (a)3000-3700 cm^{-1} and (b)1600–1800 cm^{-1}.

hydrogen bonding would decrease the vibration frequency of the N—H and C=O groups [47—49]. As shown in Fig. 4a, the broad band centered at 3428 cm^{-1} corresponds to mainly free N—H groups for RPU, this absorption decreases and undergoes a red-shift to 3330 cm^{-1}, which assigns to the hydrogen bonded N—H groups for LPU and DPU. This phenomenon indicates that most of the free N—H groups have changed to be hydrogen bonded. It is noteworthy that compared with the enveloping of N—H stretching region by the absorptions of hydrogen bonded N—H groups in DPU, the presence of free and hydrogen bonded N—H groups can be observed in LPU. This probably originated from the slightly different degrees of hydrogen bonding in chiral polymers with the opposite conformation [50]. The carbonyl stretching regions of the spectra of PUs are showed in Fig. 4b, there are two overlapping bands, apparently centered near 1741 and 1712 cm^{-1}, due to the free carbonyl groups belonging to esters and carbamates, respectively. A hydrogen bonded carbonyl band is observed at a lower frequency of 1662 cm^{-1} whereas it is weak in the RPU. Compare to the free ester carbonyl peak, the free carbamate carbonyl absorption decreases as the hydrogen bonded carbonyl band increases in the spectrum of LPU and DPU, which indicates that the N—H groups are involved in hydrogen bonding with carbonyl groups in the carbamate.

The solubility of PUs in many common organic solvents allowed us to investigate their properties by “wet” spectroscopic methods. The IR spectrum of LPU is also conducted in CHCl$_3$ (Fig. 5) in order to demonstrate which kind of hydrogen bond is formed in the optically active polyurethanes [14,15]. The peak of hydrogen bonded N—H groups in CHCl$_3$ diminishes remarkably comparing to that in the solid state. With the decrease of the concentrations from 5 to 1 mM (Fig. 5a—d), the absorptions of hydrogen bonded N—H groups reduce together with the increasing of free N—H groups. Meanwhile, the bands of carbonyl groups become narrower. This indicates that the hydrogen bondings are mostly intermolecular. However, there are no significant differences when the concentrations are below 1 mM, and some degree of hydrogen bonding exists even at a very low concentration, which implies the existence of intra-molecular hydrogen bonding.

The formation of hydrogen bond is also investigated by ^{1}H NMR spectra obtained from CDCl$_3$ solutions in Fig. 6. Although the inter-chain hydrogen bond has been disrupted by the solvent, the peak of N—H proton becomes slightly broader and shifts to lower field upon hydrogen bonding association with the carbonyl. These data lead to a reasonable conclusion that both inter- and intra-molecular hydrogen bondings are constructed in optically active polyurethanes. From the IR and NMR analyses, the existence of plentiful hydrogen bonds can be concluded in the optically active LPU and DPU, and their enhanced properties will be further demonstrated.

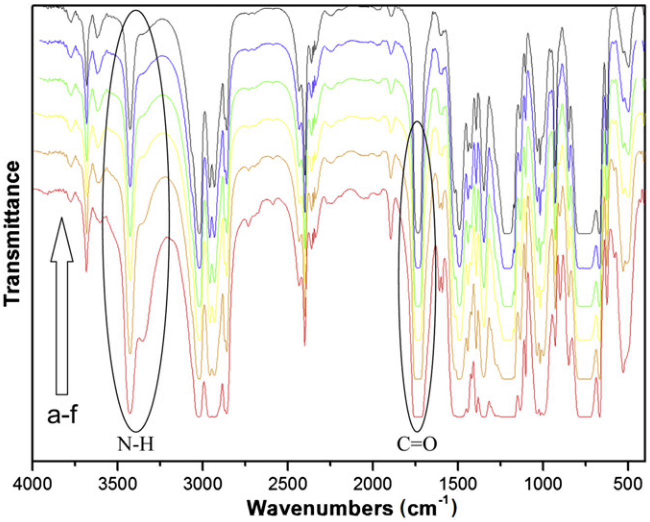


Fig. 5. IR spectra of LPU in CHCl$_3$ at the concentrations of (a)5 mM, (b)3 mM, (c)2 mM, (d)1 mM, (e)0.5 mM and (f)0.1 mM.

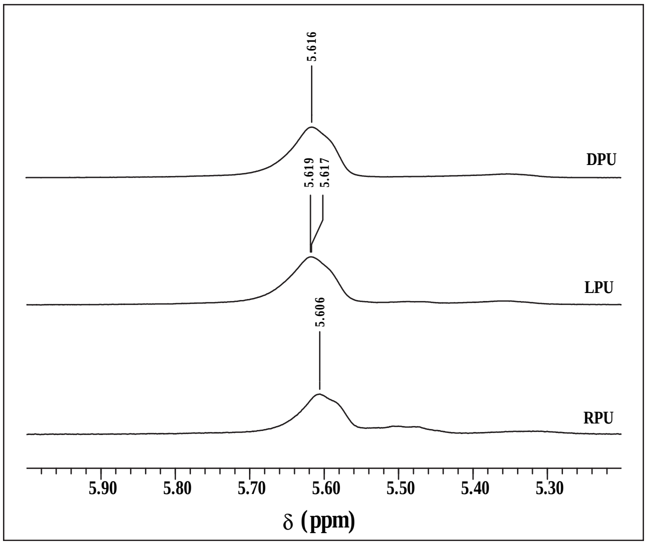


Fig. 6. ^{1}H NMR spectra of PUs in CDCl$_3$ at 5.20—6.00 ppm.

3.4. Optically activity and secondary structure of polymers

The secondary structure of PUs was examined by polarimetry, CD, and UV—vis spectroscopies. Table 1 summarizes the specific rotations of optically active and racemic polyurethanes measured in CH$_2$Cl$_2$. In contrast to the corresponding HCl salts, the LPU and DPU display large optical rotations with an opposite value to each other, suggesting that they took a helical structure with predominantly one-handed screw sense. However, the RPU still has no optical activity.

Fig. 7 depicts the CD and UV—vis spectra of LPU, DPU and RPU measured in CH$_2$Cl$_2$ at room temperature. The three polymers almost have the same UV—vis absorption. The peak at 235 nm corresponds to the π-π* transition of the aromatic rings, and the broad absorption peak at about 265 nm is assigned to the n-π* transition of carbonyl groups. The CD spectroscopic analysis is important for the investigation of secondary structure [51,52]. Hence, we conduct it to confirm the helicity of the PUs. The LPU and DPU exhibit similar strong Cotton effects with wonderful mirror image symmetry at 235 and 265 nm. The result unambiguously proves that the polyurethanes based on L and D-tyrosine are a couple of enantiomorphs which have the right handed and left-handed helical conformation with a preferred screw sense, respectively. On the contrary, the RPU is CD inactive which resulted from the random coiled molecular chain or 1:1 mixture of both left and right handed helices (see below for detail discussion).

3.5. Crystallizability properties

Wide-angle X-ray diffractograms for the polymers are displayed in Fig. 8. As it can be seen, the diffraction pattern for every PU shows a main crystalline peak A at 21 ° as well as amorphous region. Peak A is present regardless of the optical activity of polymers, thus it can be assigned to the presence of hard segments of aromatic ring in the PUs. It is worth noting that a crystalline peak B appeared at about 12 ° for the optically active LPU and DPU. All of the PUs with

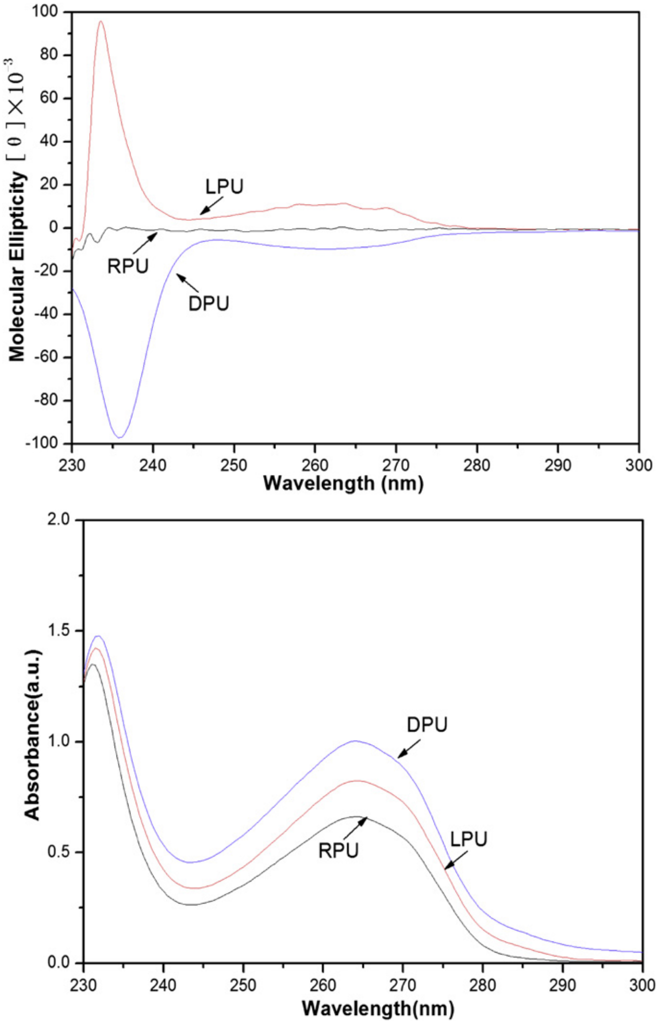


Fig. 7. CD and UV–vis spectra of PUs measured in CH_2Cl_2 ($c = 0.5$ g/dL) at room temperature.

the same composition are obtained by the self-polyaddition of monomers derived from tyrosine. There are no other ingredients which could bring about crystallinity. It can be inferred that the emergence of peak B is perhaps attributed to the formation of regular helical secondary structure of the molecular chain in the light of CD analysis above. The result indicates that the asymmetric force field generated by the chiral compound could induce more crystallinity as well as optical activity in resulting polymers, consequently generated orderliness in new region. In addition, the crystallinity of LPU and DPU are better than RPU which doesn't have this crystalline region, the random coiled macromolecular chain but not the equivalent left and right handed helices in the RPU can thus be proved.

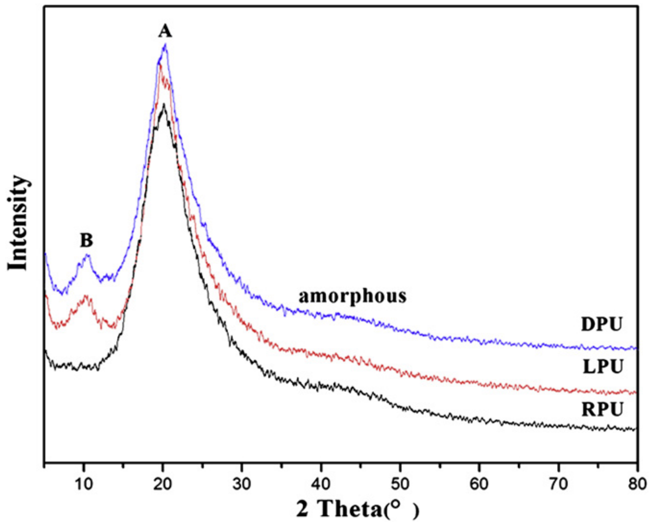


Fig. 8. WAXS Pattern for PUs.

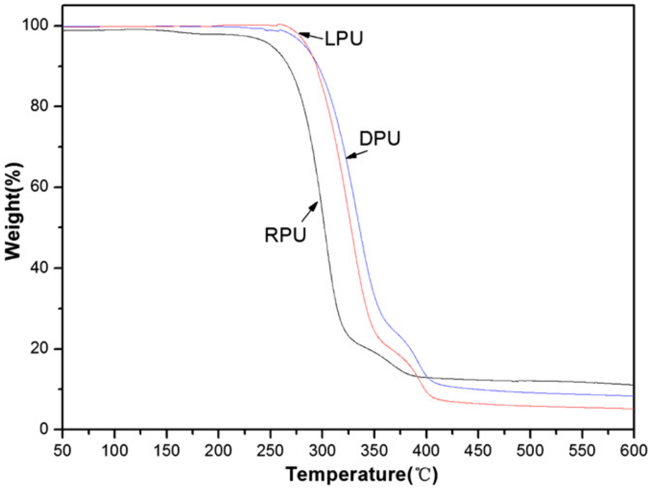


Fig. 9. TGA curves of PUs.

3.6. Thermal stability analysis

The thermal properties of PUs were investigated by TGA techniques at a heating rate of 10 °C/min under a nitrogen atmosphere. As shown in Fig. 9, the TGA curve for each sample exhibits a smooth, stepwise manner, suggesting a two-step thermal degradation. The thermogravimetric data of these polymers are summarized in Table 2. The temperature of 5% and 10% weight loss (T_5, T_{10}) of the polymers have been calculated by means of thermograms and used as criterion for evaluation of thermal stability of the polymers. Although LPU, DPU and RPU have the same repeating units and compositions, their thermal stabilities are different. The RPU shows initial weight loss around 150 °C, whereas, LPU and DPU show no decomposition until 265 °C. It is clear that optically active polymers have higher thermal stability than the racemic one, and this could be pertained to their different chain conformations. LPU and DPU have better ability to damping the internal thermal energy which benefit from the more regulated secondary structure. Furthermore, the higher crystallinity of LPU and DPU which confirmed by the XRD study would increase closer chain interactions, and therefore enhances the thermal stability. On the other hand, random coiled polymer chains can bring about chain separation and decrease the inter-chain interactions. This is why the degree of hydrogen bond of LPU and DPU is higher than that of RPU, and further supports the macromolecular chain conformations analyses above.

Table 2
Thermal properties of PUs.

Polymer	Decomposition temperature (°C) T_5	Decomposition temperature (°C) T_{10}
LPU	285	294
DPU	283	295
RPU	251	267

Table 3
Infrared emissivity values of PUs.

Polymer	Infrared emissivity (8–14 μm)
RPU	0.896
LPU	0.611
DPU	0.625

3.7. *Infrared emissivity analysis*

The infrared emissivity values of PUs at wavelength of 8–14 μm are investigated at room temperature and shown in Table 3. For RPU derived from racemic monomer, the infrared emissivity value is 0.896, while the optically active LPU and DPU have the lower values of 0.611 and 0.625 respectively. It is well known that the vibration of molecules which related to the thermal energy bring about the infrared radiation. Therefore, the thermal restraining and modification of molecular vibrational state would facilitate to the reduction of infrared emissivity [11,53]. LPU and DPU based on chiral monomers possess more regular secondary structure which favors the transmission loss of heat. Meanwhile, the single-handed helical conformation easily leads to the formation of hydrogen bond according to above analyses. This can alter the original vibration mode of molecules and reduce the index of hydrogen deficiency and the unsaturated degree, thus reduce the infrared emissivity.

4. Conclusion

Isocyanate-phenols derived from chiral and racemic tyrosine were synthesized and then polymerized in the presence of triethylamine as the catalyst, providing the corresponding optically active and racemic polyurethanes (LPU, DPU and RPU) in high yields. The LPU and DPU are a couple of enantimorphs, the optical rotations of them are reached to $+124.5\,^\circ$ and $-120\,^\circ$, respectively. The asymmetric force field in the chiral isocyanate-phenols induces orderliness in new region. They possess a helical configuration and higher degree of hydrogen bond compared to the RPU which presented random coiled molecular chain. The higher crystallinity and thermal stability of LPU and DPU provide further proofs of regular secondary structure and more inter-chain interactions. Both of them result in the reduction of infrared emissivity. The optically active polyurethanes based on amino acid could be regarded as a set of promising materials for stealthy technology and the approach to adjusting the emission rate with them is in progress.

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