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ORIGINAL PAPER

Helical polyurethane-imide with optical activity based on binaphthyl units: preparation, characterization, and study of interchain hydrogen bonds

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Abstract Helical polyurethane-imide with optical activity based on R-1,1′-binaphthyl-2′,2-diol (R-BINOL) and racemic polyurethane-imide (racemic-PUI) based on racemic 1,1′-binaphthyl-2′,2-diol (racemic-BINOL) were synthesized by hydrogen transfer addition polymerization procedure and characterized by ^{1}H NMR spectra, Fourier Transform Infrared Spectroscopy (FT-IR), thermal Fourier transform infrared spectroscopy (thermal FT-IR), X-ray diffraction (XRD), circular dichroism (CD) spectroscopy and thermogravimetric analysis (TGA). R-PUI exhibits the single-handed helical conformation and optical activity via CD spectra analysis. The optical rotation of R-PUI is +55.0°, which is larger than that of R-BINOL. The thermal stability of R-PUI is higher than that of racemic-PUI by TG analysis. According to the FT-IR and thermal FT-IR analysis, R-PUI with single-handed conformation possesses prominently interchain hydrogen bonds interactions, which plays an important role in thermal stability and optical activity.

Keywords Helical polyurethane-imide · Optical activity · Hydrogen bond · Single-handed conformation

Introduction

Macromolecules are capable of occupying a lot of different conformational forms. Conformation plays an important role in properties and applications of macromolecules. Recently, helical polymers with single-handed conformation have been attracted great attention [1, 2] due to their potential applications in chiral and sensing materials, molecular switches, data storage, optical devices, chromatographic chiral

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separation, and liquid crystals for display [3, 4]. Widely recognized natural helical structures include right-handed α-helix found in many biopolymers such as proteins, polypeptides, and so on [5]. The natural helical polymers are easily denaturalized by certain physical and chemical factors such as heat, ultraviolet irradiation, and organic solvent, although they possess excellent stereoregular and helical arrangements. On the contrast, synthetic helical polymers represent much better stability. However, most of synthetic polymers have their helicity generated from secondary interactions such as hydrogen bonds and van der Waals forces. Thus, they also undergo conformational change and helical reversal easily [6]. If the backbone of synthetic polymer is very rigid, and the sterical repulsion of side groups is large enough to maintain a stable conformation, there is a possibility to obtain optically active polymers with high stability. Binaphthyl units just can provide the rigid backbone and the chiral origin due to its axial chirality and configutational stability [6–12]. Besides, conformation and inerchain structure for synthetic polymers are key factors in dimensional and thermal stabilities. In this article, helical polyurethane-imide with single-handed conformation and optical activity was synthesized based on R-1,1′-binaphthyl-2′,2-diol (R-BINOL), and our work is focused on the single-handed conformation and the interchain hydrogen bonds on its properties.

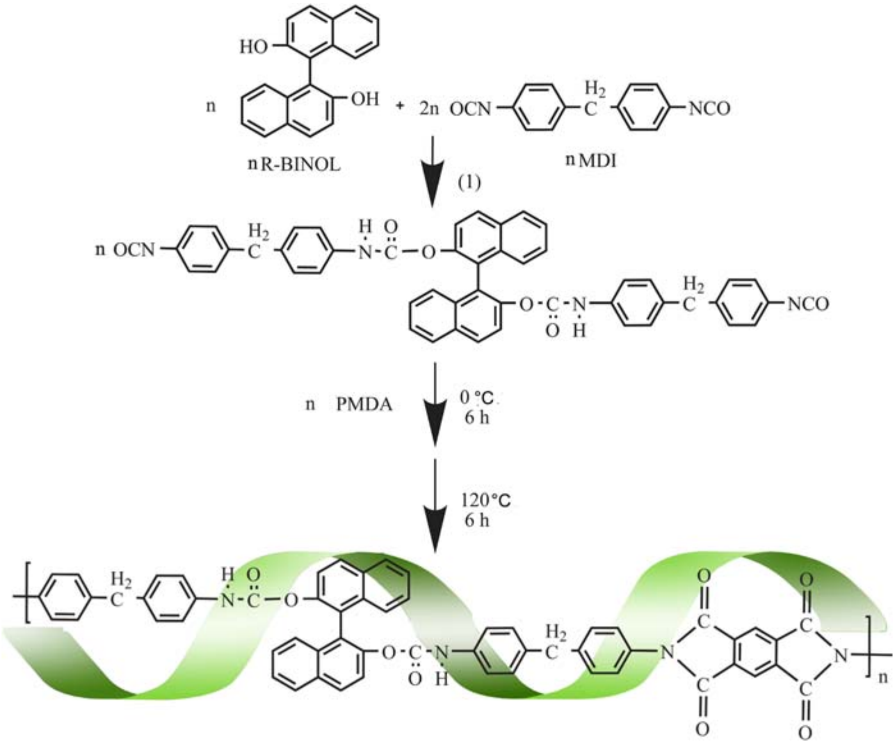
Experimental part

Materials

R-1,1′-binaphthyl-2′,2-diol (R-BINOL) and racemic 1,1′-binaphthyl-2′,2-diol (BINOL) were synthesized and resoluted according to the literature [13, 14]. 4,4′-Diphenylmethane diisocyanate (MDI, TCI Co. Ltd.) was dried and purified under vacuum. Pyromellitic dianhydride (PMDA, Shanghai Chemical Reagent Co.) was recrystallized from acetic anhydride after refluxing for 2 h. *N*,*N*-dimethylformamide (DMF, Shanghai Chemical Reagent Co.) was dried over 40 nm molecular sieves for 1 week. All of the other solvents were purchased from commercial A.R. grade.

Preparation of R-PUI and racemic-PUI

Thirty-milliliter DMF solution of 1.144 g (4 mmol) R-BINOL (or BINOL) was first conducted in a 150 mL, four-necked round-bottom flask equipped with stirrer, condenser, nitrogen inlet, and heating to 100 °C gradually. Then, 20 mL DMF solution of 8 mmol MDI was added into the reactor at 100 °C and reacted for 5 h to obtain the prepolymer. This process was with NCO/OH = 2. Then, 20 mL DMF solution of 4 mmol PMDA was added to the prepolymer at 0 °C in an ice-water bath for 6 h. Then the mixture was heated to 120 °C for 1 h, and then put in the vacuum drying oven at 120 °C for 6 h to obtain R-PUI (or racemic-PUI). The synthetic process is shown as Scheme 1. IR(KBr, cm^{-1}) data of racemic-PUI: 3,472 (free N–H), 3,374 (partial H-bonded N–H), 3,283 (H-bonded N–H), 2,924, 2,864 (–CH_2), 1,777, 1,725 (OCNCO), 1,656 (OCONH); IR (KBr, cm^{-1}) data of R-PUI: 3,472 (free N–H), 3,374 (partial H-bonded N–H), 3,283 (H-bonded N–H), 2,924, 2,864



Scheme 1 Preparation of R-PUI with single-handed conformation and racemic-PUI

($–CH_2$), 1,777, 1,725(OCNCO), 1,656(OCONH); M_w of racemic-PUI: 19,450; M_w of R-PUI: 20,100; ^{1}H NMR(DMSO-d_6, δ) data of racemic-PUI: 8.38–8.41 (m, 2H, ArH), 7.94 (m, 2H, ArH), 7.82–7.85 (m, 2H, ArH), 7.59–7.62 (m, 2H, ArH), 7.28–7.31 (m, 2H, ArH), 7.22–7.24 (m, 2H, ArH), 7.17–7.19 (m, 4H, PhH), 7.13–7.15 (m, 4H, PhH), 9.20 (m, 2H, OCONH), 6.89–6.92 (m, 2H, PhH), 3.33 (m, 4H, CH_2), 2.87 (m, 4H, PhH), 2.71 (m, 4H, PhH); ^{1}H NMR(DMSO-d_6, δ) data of R-PUI: 8.38–8.41 (m, 2H, ArH), 7.94 (m, 2H, ArH), 7.82–7.85 (m, 2H, ArH), 7.59–7.62 (m, 2H, ArH), 7.28–7.31 (m, 2H, ArH), 7.22–7.24 (m, 2H, ArH), 7.17–7.19 (m, 4H, PhH), 7.13–7.15 (m, 4H, PhH), 9.20 (m, 2H, OCONH), 6.89–6.92 (m, 2H, PhH), 3.33 (m, 4H, CH_2), 2.87 (m, 4H, PhH), 2.71 (m, 4H, PhH);

Measurements

FT-IR spectra and thermal FT-IR were carried out on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets. The temperature of sample was controlled with Watlow's series 988 controller at the heating rate of 5 K/min. FT-IR spectra were obtained at a 4 cm^{-1} resolution and recorded in the region of 4,000–400 cm^{-1}. The samples and background scanning times was both 16. ^{1}H NMR spectra measurements (in DMSO-d_6) were recorded on a DXT-500 Mhz Bruker spectrometer with

TMS as internal standard. Molecular weights were determined by gel permeation chromatography (GPC, Agilent 1100, USA) at room temperature in DMF. X-ray diffraction (XRD) measurements were recorded using a Rigaku D/MAX-R with a copper target at 40 kV and 30 mA. The power samples were spread on a sample holder and the diffractograms were recorded in the range 4–60° at the speed of 5°/min. Circular dichroism (CD) spectroscopies in the UV–visible region were carried on JASCO J-810 spectropolarimeter at 20–25 °C. The samples of R-PUI (racemic-PUI) were dissolved in DMF with the concentration 0.40 g/L. UV spectra were measured on a Shimadzu UV 3600 spectrometer. The optical rotation was measured in a WZZ-2S (2SS) Digital Automatic Polarimeter. The wavelength of sodium lamp was 589.44 nm and the solvent was DMF. Thermal analysis experiments were performed using a TGA apparatus operated in the conventional TGA mode (TA Q-600, TA Instrument) at the heating rate of 10 K/min in a nitrogen atmosphere and sample size was about 50 mg.

Results and discussion

FT-IR analysis of R-PUI and racemic-PUI

FT-IR spectra of R-PUI and racemic-PUI are shown in Fig. 1. As can be seen, both R-PUI and racemic-PUI almost have the same absorption. The bands at 1,777 and 1,725 cm^{-1} are assigned to the stretching vibration of carbonyl groups for the imide circle. The absorption of amide I and amide II appears at 1,545 and 1,510 cm^{-1}, respectively. The band at 1,210–1,270 cm^{-1} corresponds to C–N with NH (amide III).

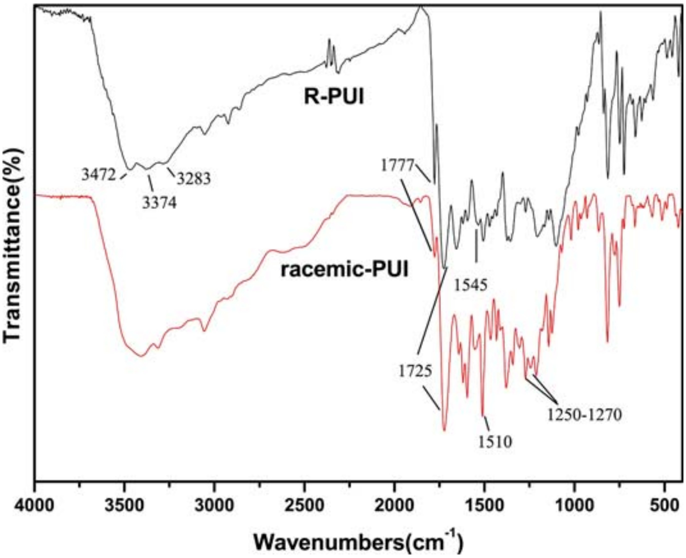


Fig. 1 FT-IR spectra of R-PUI and racemic-PUI

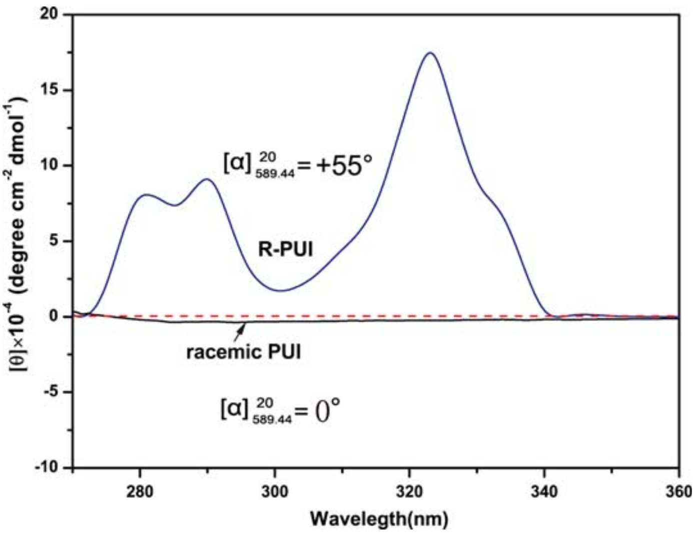


Fig. 2 CD spectrum and the optical rotation of R-PUI with single-handed conformation

The bands at 2,230 cm^{-1} belonging to N=C=O groups have disappeared. These results indicate that the reaction has taken place as expected. There are some differences in the region from 3,000 to 3,600 cm^{-1} corresponding to N–H stretching. As seen in Fig. 2, the bands at 3,374 and 3,283 cm^{-1} are assigned to the partly hydrogen-bonded N–H groups and the completely hydrogen-bonded N–H groups. The band at 3,472 cm^{-1} belongs to the free N–H groups. These three bands display different intensities. The structural changes of the polymer are fundamentally important for the IR study. Participation in hydrogen bonding decreases the frequency of the N–H vibration but increases its intensity, making this absorption useful in the study of hydrogen-bond effects [15]. These results indicate that the degree of hydrogen bonded of R-PUI is larger than that of racemic-PUI due to the more orderly conformation of R-PUI.

Optical activity of R-PUI

The method of proving the presence of a single-handed helical structure varies depending on the type of study and the structure of the polymer, and the structural questions can be addressed by optical activity and circular dichroism (CD) when the helix has an excess screw sense [16]. The chiroptical properties of the optically active polyurethane-imide were investigated by CD spectroscopy.

Figure 2 shows the CD spectra of R-PUI and racemic-PUI. R-PUI appears to possess a predominantly one-handed helical conformation so that it exhibits an intense CD in the absorption region. R-PUI appears two positive value peaks corresponding to positive Cotton effect in the CD spectra. The absorption at 322 nm corresponds to the л–л* transition of the naphthalene rings and a high rigidity backbone in the polymer chains [17]. The broad absorption peaks at about 285 nm

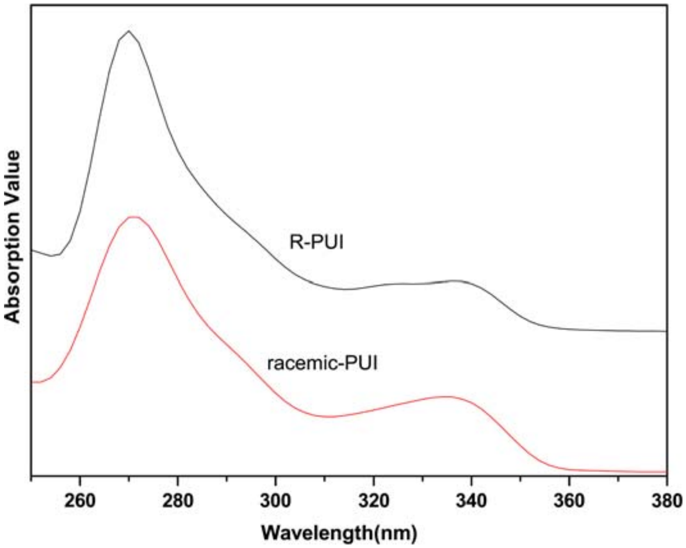


Fig. 3 UV spectra of R-PUI and racemic-PUI

is assigned to the n–π^* transition of carbonyl groups [18–21]. There are no CD signals in the spectra for racemic-PUI based on racemic-BINOL. It indicates that the polymeric conformation of racemic-PUI is racemic without Cotton effect. Racemic-PUI possesses the helical structure derived from BINOL; however, the conformation is racemic and the stereo structure is out of order. However, as seen in Fig. 3, R-PUI and racemic-PUI exhibit the same absorption in UV spectra. The optical rotation values of racemic-PUI and R-PUI were measured to obtain a further proof that R-PUI has the single-handed conformation and optical activity. The optical rotation value ([α] 20 589.44) of R-BINOL is +35.1°, but the optical rotation value of its corresponding polymer (R-PUI) is enhanced to +55.0°. It is not very large, and this is maybe attributed to the origin of the helical structure. For R-PUI based on R-BINOL, the helicity generates from the chiral axis of main chain. In other words, R-BINOL is the origin of helical structure. R-PUI contains three monomers, thus the helical origin is dispersed and the rotation degree is not very large. For some similar main chain helical polymers, the rotation degree is also not very large [7, 17]. Although the rotation degree is not very large, the helical structure possesses high stability compared with the helical structure based on the side chains or weak force. In contrast, the optical rotation value of racemic-PUI is 0°. On the basis of these analyses, it is found that R-PUI is the optically active polymer and has the single-handed helical structures, while racemic-PUI possesses racemic conformation as a whole.

Crystallizability and thermal stability analysis

Figure 4 displays the XRD patterns of R-PUI and racemic-PUI. The XRD patterns show that R-PUI and racemic-PUI are partially crystalline in nature. This is perhaps

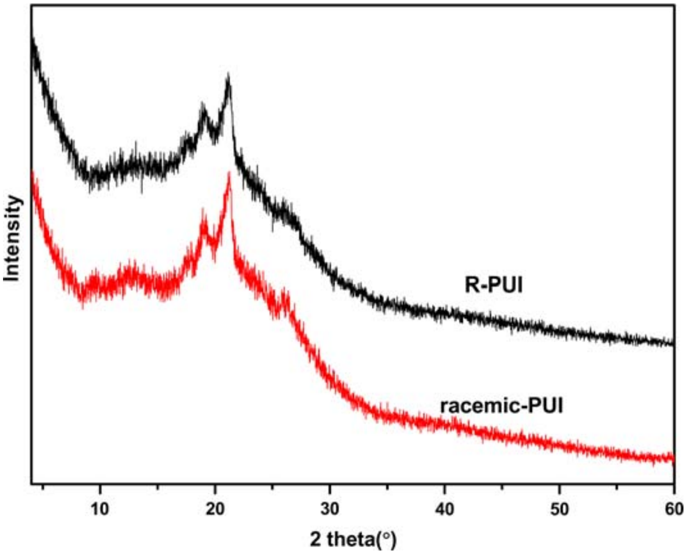


Fig. 4 XRD patterns of R-PUI and racemic-PUI

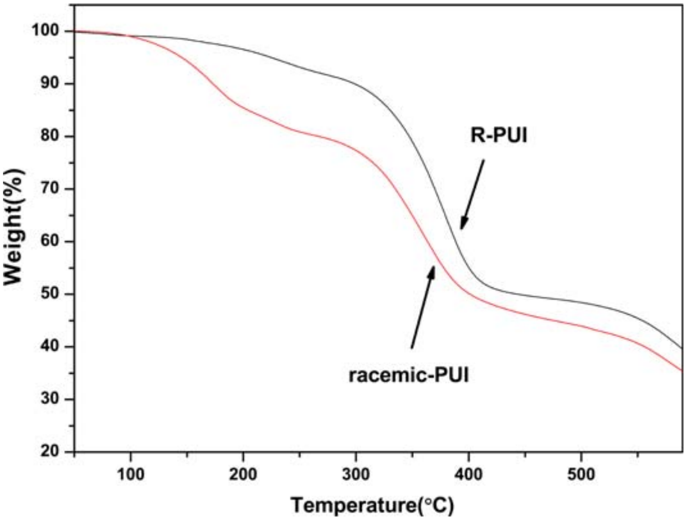


Fig. 5 TG curves of R-PUI and racemic-PUI

due to the presence of the hard segment such as naphthalene rings as well as the interchain hydrogen bonds. TG curves of R-PUI and racemic-PUI are shown in Fig. 5. As can be seen in Fig. 5, below 285 °C, racemic-PUI appears more weight loss than R-PUI. R-PUI possesses better thermal stability than racemic-PUI. The effect could be attributed to more regular structures of single-handed polymer than that of the racemic polymer. This could also be attributed to the hydrogen bonds

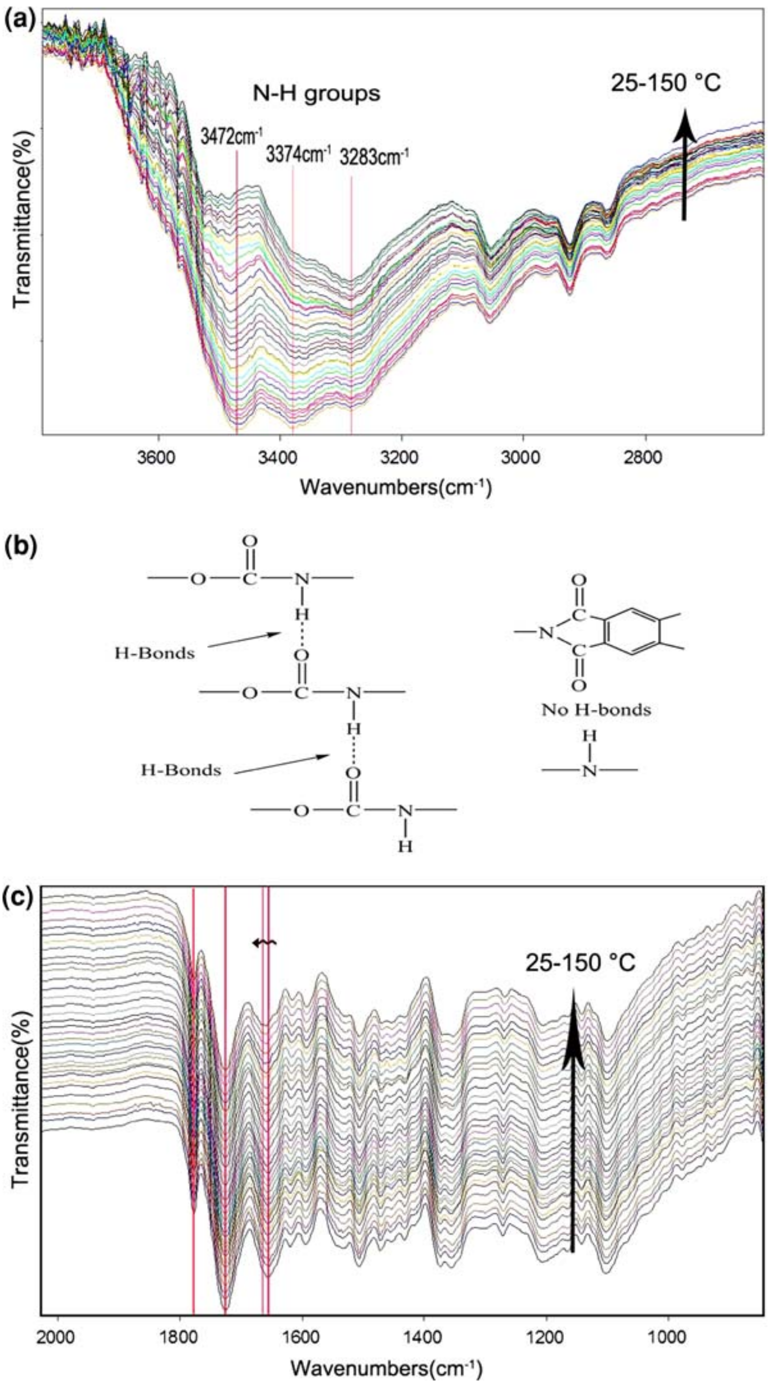


Fig. 6 **a** Thermal FT-IR spectra of R-PUI at 900–2,000 cm^{-1}. **b** Scheme of interchain H-bonds. **c** Thermal FT-IR spectra of R-PUI at 2,600–4,000 cm^{-1}

interchain. Conformation and interchain hydrogen bonds are important factors on the thermal stability of helical polymers.

Thermal FT-IR and H-bonds analysis of R-PUI

Thermal FT-IR was performed in order to investigate the effect of helical conformation on hydrogen bonds, and the spectra are shown in Fig. 6. As can be seen in Fig. 6a, the peak at 3,283 cm^{-1} belonging to the hydrogen-bonded N–H groups are in high intensity and hydrogen bonds are still active in the polymeric structure when R-PUI have been heated to 150 °C. However, the peak at 3,472 cm^{-1} corresponding to the free N–H groups and the peak at 3,374 cm^{-1} have already disappeared at about 150 °C. In Fig. 6c, the peak at 1,656 cm^{-1} corresponding C=O groups is increased in the frequency along with the increased temperature above 150 °C. Because the hydrogen-bonded N–H groups are associated to the C=O groups from NHCOO, the disappearance of hydrogen bonds causes the increased the frequency for C=O groups. However, the peaks at 1,727 cm^{-1} and 1,777 cm^{-1} corresponding to the C=O groups from the imide circle have not changed above 150 °C. This result proves that the participation of hydrogen bonds is active between N–H groups and C=O groups from the structure of –NHCOO– in R-PUI. The interchain hydrogen bonds of R-PUI are form in a special way shown in Fig. 6b.

Conclusion

Optically active R-PUI with single-handed helical conformation and racemic-PUI were prepared successfully based on binaphthyl units. R-PUI possesses higher degree of hydrogen bonds owing to its single-handed conformation. The thermal stability of R-PUI is higher than that of racemic-PUI due to the higher degree of hydrogen bond for R-PUI. R-PUI shows optical activity, excellent thermal stability, and the interchain hydrogen bonds which provide the foundation for many potential applications.

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