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ARTICLE

Optically Active Helical Polyurethane−Urea with Single-Handed Conformation for Infrared Low Emissivity

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ABSTRACT: Optically active polyurethane−urea (S-PUU) based on S-1,1′-binaphthyl-2′,2-diol (S-BINOL) and polyurethane−urea (PUU) based on racemic 1,1′-binaphthyl-2′,2-diol (BINOL) were synthesized by hydrogen transfer addition polymerization procedure and characterized by Fourier transform infrared spectroscopy (FT-IR), thermal Fourier transform infrared spectroscopy (thermal FT-IR), X-ray diffraction (XRD), circular dichroism (CD) spectroscopy, and vibrational circular dichroism (VCD) spectroscopy. The infrared emissivity values of S-PUU and PUU were investigated at 8−14 μm. S-PUU with single-handed helical conformation possesses prominently interchain hydrogen bonds interactions, which is impactful for the reduction of infrared emissivity value. Thus, the infrared emissivity value of S-PUU is lower than that of PUU. The increasing rate of the infrared emissivity value of S-PUU is affected by hydrogen bonds, while S-PUU is heated up from 25 to 150 °C, and the rate is much higher after disappearance of hydrogen bonds interchain above 100 °C than that below 100 °C.

Introduction

In recent years, materials with infrared low emissivity have attracted great attention due to their increasingly important application in both thermal control and military stealthy.[1] In present application for infrared materials, inorganic or metallic materials are used very widely because of their high reflectance, while the organics and polymers with highly absorptive groups such as C═O and N−H are hardly used owing to the high emissivity resulting from the high absorption. However, organic polymers possess unique properties such as low density, tractability, and the most value, their adjustable structure, which can provide the possibility of adjusting the infrared emissivity efficaciously according to our need. Thus, there is a great need to develop the organic polymers that can be used in infrared low-emissivity materials.

Meanwhile, helical polymers possess not only the advantages of any other polymers but also the unique structure[2] and optical activity.[3] Their precisely ordered stereo structures and optical activity can induce the unique properties[4] and provide potential applications for certain.[5] They have attracted great attention due to their chiro-optical structure and properties, intriguingly various architectures, and, more importantly, their potential applications in chiral and sensing materials, molecular switches, data storage, optical devices, chromatographic chiral separation, and liquid crystals for display.[6] Synthetic polymers with right- or left-handed helical conformation can be optically active without any chiral component because they are chiral.[7] If the polymer backbone is rigid enough, or the steric repulsion of side groups is large enough to maintain a stable conformation, there is the possibility of obtaining helical optical polymers. Binaphthyl units can just provide the rigid backbone and the chiral origin owing to its axial chirality and conformational stability.[8] Two naphthyls can not be coplanar and possess an angle because of the huge steric hindrance.

In this study, helical polyurethane−urea (S-PUU and PUU) based on S-1,1′-binaphthyl-2′,2-diol (S-BINOL) and racemic 1,1′-binaphthyl-2′,2-diol (BINOL) were synthesized and characterized. Although polyurethane−urea contains the groups (N−H and C═O) with high absorption, S-PUU with helical structure and single-handed conformation has a lower value of infrared emissivity compared with PUU based on BINOL. When the temperature is increased, the value of infrared emissivity for S-PUU displays an interesting inflection impacted by interchain hydrogen bonds. This work is focused on the effect of single-handed helical conformation and interchain hydrogen bonds on infrared emissivity, and it provides a novel method to investigate infrared low-emissivity materials.

Experimental Part

Materials. S-1,1′-Binaphthyl-2′,2-diol (S-BINOL) and racemic 1,1′-binaphthyl-2′,2-diol (BINOL) were synthesized and resoluted according to the literature.[9] 4,4′-Diphenylmethane diisocyanate (MDI, TCI Co. Ltd.) was dried and purified under vacuum. 1,4-Diaminobenzene (PhDA, Shanghai Chemical Reagent Co.) was used without further purification. *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 S-PUU (PUU). The progress of preparation of S-PUU (PUU) is shown in Figure 1. 40 mL of DMF solution of 1.144 g of S-BINOL (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 of DMF solution of 2.0 g MDI was added dropwise into the reactor at 100 °C and reacted for 5 h to obtain the prepolymer. Then, 20 mL of DMF solution of 0.432 g (4 mmol) PhDA was added to the prepolymer at 80 °C for 8 h. The total process was done under a nitrogen atmosphere and with NCO/OH/NH_2 = 2/1/1. Then the mixture was put in the vacuum drying oven at 75 °C for 24 h after being distilled under reduced pressure to remove most of DMF. Then, the production was washed with anhydrous ethanol several times. Further purification could be conducted by dissolving the polymer in DMF to precipitate in anhydrous ethanol again. ^{1}H NMR (DMSO-d_6, δ) data of PUU: 3.37 (s, 4H, CH_2), 3.15 (s, 2H, CONHPh), 3.25 (s, OCONHPh),

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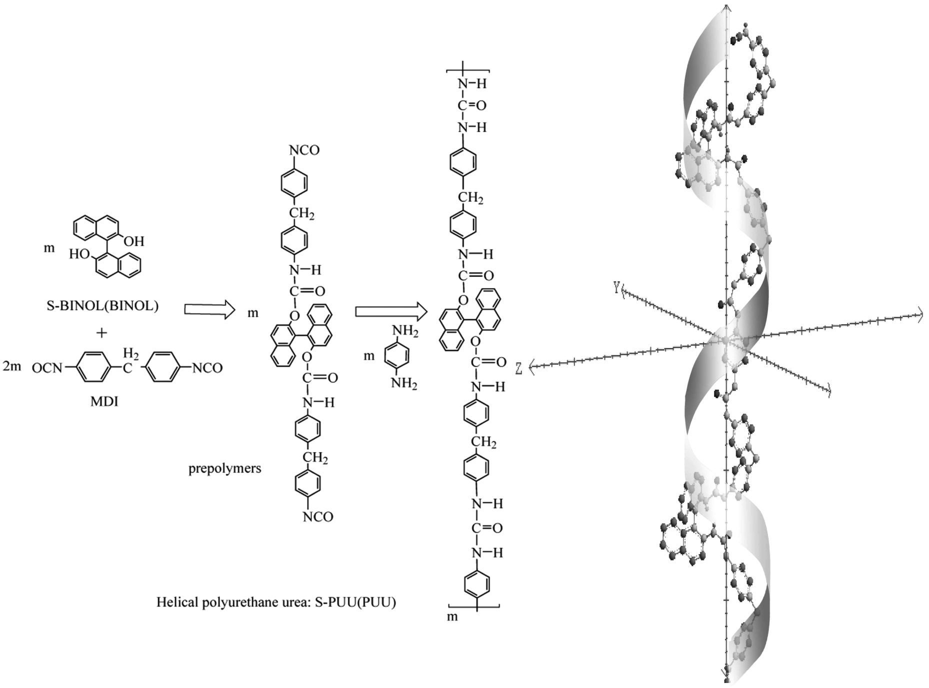

Figure 1. Scheme of preparation of S-PUU and PUU.

2.88 (s, 2H, PhH), 2.75 (s, 2H, CONHPh), 2.30 (s, 2H, PhH), 6.93−6.98 (m, 8H, PhH), 7.15−7.18 (m, 8H, PhH), 7.22−7.24 (m, 2H, ArH), 7.32 (m, 2H, ArH), 7.35 (d, 2H, ArH), 7.84 (m, 2H, ArH), 7.85 (m, 2H, ArH), 7.94 (s, 2H, ArH). ^{1}H NMR (DMSO-d_6, δ) data of S-PUU: 3.37 (s, 4H, CH_2), 3.15 (s, 2H, CONHPh), 3.25 (s, OCONHPh), 2.88 (s, 2H, PhH), 2.75 (s, 2H, CONHPh), 2.30 (s, 2H, PhH), 6.93−6.98 (m, 8H, PhH), 7.15−7.18 (m, 8H, PhH), 7.22−7.24 (m, 2H, ArH), 7.32 (m, 2H, ArH), 7.35 (d, 2H, ArH), 7.84 (m, 2H, ArH), 7.85 (m, 2H, ArH), 7.94 (s, 2H, ArH).

Measurements. FT-IR spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer at room temperature 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 4000−400 cm^{-1}. The sample and background scanning times were 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. 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 5°−70° at the speed of 5°/min. Vibrational circular dichroism (VCD) spectra were carried out on a Bruker Tensor 27 FT-IR spectrometer attached by PMA50 (Bruker) at room temperature using KBr pellets, and the scanning time is 8 h. Circular dichroism (CD) spectroscopies in the UV−vis region were carried on JASCO J-810 spectropolarimeter at 20−25 °C. The samples of S-PUU (PUU) were dissolved in DMF with the concentration 0.40 g/L. UV spectra were measured on a Shimadzu UV 3600 spectrometer. The optical rotation of R/S-HPUU 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 Instruments) at the heating rate of 10 K/min in a nitrogen atmosphere, and the sample size was about 50 mg. Infrared emissivity values of the samples were carried out at the heating rate of 5 K/min on IRE-I infrared emissivity measurement instrument of Shanghai Institute of Technology and Physics, China.

Results and Discussion

Hydrogen Bonds Analysis of S-PUU and PUU. 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.[10] FT-IR spectra of S-PUU and PUU are shown in Figure 2a. As can be seen, both S-PUU and PUU almost have the same absorption. The strong band at 1643 cm^{-1} is assigned to the C=O groups. The absorption of amide I and amide II appears at 1545 and 1510 cm^{-1}, respectively. The band at 1210−1270 cm^{-1} corresponds to C—N with NH (amide III). The bands at 2230 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 of 3000−3600 cm^{-1} corresponding to N−H stretching. For PUU as seen in Figure 2a (2), the bands at 3305 and 3395 cm^{-1} are assigned to the completely hydrogen-bonded N−H groups and the partly hydrogen-bonded N−H groups. The broad band at 3465 cm^{-1} belongs to the free N−H groups. For S-PUU in Figure 2a (1), the disappearance of absorption at 3395 cm^{-1} and increased intensity at 3305 cm^{-1} indicate that some partly associated N−H groups have changed to be hydrogen bonding completely. Compared with the board band at 3465 cm^{-1} of PUU, there are two absorptions (3433 and 3511 cm^{-1}) in for S-PUU. This result indicates that some free N−H groups have changed to be hydrogen bonding to a certain extent.[11]

Figure 2b displays the XRD patterns of S-PUU and PUU. The XRD patterns show that S-PUU and PUU are partially crystalline in nature. This is may be due to the presence of the hard segment such as naphthalene rings. The crystal layer spacing related to the plane bifurcated hydrogen bonds structures at about 22° of S-PUU is smaller (4.14 nm) than that of PUU (4.16 nm). The structures of interchain hydrogen bonds could be arrayed in the special way (Figure 2b). This result is another proof that the degree of hydrogen bonds of S-PUU is higher than that of PUU. Parts c and d of

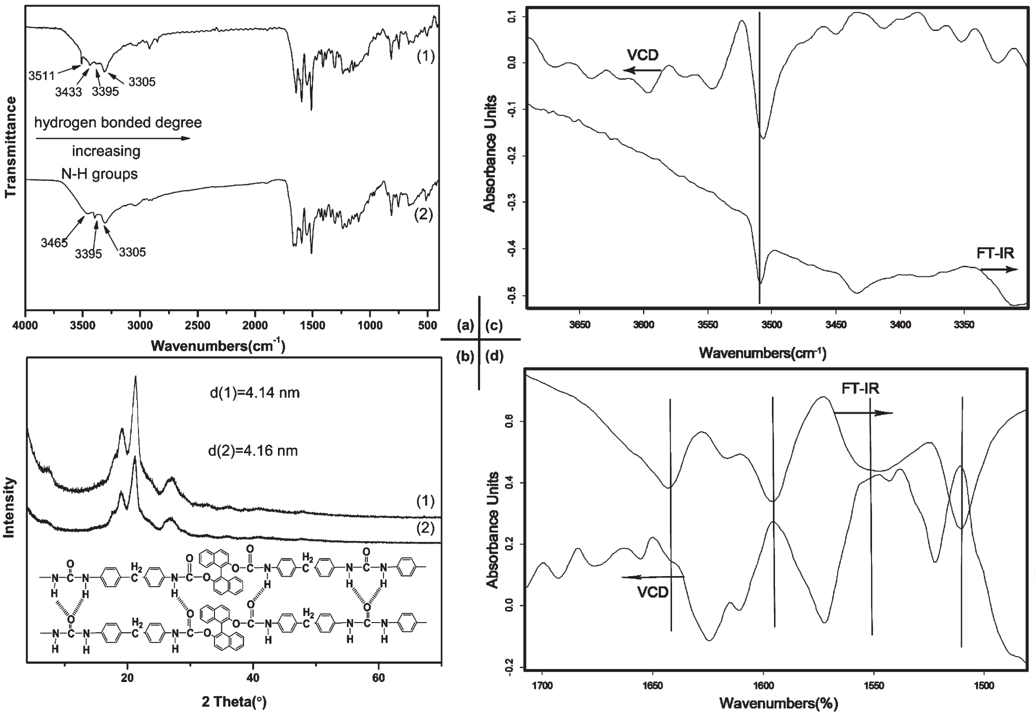

Figure 2. (a) FT-IR spectra of (1) S-PUU and (2) PUU. (b) XRD patterns of (1) S-PUU and (2) PUU. (c) VCD and FT-IR spectra of S-PUU at 3300−3700 cm^{-1}. (d) VCD and FT-IR spectra of S-PUU at 1500−1700 cm^{-1}.

Figure 2 display the FT-IR spectra and VCD spectra of S-PUU, respectively. It is found that VCD signal of S-PUU displays an obvious Cotton effect for N−H and C=O groups. This result suggests that S-PUU possesses single-handed conformation, which is more orderly than that for PUU. That is why the degree of hydrogen bonds of S-PUU is higher than that of PUU.

Optical Activity and Single-Handed Conformation of S-PUU. The helical structural questions can be addressed and proved by optical activity and circular dichroism (CD) when the helix has an excess screw sense.[12] The chiro-optical properties of the optically active polymers were investigated by CD spectroscopy. CD and UV spectra of S-PUU and PUU are displayed in Figure 3. The absorption at about 340 nm corresponds to the $\pi-\pi^*$ transition of the naphthalene rings and a high rigidity backbone in the polymer chains.[13] The broad absorption peaks at about 285 nm is assigned to the $n-\pi^*$ transition of carbonyl groups.[14] S-PUU appears to possess a predominantly one-handed helical conformation so that they exhibit an intense CD in the absorption region. S-PUU appears two negative values peaks corresponding to a negative Cotton effect in the CD spectra. There are no CD signals in the spectra for PUU based on racemic BINOL. It indicates that the polymeric conformation of PUU is racemic without a Cotton effect. PUU possess the helical structure derived from BINOL; however, the conformation is racemic, and the stereo structure is out of order. The optical rotation values of BINOL, S-BINOL, PUU, and S-PUU were measured to obtain a further proof that S-PUU has the single-handed conformation and optical activity. The optical rotation value ($[\alpha]_{589.44}^{20}$) of S-BINOL is −35.4°, but the optical rotation value of its corresponding polymer (S-PUU) is enhanced to −75.2°. PUU has no single-handed conformation owing to the racemic BINOL without optical activity.

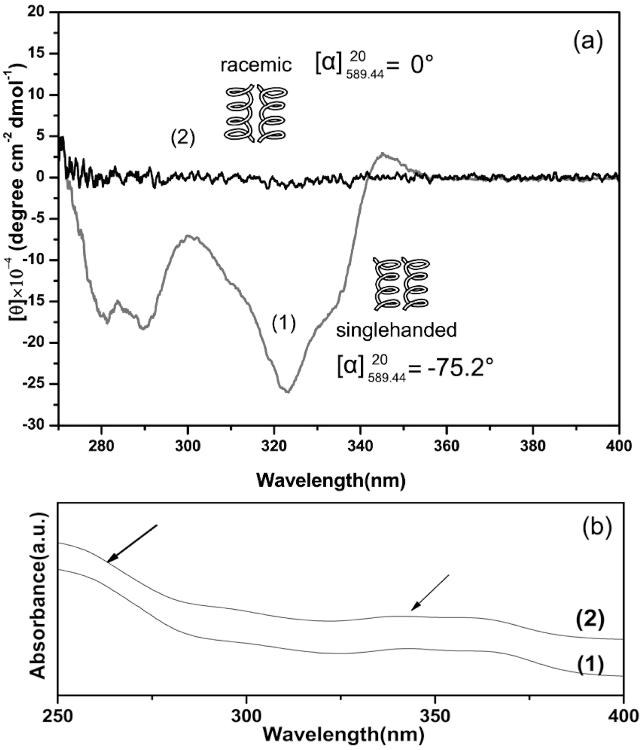

Figure 3. CD and UV spectra of (1) S-PUU and (2) PUU.

Infrared Emissivity Analysis. The infrared emissivity values of S-PUU and PUU at wavelength of 8−14 μm are investigated and shown in Figure 4 from 25 to 150 °C. As can be seen from TG curve of S-PUU, below 200 °C no thermal decomposition has occurred. PUU based on racemic BINOL has a higher infrared emissivity value of 0.827 at room temperature (25 °C), while S-PUU with single-handed conformation structure possesses a lower value of 0.686. Obviously, the single-handed helical conformation is favored to the reduction of infrared emissivity value due to the more regular structure and ordered stereo structures based on S-BINOL.

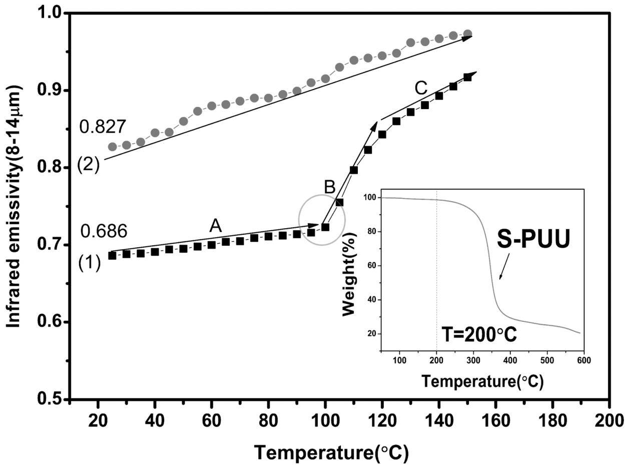

Figure 4. Infrared emissivity values of (1) S-PUU and (2) PUU at 25−150 °C.

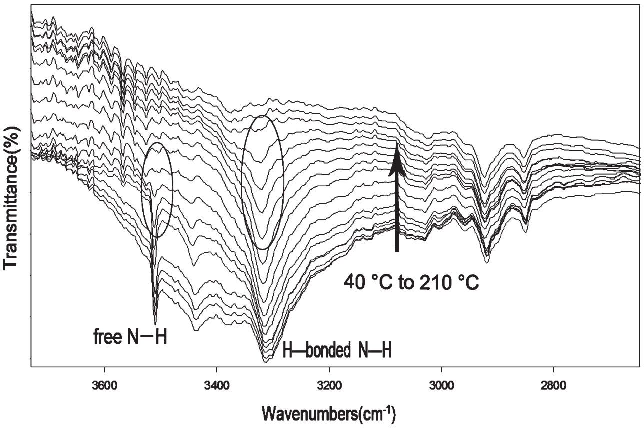

Figure 5. Thermal FT-IR spectra of S-PUU at 2700−3700 cm^{-1}.

Generally, organic polymers possess high infrared emissivity values because of the high unsaturated groups (−NHCO− and −NHCONH− in polyurethane−urea) in the structure of polymer chain. According to FT-IR and XRD analysis, there are interchain hydrogen bonds with different degree between C=O and N−H groups for S-PUU and PUU. The oxygen atom in C=O provides the lone pair electrons, and the hydrogen atom provides the unoccupied orbital. The lone pair electrons are seized by both hydrogen atom and oxygen atom; thus, to some extent the index of hydrogen deficiency and the unsaturated degree would be reduced after forming hydrogen bonds between −NH and C=O groups in the polymeric structures. The orderly structure of S-PUU with single-handed conformation could more easily lead to form hydrogen bonds among the high unsaturated groups, and the degree of hydrogen bonding in S-PUU is higher than that in PUU. To some extent, the index of hydrogen deficiency and the unsaturated degree would be reduced after forming hydrogen bonds between −NH and C=O groups in the polymeric structures. Thus, the infrared emissivity value of S-PUU is lower than that of PUU.

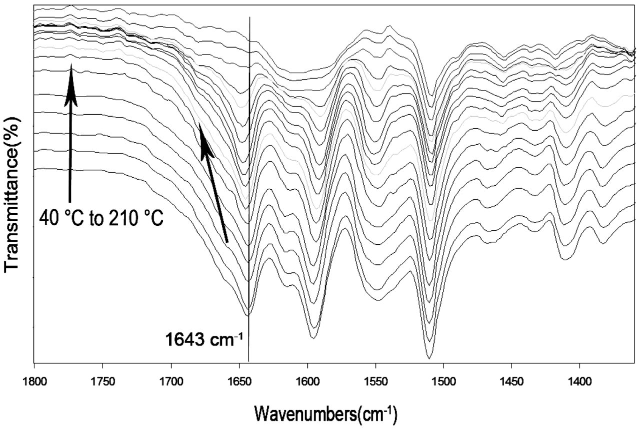

Figure 6. Thermal FT-IR spectra of S-PUU at 1400−1800 cm^{-1}.

Thermal FT-IR was performed in order to investigate the effect of hydrogen bonds on infrared emissivity value, and the spectra are shown in Figures 5 and 6. As can be seen, the peak at 3305 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 S-PUU have been heated to 100 °C. However, the peak at 3511 cm^{-1} corresponding to the free N−H groups has already disappeared at about 100 °C. From Figure 4, we can see the infrared emissivity value of S-PUU has not increased at a high speed below 100 °C. This indicates that the disappearance of free N−H groups does not impact the infrared emissivity of S-PUU. Above 100 °C, the absorption band at 3305 cm^{-1} are weakening along with the temperature increasing. Therefore, hydrogen bonds have disappeared gradually above 100 °C. Correspondingly, in Figure 4, the infrared emissivity value of S-PUU is increased rapidly over 100 °C, and there is an obvious inflectional point at about 100 °C. In Figure 6, the peak at 1643 cm^{-1} corresponding C=O groups is increased in the frequency along with the increased temperature above 100 °C. Because the hydrogen-bonded N−H groups are associated with the C=O groups, the disappearance of hydrogen bonds causes the increased the frequency for C=O groups. This result also proves that the participation of hydrogen bonds plays an important role in the infrared emissivity value for S-PUU.

Conclusion

Optically active S-PUU with single-handed helical conformation was present, and infrared emissivity values of S-PUU exhibit different rate of increasing in different temperature range. Below 100 °C, in which hydrogen bonds are still associating the polymeric chain, the increasing rate is very small. And when S-PUU is heated up above 100 °C, where the hydrogen bonds have disappeared gradually, the infrared emissivity value is increased at a very large rate. The interchain hydrogen bonds are controlled and changed in the synthesized progress, and they are affected by the helical conformation and the optical activity. This paper provides the possibility to obtain polymers with infrared low emissivity and to adjust the infrared emissivity according to our need by means of designing the polymeric structure.

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