

# Synthesis and Characterization of Novel Optically Active Poly(urethane urea)s: Effect of Left/Right Rotation Conformation

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**ABSTRACT:** Helical *R/S*-poly(urethane urea)s (*R/S*-HPUUs) were synthesized successfully with *R/S*-1,1'-binaphthyl-2',2'-diol, toluene 2,4-diisocyanate, and 1,4-diaminobenzene by a simple hydrogen-transfer addition reaction. The structure and optical properties of *R/S*-HPUUs were investigated systematically with Fourier transform infrared spectroscopy, <sup>1</sup>H-NMR spectra, absorption and circular dichroism, thermogravimetry, differential scanning calorimetry, and X-ray diffraction measurements. Fourier transform infrared spectra showed that all the —NH and carbonyl groups in *R/S*-HPUUs were hydrogen-bonded. *R*-HPUU and *S*-HPUU were two enantiomorphs with wonderful mirror-image symmetry according to circular dichro-

ism spectroscopy analysis. *R/S*-HPUUs exhibited optical activity, and the optical rotations were +54.7 and –60.7°, respectively. *R/S*-HPUUs showed excellent thermal stability because of the plane-bifurcated interchain hydrogen bonds and helical stereostructures according to thermogravimetry, differential scanning calorimetry, and X-ray diffraction analysis. Moreover, the left-handed rotation was more stimulative for the construction of hydrogen bonds than the right-handed rotation, so *S*-HPUU showed higher thermal stability and better crystallizability. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2134–2140, 2009

**Key words:** chiral; optics; FTIR; thermal properties

## INTRODUCTION

Helical polymers existing in genes, proteins, enzymes, and polypeptides are frequently found in nature. The high functionalities of naturally occurring polymers and supramolecules arise from their precisely ordered stereostructures. They have attracted great attention because of their chiro-optical structure and properties, their intriguingly varied 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.<sup>1–5</sup>

Although their helical structure is stabilized by hydrogen bonds, natural helical polymers are easily denaturalized by certain physical factors such as

heat, ultraviolet irradiation, and high pressure and by other chemical factors such as organic solvents. In contrast, synthetic polymers represent much better stability. Therefore, there is a strong need to develop new helical polymers with high stability. In recent years, a series of chiral polybinaphthalene polymers has been prepared enantioselectively from optically active 1,1'-binaphthyl-2',2'-diol (BINOL) because of its axial chirality and configurational stability.<sup>6–13</sup>

Poly(urethane urea)s (PUUs) consisting of alternating segments have been heavily investigated because of their wide range of properties.<sup>14</sup> They have been applied in many fields, such as adhesives, protective coatings, biomaterials, textile fibers, and high-performance elastomers.<sup>15</sup> In our study, novel helical poly(urethane urea)s (HPUUs) were designed and synthesized. These novel HPUUs possess ordered helical stereostructures, outstanding solvent resistance, and high thermal stability. HPUUs are steadied by hydrogen bonds just like natural helical polymers are.

## EXPERIMENTAL

### Materials

*R/S*-BINOL was synthesized and resolved according to the literature.<sup>16,17</sup> Toluene 2,4-diisocyanate

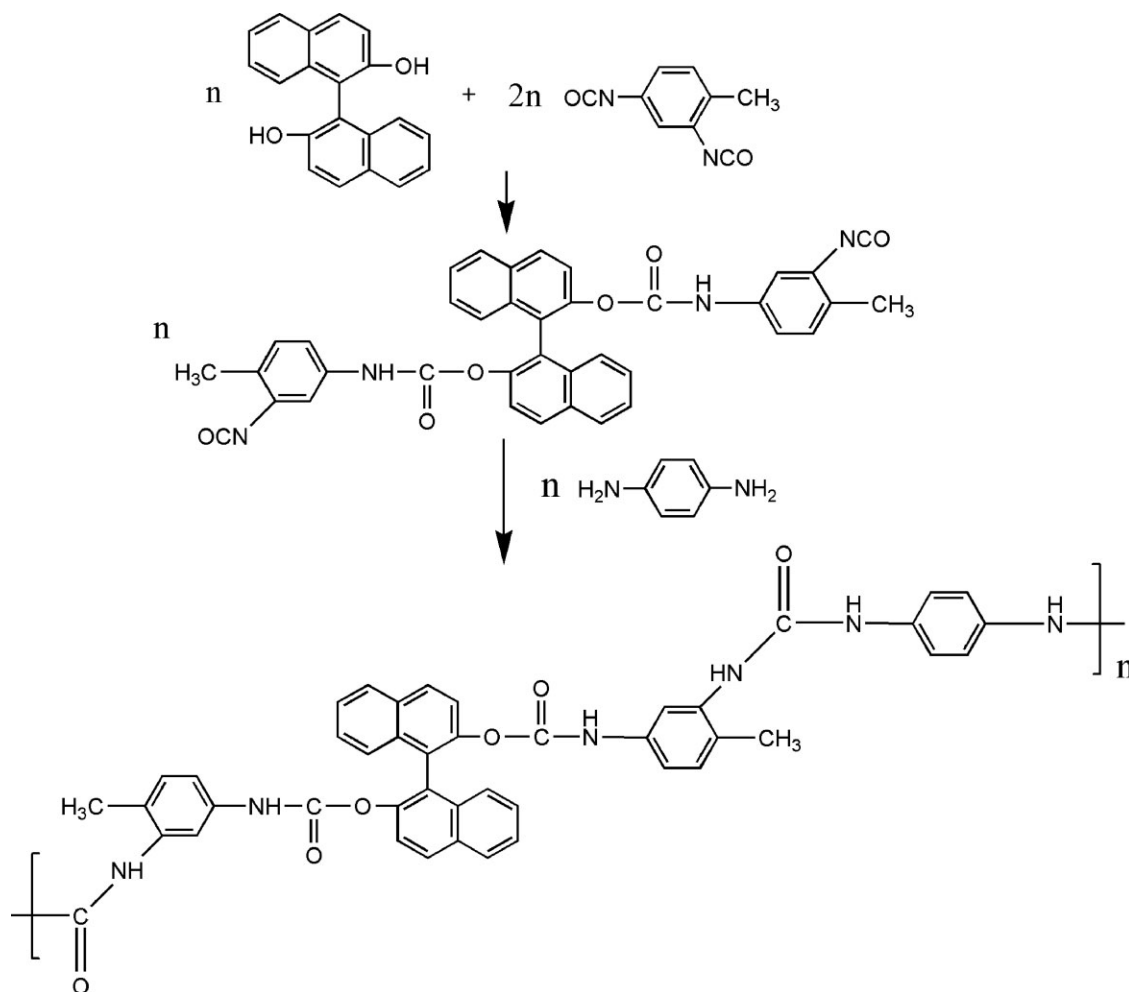
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**Scheme 1** Synthesis of *R/S*-HPUUs.

(TDI; Shanghai Chemicals Co., Shanghai, China) was distilled under reduced pressure. 1,4-Diaminobenzene (PhDA; Shanghai Chemical Reagent Co., Shanghai, China) was used without further purification. *N,N*-Dimethylformamide (DMF; Shanghai Chemical Reagent) was dried over 40-nm molecular sieves for 1 week. All the other solvents were purchased from commercial sources and were analytical-reagent-grade.

### Preparation of *R/S*-HPUUs

*R/S*-HPUUs with right-handed rotation and left-handed rotation configurations were prepared in this study. They were synthesized by a two-step hydrogen-transfer addition polymerization procedure, as shown in Scheme 1.

A 40-mL DMF solution of 1.144 g (4 mmol) of *R(S)*-BINOL was first placed in a 150-mL, four-necked, round-bottom flask equipped with a stirrer, a condenser, and a nitrogen inlet and heated to 100°C gradually. Then, a 20-mL DMF solution of 1.2 mL (8 mmol) of TDI was added dropwise into the reactor

at 100°C and reacted for 5 h to obtain the prepolymer. This process was done with NCO/OH = 2. Then, a 20-mL DMF solution of 0.432 g (4 mmol) of PhDA was added to the prepolymer at 80°C for 8 h. The entire process was conducted under a nitrogen atmosphere and with NCO/OH/NH<sub>2</sub> = 2/1/1. Then, the mixture was put in a vacuum-drying oven at 75°C for 24 h after being distilled under reduced pressure to remove most of the DMF. Then, the product was washed with anhydrous ethanol several times. Further purification could be conducted by the dissolution of the polymer in DMF to precipitate in anhydrous ethanol again.

### *R*-HPUU

<sup>1</sup>H-NMR [dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>, δ)]: 3.39 (s, 6H, CH<sub>3</sub>), 3.18 (s, 2H, CONHPh), 3.26 (s, 2H, PhH), 2.89 (s, 2H, PhH), 2.76 (s, 2H, CONH), 2.33 (s, 2H, PhH), 9.25 (s, 2H, OCONH), 6.94–6.98 (m, 4H, PhH), 7.16–7.18 (m, 2H, ArH), 7.23–7.25 (m, 2H, ArH), 7.33 (m, 2H, ArH), 7.36 (d, 2H, ArH), 7.85–7.86 (m, 2H, ArH), 7.96 (s, 2H, ArH).

## S-HPUU

$^1\text{H-NMR}$  (DMSO- $d_6$ ,  $\delta$ ): 3.39 (s, 6H,  $\text{CH}_3$ ), 3.18 (s, 2H, CONHPh), 3.26 (s, 2H, PhH), 2.89 (s, 2H, PhH), 2.76 (s, 2H, CONH), 2.33 (s, 2H, PhH), 9.25 (s, 2H, OCONH), 6.94–6.98 (m, 4H, PhH), 7.16–7.18 (m, 2H, ArH), 7.23–7.25 (m, 2H, ArH), 7.33 (m, 2H, ArH), 7.36 (d, 2H, ArH), 7.85–7.86 (m, 2H, ArH), 7.96 (s, 2H, ArH).

## Measurements

Fourier transform infrared (FTIR) spectra were carried out on a Nicolet (Nicolet Co., Madison, WI) Magna-IR 750 spectrometer (Nicolet Co., Madison, WI) at room temperature with KBr pellets. FTIR spectra were obtained at a  $1\text{-cm}^{-1}$  resolution and recorded in the region of  $4000\text{--}400\text{ cm}^{-1}$ . The sample and background scanning times were both 32.

$^1\text{H-NMR}$  spectra measurements (in DMSO- $d_6$ ) were recorded on a Bruker DXT 500-MHZ spectrometer (Bruker Optic Co., Fällanden, Switzerland) with tetramethylsilane as the internal standard.

The absorption and circular dichroism (CD) spectroscopy in the ultraviolet–visible region was carried out on a Jasco J-810 spectropolarimeter (Jasco Co., Ltd., Tokyo, Japan) at  $20\text{--}25^\circ\text{C}$ . The *R/S*-HPUU samples were dissolved in DMF with a concentration of  $0.40\text{ g/L}$ .

The optical rotation of *R/S*-HPUUs was measured with a WZZ-2S (2SS) digital automatic polarimeter (Shanghai, China) (the wavelength of the sodium lamp was  $589.44\text{ nm}$ , and the solvent was DMF).

X-ray diffraction (XRD) measurements of *R/S*-HPUUs were recorded with a Rigaku D/MAX-R (Rigaku Co., Tokyo, Japan) with a copper target at  $40\text{ kV}$  and  $30\text{ mA}$ . The power samples were spread on a sample holder, and the diffractograms were recorded in the range of  $5\text{--}70^\circ$  at the speed of  $5^\circ/\text{min}$ .

Thermal analysis experiments were performed with a thermogravimetric analysis (TGA) apparatus (TA Instruments, New Castle, DE) operated in the conventional TGA mode (TA Q-600, TA Instrument) at a heating rate of  $10\text{ K/min}$  in a nitrogen atmosphere, and the sample size was about  $50\text{ mg}$ . The differential scanning calorimetry (DSC) measurements involved a temperature range of  $50\text{--}600^\circ\text{C}$ , a PerkinElmer 7 series differential scanning calorimeter, purging with a nitrogen atmosphere, and chilling with liquid  $\text{N}_2$ . Runs were conducted on samples of about  $10\text{ mg}$  at a heating rate of  $10\text{ K/min}$ .

## RESULTS AND DISCUSSION

## Solubility

The solubility of *R/S*-HPUUs was tested in various polar and nonpolar solvents, as listed in Table I. *R/*

TABLE I  
Solubility of *R/S*-HPUUs in Various Solvents

Solvent	<i>R</i> -HPUU	<i>S</i> -HPUU
DMSO	+	+
DMF	+	+
DMAc	+	+
NMP	+	+
$\text{H}_2\text{O}$	–	–
THF	–	–
$\text{CH}_3\text{CN}$	–	–
$\text{CHCl}_3$	–	–
$\text{CH}_2\text{Cl}_2$	–	–
Acetone	–	–

+, soluble; –, insoluble; DMAc, dimethyl acetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; NMP, *N*-methylpyrrolidone; THF, tetra-hydrofuran.

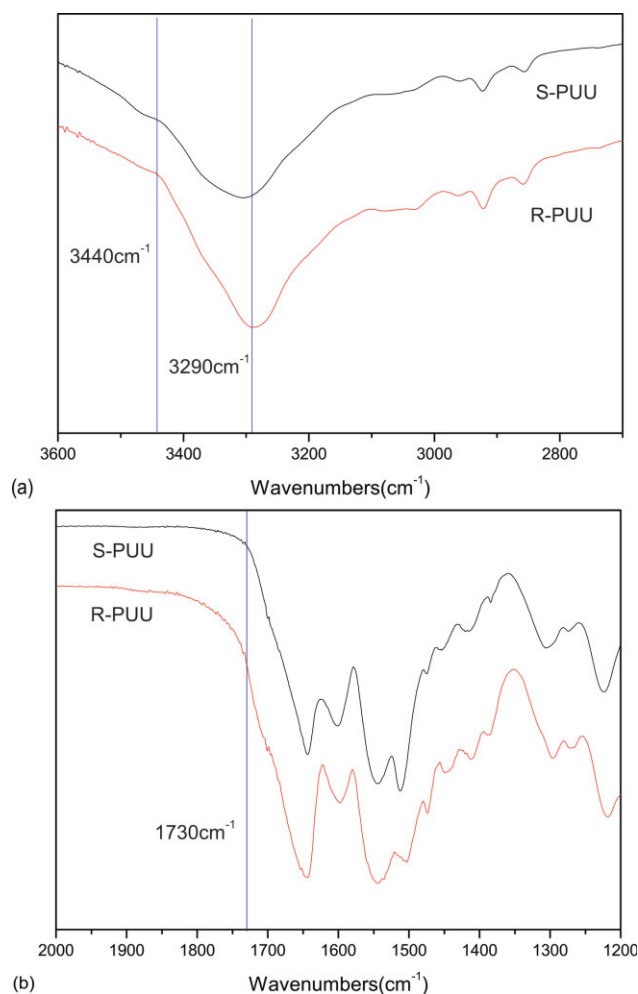
*S*-HPUUs facilitated solubility in polar solvents such as dimethyl sulfoxide and DMF, whereas in  $\text{H}_2\text{O}$ , tetrahydrofuran,  $\text{CHCl}_3$ , and so forth, *R/S*-HPUUs were insoluble. The outstanding solvent resistance of the HPUUs might be due to the presence of hard segments.

FTIR analysis of *R/S*-HPUUs

The structural changes of the polymer are fundamentally important for IR study. The hard-segment structure of PUUs can be characterized by the carbonyl group and NH group located entirely in the hard segment. Participation in hydrogen bonding decreases the frequency of the NH vibration but increases its intensity, making this absorption useful in the study of hydrogen-bond effects.<sup>18</sup>

The FTIR spectra of *R/S*-HPUUs are shown in Figure 1(a,b). As can be seen in Figure 1(a), both *R*-HPUU and *S*-HPUU have the same absorption. The absorption at  $3290\text{ cm}^{-1}$  corresponds to hydrogen-bonded NH groups, and the absorption at  $3440\text{ cm}^{-1}$  corresponds to the free NH groups. The disappearance of absorption at  $3440\text{ cm}^{-1}$  indicates that almost all the NH groups have formed hydrogen bonds. The absorptions at  $2930$  and  $2850\text{ cm}^{-1}$  correspond to asymmetric and symmetric C–H stretching, respectively.

In Figure 1(b), the strong band at  $1643\text{ cm}^{-1}$  is assigned to the C=O groups. No absorption at  $1730\text{ cm}^{-1}$ , which belongs to the free C=O, suggests that all the C=O groups are associated in HPUUs. The frequencies of the peaks for both NH and C=O absorptions suggest that all of the –NH and C=O groups in *R/S*-HPUUs are hydrogen-bonded. The absorption of amide I and amide II appears at  $1545$  and  $1510\text{ cm}^{-1}$ , respectively. The band at  $1210\text{--}1270\text{ cm}^{-1}$  corresponds to C–N with NH (amide III).



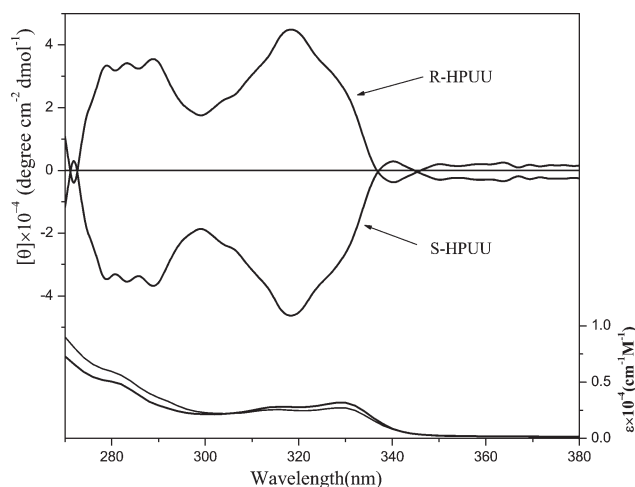
**Figure 1** FTIR spectra of R-HPUU and S-HPUU. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Furthermore, important influencing factors on the intensity of the IR bands are the conformation and configuration.<sup>19</sup> Thus, the intensity of certain groups is not coincident perfectly between R-HPUU and S-HPUU. The right-handed and left-handed rotations make the groups' chemical conditions different. The space effect of polymer structures is very fundamental in the chiral polymers.

### Chiro-optical properties of R/S-HPUUs

The method and accuracy of proving the presence of a helical structure vary, depending on the type of study and the structure of the polymer, and the structural questions can be addressed by optical activity and CD when the helix has an excess screw sense.<sup>20</sup> The chiro-optical properties of the optically active polymers were investigated by absorption and CD spectroscopy.

Figure 2 shows the CD and absorption spectra of R/S-HPUUs. R/S-HPUUs appear to possess a pre-



**Figure 2** CD and absorption spectra of R/S-HPUUs.

dominantly one-handed helical conformation, so they exhibit intense CD signals in the absorption region. R-HPUU appears to have two positive peaks, and S-HPUU has two corresponding negative Cotton effects in the CD spectra. The absorption at 322 nm corresponds to the  $\pi$ - $\pi^*$  transition of the naphthalene rings and a highly rigid backbone in the polymer chains.<sup>21</sup> The broad absorption peaks at about 285 nm are assigned to the  $n$ - $\pi^*$  transition of carbonyl groups.<sup>22-25</sup>

The wonderful mirror-image symmetry between R-HPUU and S-HPUU, presented in Figure 2, suggests that they are two enantiomorphs and have right-handed rotation and left-handed rotation helical structures, respectively.

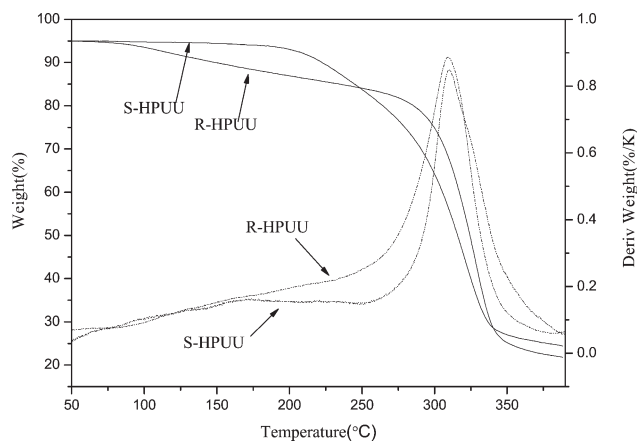
The optical rotation ( $[\alpha]_{589.44}^{20}$ ) values of R/S-HPUUs were measured to obtain further proof that HPUUs have helical structures and optical activity. The  $[\alpha]_{589.44}^{20}$  values of R-BINOL and S-BINOL are +35.1 and -35.4°, but the  $[\alpha]_{589.44}^{20}$  values of their corresponding polymers (R-HPUU and S-HPUU) are enhanced. The  $[\alpha]_{589.44}^{20}$  and maximum absorbency  $[\theta]$  ( $[\theta]_{\max}$ ) values of R/S-HPUUs are listed in Table II. The  $[\alpha]_{589.44}^{20}$  and  $[\theta]_{\max}$  values of R/S-HPUUs are nearly equal in absolute value, and the higher absolute values of S-HPUU show agreement between  $[\alpha]_{589.44}^{20}$  and  $[\theta]_{\max}$ .

On the basis of these analyses, R/S-HPUUs are optically active polymers and have helical structures. R-HPUU and S-HPUU are two enantiomorphs with wonderful mirror-image symmetry. The optical

**TABLE II**  
 $[\theta]_{\max}$  and  $[\alpha]_{589.44}^{20}$  Values of R/S-HPUUs

Polymer	$[\theta]_{\max}$ ( $^{\circ}$ $\text{cm}^{-2}$ $\text{dmol}^{-1}$ )	$[\alpha]_{589.44}^{20}$ ( $^{\circ}$ )
R-HPUU	4.48	+54.7
S-HPUU	-4.62	-60.7





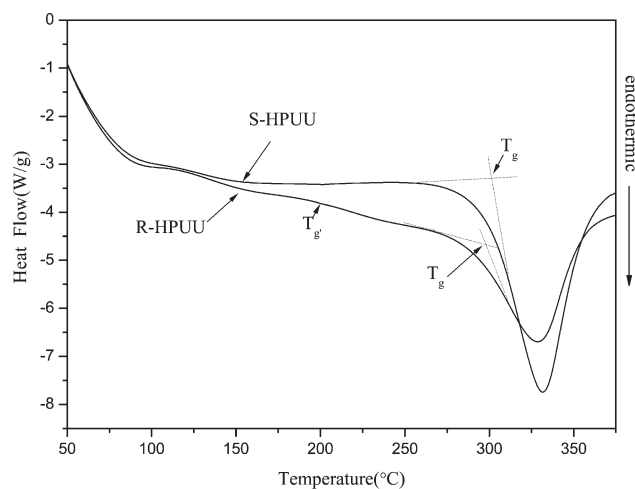
**Figure 3** TG and DTG curves of R/S-HPUUs.

rotation of S-HPUU is a little higher than that of R-HPUU in absolute value.

### Thermal properties of R/S-HPUUs

It has been proposed that the thermal degradation of PUUs is primarily a depolycondensation process.<sup>18</sup> The thermal stability of R/S-HPUUs was investigated with TGA. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves for the formulations are presented in Figure 3. The initial decomposition occurred at 200°C for S-HPUU and at 125°C for R-HPUU.

R-HPUU and S-HPUU have the same molecular formula, so the peculiarity in conformation is the origin of the different thermal stabilities in different temperature ranges. The left-handed rotation helical structure in S-HPUU is the favorable factor in thermal stability below 250°C, and when the temperature reaches 250°C, R-HPUU and S-HPUU are reversed in the thermal stability. This suggests that the right-handed one has more influence on the thermal stability above 250°C. This effect also occurs below 250°C, being just weaker than the impact of the left-handed rotation. The right-handed and left-handed ones are exactly alike in the backbone, and the only differences are the direction and condition of side bifurcations such as C=O, N—H, and naph-



**Figure 4** DSC curves of R/S-HPUUs ( $T_g$  = glass-transition temperature;  $T_{g'}$  = lower glass-transition temperature).

thalene rings. This could cause the otherness of the interchain hydrogen bonds and the steric affection. The left-handed rotation is more stimulative for the construction of hydrogen bonds than the right-handed rotation. Thus, S-HPUU is more thermally stable than R-HPUU. Above 250°C, the hydrogen bonds are broken off, and the right-handed rotation makes R-HPUU more stable than S-HPUU.

DSC scans (Fig. 4) show that S-HPUU exhibits a single glass-transition temperature, but R-HPUU has two glass-transition temperatures, a lower one and a higher one. The thermal property data for R/S-HPUUs are listed in Table III. Below the lower glass-transition temperature, R-HPUU has a slow endothermic transition, which is related to the breakup of interurethane hydrogen bonds.<sup>26</sup> R/S-HPUUs exhibit a prominent endothermic transition at 335°C, which can be ascribed to the melting of microcrystalline regions within the hard microdomains for R-HPUU and to both the breakup of interchain hydrogen bonds and the melting of microcrystalline regions within the hard microdomains for S-HPUU. Both R-HPUU and S-HPUU exhibit the same thermal decomposition temperature of the polymer backbone at 335°C, but R-HPUU has

**TABLE III**  
Thermal Properties of R/S-HPUUs

Polymer	$T_{g'}$ (°C)	$T_g$ (°C)	$T_d$ (°C)	Major weight-loss transition (°C)	Heat flow range (°C)
S-HPUU	—	300	335	200–330	275–350
R-HPUU	200	298	335	125–330	150–350

$T_d$ , thermal decomposition temperature of the polymer backbone;  $T_g$ , glass-transition temperature;  $T_{g'}$ , lower glass-transition temperature.

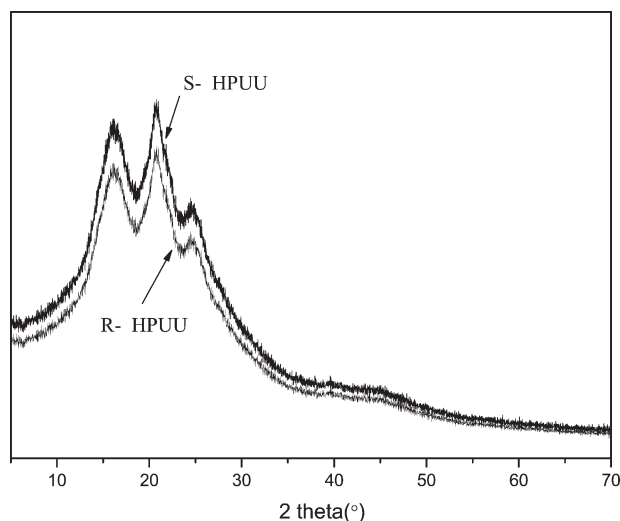


Figure 5 XRD patterns of *R/S*-HPUUs.

a lower and inconspicuous glass-transition temperature at 298°C, and *S*-HPUU has one at 300°C. As can be seen in Table III, the left-handed rotation is more stimulative for the formation of hydrogen bonds than the right-handed rotation in *R/S*-HPUUs.

#### XRD analysis and hydrogen-bond analysis

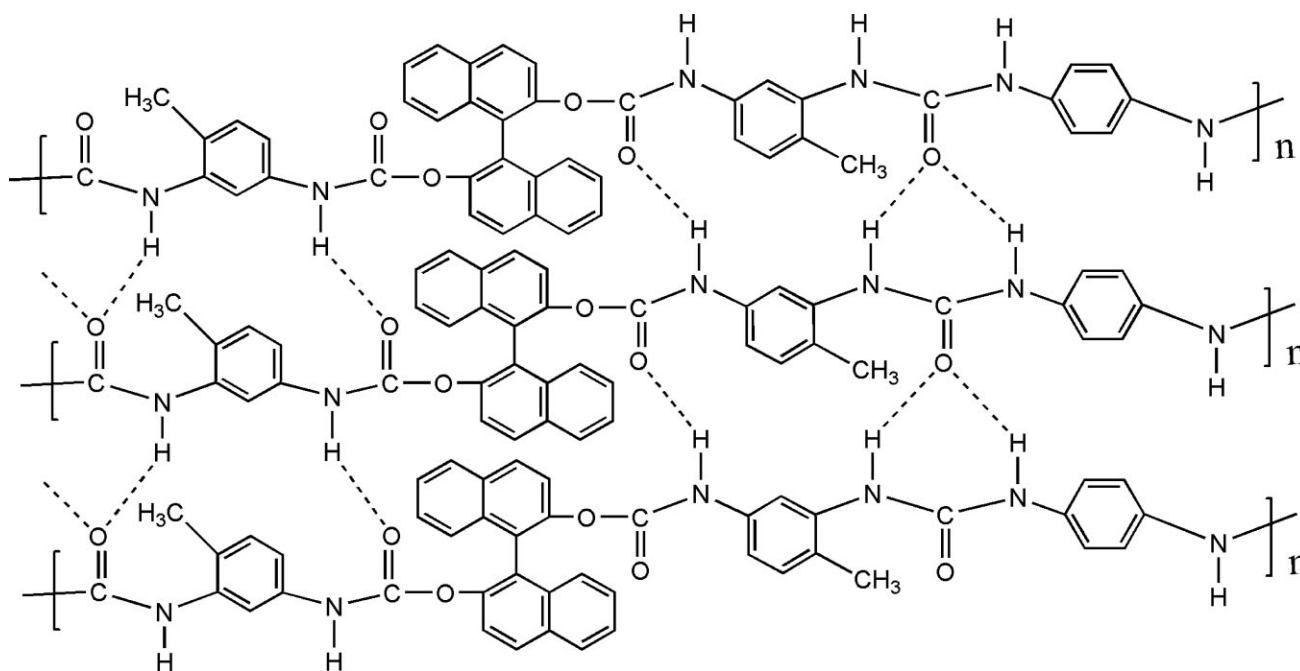
Figure 5 displays the XRD patterns of *R/S*-HPUUs. The XRD patterns show that *R/S*-HPUUs are partially crystalline in nature. This may be due to the presence of hard segments such as naphthalene

rings and more importantly to the presence of interchain hydrogen bonds. The crystallizability of *S*-HPUU is better because of the more orderly hydrogen bonds resulting in the interchain effects in *S*-HPUU. According to the Bragg equation,

$$2d \sin \theta = \lambda$$

where  $d$  is the crystal layer spacing,  $\theta$  is the angle of incidence ( $^{\circ}$ ), and  $\lambda$  is the X-ray wavelength. It can be obtained from the strongest diffraction peaks at  $2\theta = 20.91^{\circ}$  in Figure 5 that the crystal layer spacings of *R/S*-HPUUs are 4.24 nm.

The interchain hydrogen bonds of *R/S*-HPUUs were further analyzed according to FTIR, TGA/DSC, and XRD. As shown in the FTIR spectra, all the  $-\text{NH}$  and  $\text{C}=\text{O}$  groups in HPUUs are hydrogen-bonded. The rate of  $\text{C}=\text{O}$  and  $\text{N}-\text{H}$  in *R/S*-HPUUs is 4/6, so the hydrogen bonds are not arranged in a simple formation of 1/1. The crystal layer spacing (4.24 nm) at about  $20.91^{\circ}$  is related to the plane-bifurcated hydrogen-bond structures. Therefore, the structures of interchain hydrogen bonds could be arrayed in a special way (Scheme 2). Because of the plane-bifurcated hydrogen bonds, *R/S*-HPUUs display excellent thermal stability and good crystallizability. The plane-bifurcated hydrogen bonds are much firmer than normal hydrogen bonds between helical chains, and they make the helical structure more locked in, avoiding distortion and degradation. The three-dimensional network helical structures



Scheme 2 Structures of hydrogen bonds in *R/S*-HPUUs.

could be constructed in *R/S*-HPUUs, and it shows potential applications in chiral and optical devices.

### CONCLUSIONS

*R*-HPUU and *S*-HPUU have been synthesized successfully with *R*-BINOL and *S*-BINOL, and they possess outstanding solvent resistance. *R*-HPUU and *S*-HPUU are two enantiomorphs with wonderful mirror-image symmetry. The  $[\alpha]_{589.44}^{20}$  values are +54.7 and  $-60.7^\circ$ , respectively. *R*-HPUU and *S*-HPUU have the same thermal decomposition temperature of the polymer backbone (335°C), but *S*-HPUU has higher thermal stability at a lower temperature. *S*-HPUU displays a single glass-transition temperature at 300°C, whereas *R*-HPUU exhibits two glass-transition temperatures at 300 and 295°C. The left-handed rotation structure is more stimulative for thermal stability than the right-handed rotation below 250°C because of both conformation and interchain hydrogen bonds, and they are reversed above 250°C; this can be attributed to the breaking of hydrogen bonds. The crystallizability of *S*-HPUU is better than that of *R*-HPUU because of the more orderly hydrogen bonds resulting in the interchain effects of *S*-HPUU. The interchain hydrogen bonds are the plane-bifurcated structures, which are more stable and in-locked to the helical structures. *R/S*-HPUUs show optical activity, excellent thermal stability, and network structures, which provide the foundation for many potential applications.

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