

# Preparation and Characterization of Novel Optically Active Polyurethanes Containing 1,1'-binaphthol

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**ABSTRACT:** Novel optically active polyurethanes (BPUs) based on chiral 1,1'-binaphthol were synthesized via direct hydrogen transfer addition polymerization. The polymers were analyzed by FTIR,  $^1\text{H}$  NMR, DSC-TGA, CD spectra. The results showed that the specific rotation  $[\alpha]_D^{25}$  were  $-78.0^\circ$  and  $+54.6^\circ$  for the S-BPU and R-BPU respectively, and these polymers showed better thermal stability. The circular dichroism spectra of the chiral polymers were almost identical except that they gave opposite signals at each wavelength, and the infrared emissivity

values of the S-BPU and R-BPU were 0.618 and 0.682, they displayed low infrared emissivity. Meantime the polymers implanted with PEG group exhibit better solubility, however thermal stability reduced to some extent. Some properties of the new optically active polyurethanes were reported. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2190–2196, 2010

**Key words:** polyurethanes; chiral; binaphthol; infrared emissivity

## INTRODUCTION

Polyurethanes (PUs) have been extensively studied as high performance polymers in recent years for their unique abrasion resistance and mechanical performance, especially that polymers were widely used as basement materials in absorption materials or as binder in stealth coating,<sup>1,2</sup> however the conventional PUs are known to exhibit poor thermal stability, which limits their applications.<sup>3</sup> For example, the acceptable mechanical properties disappear above 80–90°C, Attempts to improve the thermal stability of PUs have been made over a long period.<sup>4,5</sup>

Optically active polymer as one novel functional materials gained large development in the recent years, and they are widely used in asymmetric synthesis, medicine, chiral resolution, nonlinear optical materials and so on.<sup>6,7</sup> Optically active 1,1'-binaphthyl has been extensively used as the starting materials for obtaining optically active polymer for its non-coplanar and torsion con-

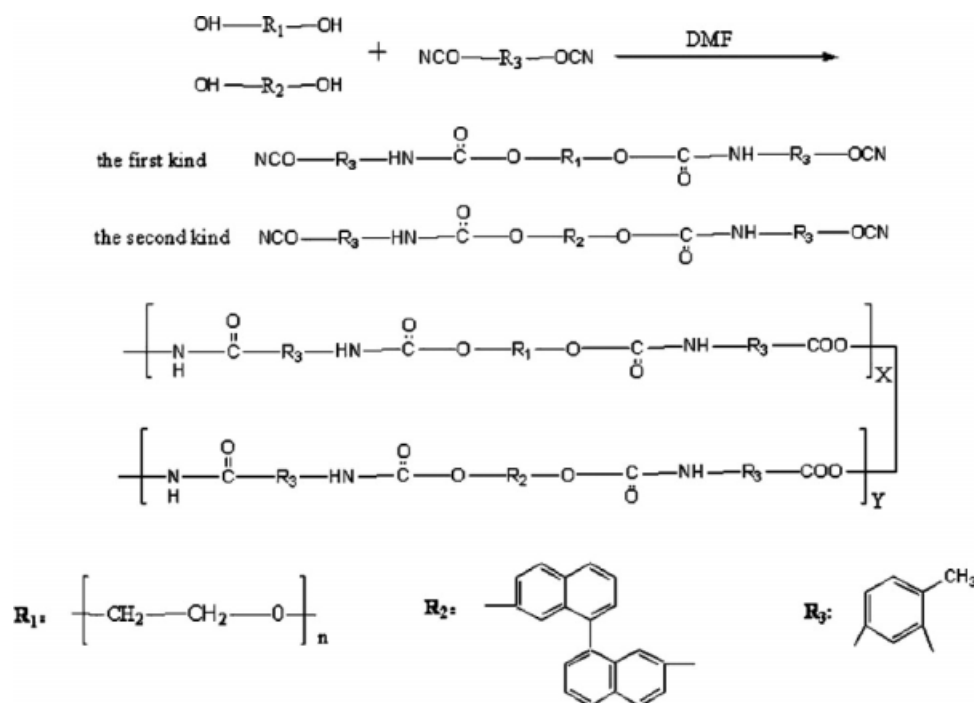
struction,<sup>8</sup> furthermore the 1,1'-binaphthyl group with its almost rigid structure can also improve the polymer thermal stability, over the past several years, Cheng's groups has devoted sustained efforts to investigate the synthesis, structure, and properties of chiral polymer based on binaphthol group,<sup>9,10</sup> for example Song et al.<sup>11</sup> reported the preparation of optically active polybinaphthyl from chiral (R) or (S)-1,1'-binaphthyl and oxadiazole by Heck Reaction and found that the novel polymers had strong blue fluorescence, which have potential application in the materials of fluorescent. Gong<sup>12,13</sup> et al. also synthesized cyclic and linear poly(aryl-esters) and poly(ether-sulfone)s based on 1,1'-bi-2-naphthol and the different cyclic polymers had been separated from their homologous compounds by TLC successfully. Optically active polyurethane is a kind of promising materials, its chiroptical effect can be combined with good mechanical properties and abrasion resistance. The general method to obtain optically active polyurethanes is through hydrogen transfer addition polymerization, which selected natural carbohydrates or polybasic alcohol or the derivants of amino acid and isocyanate as raw materials.<sup>14–17</sup> However seldom researches had been reported that binaphthol as a chiral agent was incorporated into polyurethanes. In this article, the chiral binaphthol groups were introduced into the optically active polyurethanes, the properties of the polymer were also studied.

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Scheme 1 Route of synthesis of the novel polyurethanes.

## EXPERIMENTAL

### Material

The monomer (S)-1,1'-binaphthol and (R)-1,1'-binaphthol were synthesized as previously reported.<sup>18–20</sup> Toluene diisocyanate (TDI, mixture of 80% 2,4 and 20% 2,6 isomers, Merck was purchased from Lingfeng Chemical Reagent and distilled before used. Polyethylene glycol 400 was dried under vacuum at 80°C for 6 h, DMF was purified, dried, and stored under nitrogen. *N,N*-dimethyl acetamide (DMAC), *N*-methyl-2-pyrrolidone (NMP) and other solvents were from commercial A.R. grade and used as received.

### Measurements

FTIR spectra were recorded on a Perkin–Elmer 1750 instrument. The <sup>1</sup>H and <sup>13</sup>C NMR (500 MHz) spectra were obtained using a Varian NMR Gemini 500 spectrometer, specific rotation measurements were accomplished at 25°C on DMF solutions (C = 0.25g/dL) with a WZZ-2S digital polarimeter. Circular dichroism (CD) spectra were carried out at 25°C in DMF solutions on a Jasco 810A dichrograph. TG and DSC analysis were performed on Perkin–Elmer TG-7 thermogravimetric analyzer with heating rate of 10°C/min in air. Inherent viscosities of polymers were determined for solutions of 0.5 g/dL in DMF at 30°C using Ubbelohde viscometer.

### Synthesis of polyurethanes

Hydrogen transfer addition polymerization is a versatile method for preparation of polyurethanes, using this method the optically active polyurethanes containing binaphthol groups was synthesized as shown Scheme 1, firstly an appropriate amount of chiral binaphthol (or PEG400 or the mixture of binaphthol and PEG400) was dissolved in 10 mL of DMF to form solution, under N<sub>2</sub> gas at 80°C. Then, one equivalent molar quantities of TDI (6 mmol) was added dropwise into solution under stirring. The solution was heated and kept at 100°C for 16 h with constant stirring and cooled to room temperature. To this solution, NaOH was added until test reaction for the chiral binaphthol was negative. The mixture was poured into 150 mL of ethanol, the pH of the solution was adjusted to neutrality by adding drops of hydrochloric acid (the concentration of hydrochloric acid is 37%). The resulted material was then filtered and washed three times with ethanol and subsequently dried in vacuum at 80°C. The obtained polymers were dissolved in DMF and precipitate in ethanol for purification. Characterizations were as follow:

R-BPU(yield 62.3%  $[\alpha]_D^{25}$ :+54.6°);  $\nu_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3279.1, 3056.3, 2925.2, 1649.5, 1544.7, 1501.0, 1387.4, 1234.5, 1212.6, 815.0, 753.9 (Fig. 1). <sup>1</sup>H-NMR in DMSO- $\delta$  3.36 (s, 3H, CH<sub>3</sub>), 3.25 (s, 1H, Ph-H), 2.74 (s, 1H, OCONH), 2.51 (s, 1H, Ph-H), 9.25 (s, 1H, Ph-H), 6.93–7.05 (m, 2H, Ar-H), 7.15–7.18 (m, 2H, Ar-H), 7.22–7.24 (m, 2H, Ar-H), 7.33–7.35 (d, 2H, Ar-H),

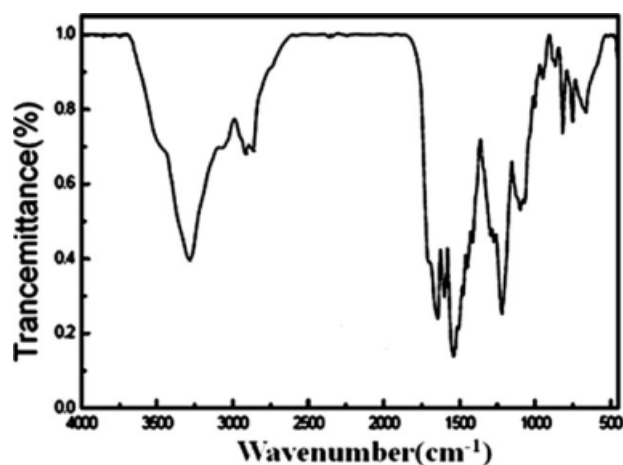


Figure 1 FTIR spectra of R-BPU.

7.84–7.87 (m, 2H, Ar-H), 7.96 (s, 2H, Ar-H). (Fig. 2).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  152.3, 153.0, 133.4, 130.3, 129.5, 129.8, 128.2, 127.0, 125.9, 124.7, 125.6, 124.1, 122.9, 119.7, 116.2, 86.9, 58.5, 52.0.

S-BPU (yield 60.4% [ $\alpha$ ] $_D^{25}$ :  $-78.0^\circ$ );  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3283.5, 3060.7, 2920.9, 1649.5, 1544.7, 1501.0, 1431.1, 1273.8, 1217.0, 823.8, 753.0.  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  3.36 (s, 3H,  $\text{CH}_3$ ), 3.25 (s, 1H, Ph-H), 2.89 (s, 1H, OCONH), 2.74 (s, 1H, OCONH), 2.51 (s, 1H, Ph-H), 9.24 (s, 1H, Ph-H), 6.93–7.05 (m, 2H, Ar-H), 7.15–7.18 (m, 2H, Ar-H), 7.22–7.24 (m, 2H, Ar-H), 7.33–7.35 (d,

2H, Ar-H), 7.84–7.87 (m, 2H, Ar-H), 7.96 (s, 2H, Ar-H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  152.8, 152.1, 133.7, 130.3, 129.7, 129.5, 128.6, 128.0, 127.0, 126.9, 125.8, 125.6, 124.2, 122.9, 119.5, 116.3, 87.1, 58.0, 52.2.

## RESULTS AND DISCUSSION

### The effect of optical purity on the specific rotation of the polymers

The effect of optical purity on the specific rotation of the polymers was studied in Figure 3, and the result showed that the specific rotation of the polymer kept increasing with the optical purity, it may be explained that the increment of the optical purity caused a bigger chiral groups density. Moreover as it could be seen from Figure 3, the rotation orientation of the polymer coincide with the binaphthol monomer, which seemed that the rotation ability of the polymer mostly came from the monomer.

### The effect of optical purity on the intrinsic viscosity of the polymers

The effect of optical purity on the intrinsic viscosity of the polymers is shown in Figure 4. The inherent viscosity was crescent with the optical purity, it could be explained the flowing aspects. Firstly, in the polymerization process, when the optical purity

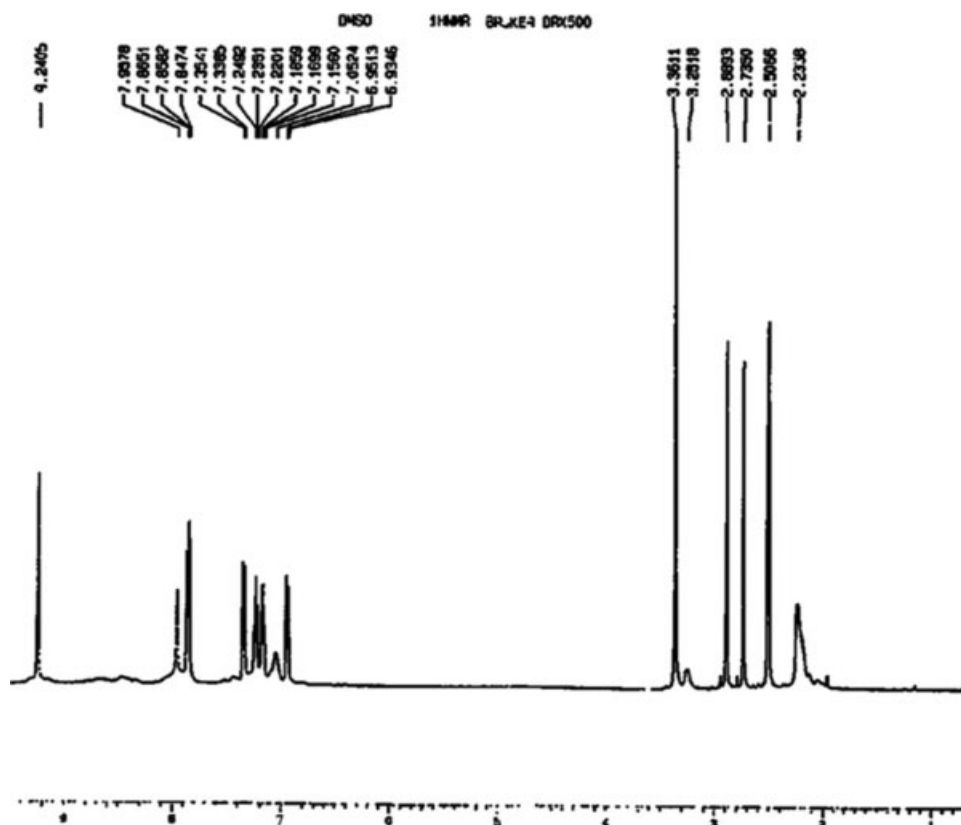
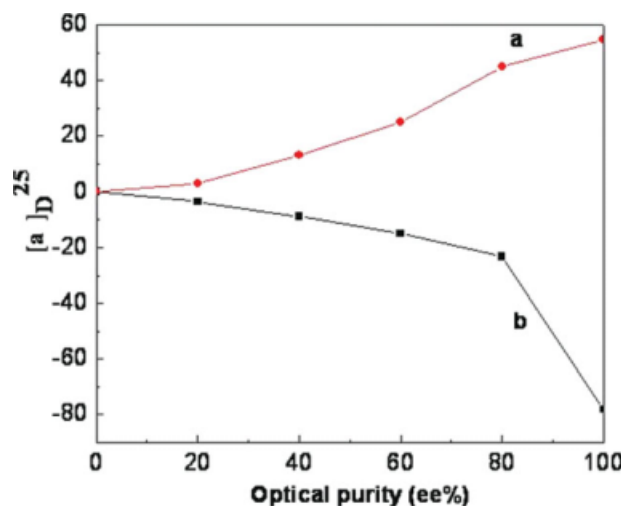
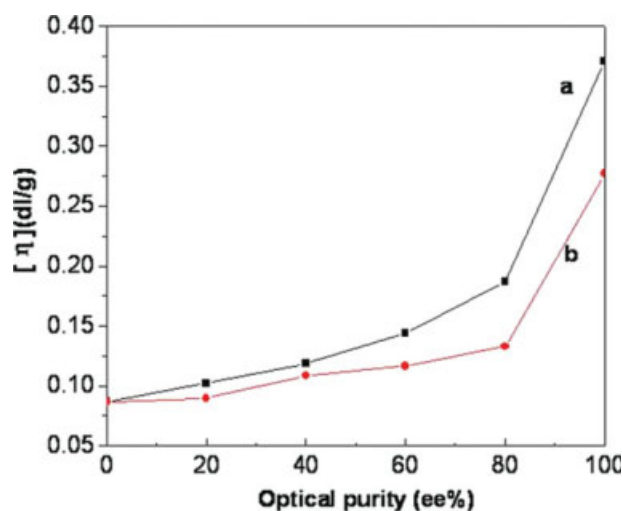


Figure 2  $^1\text{H}$ NMR spectra of R-BPU.



**Figure 3** The optical purity of the BINOL effects on specific rotation of (a) R-BPU and (b) S-BPU. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

was low, the reactant contained some racemic monomer, two kinds of different and unequal helix chains will be obtained, the helix chains with converse conformation will get a spatial complement, the fluid volume in solution state connected to the inherent viscosity would get smaller, thus the polymer exhibit a low intrinsic viscosity. On the other hand, the polymer could easily form single helix chain while the binaphthol kept a high optical purity, moreover the binaphthol units in the polymer were rigid structures, which caused a bigger fluid volume in solution state, accordingly the polymer showed high inherent viscosity. According to Figure 4, the inherent viscosity of R-polymer is bigger than



**Figure 4** The optical purity effects on the intrinsic viscosity of (a) R-BPU and (b) S-BPU. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
The Effect of the Charging-up Mode on the Specific Rotation

No.	1	2	3
[α] <sub>D</sub> <sup>25</sup>	-15.2°	-11.3°	-10.2°

the S-polymer with the same optical purity that maybe attributed to different polymer chains. The inherent viscosity of the BPUs were in the range of 0.08–0.35dL/g, considering inherent viscosity of polymer of polymer solution as a measure of the molecular weight, the BPUs exhibited low to moderate molecular.

### An optimized method for charging-up

To gain an optimized method for charging-up, an investigation was carried out under three methods and the result can be seen in Table I. If method 3 was selected, the PEG400 with much higher activity of alcohol hydroxyl group than the phenol hydroxyl groups could react with TDI quickly, then only a few active –NCO groups were left to react with binaphthol, Meanwhile the spatial resistance to react between longer chains and binaphthol monomer was bigger than the smaller chains, thus only few binaphthol could keep on reacting with the pre-formed polymer chains. However method 1 was better, there were enough active –NCO groups left and the resistance of the polymer chains was much smaller, combined with the two reasons, the chiral polyurethanes chains could be obtained, method 1 was a better choice for this preparation.

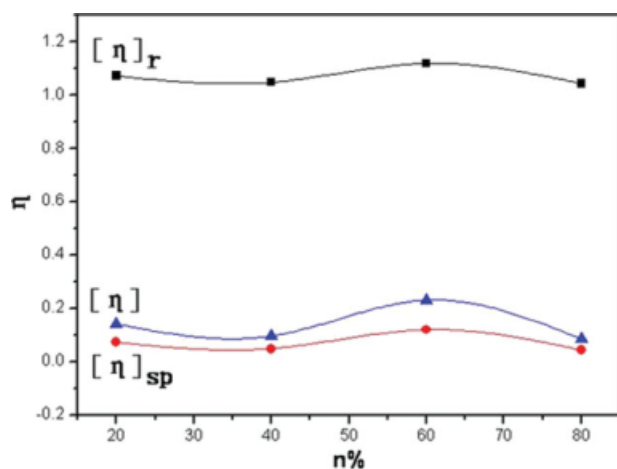
### A better monomer ratio

In an attempt to obtain a better monomer ratio for PBPU, investigations were carried out at different monomer ratio. The results were collected in Table II, the specific rotation [α]<sub>D</sub><sup>25</sup> of the polymer decreased with the increasing of PEG400, it might be explained that the number of chiral binaphthol groups in the polymer chains had reduced. However the increment of the PEG400 didn't keep line with the decrease for the specific rotation of the polymer. It was coincided with the complexity of the

**TABLE II**  
The Effect of the Monomer Ratio on the Specific Rotation

n%	100	80	60	40	20
S-BPU	-78.0°	-15.2°	-14.9°	-14.6°	-11.4°
R-BPU	+45°	+20°	+18.0°	+7.6°	+4.3°

n% represents the ratio of the monomer. Nbinol/(R-Nbinol + S-Nbinol).



**Figure 5** The effect of the monomer ratio on the intrinsic viscosity  $[\eta]_{sp}$  represents viscosity number;  $[\eta]_r$  represents logarithmic viscosity number;  $[\eta]$  represents inherent viscosity number;  $n\%$  represents the ratio of the monomer: Nbinol/(R-Nbinol +S-Nbinol). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

polymerization process. Meantime, at the beginning of the polymerization the reduced extent of the specific rotation of polymer was much bigger, this phenomenon could be guessed that the hydrogen groups of the PEG400 had higher activity, they got a priority when reacted with the TDI monomer.

#### The monomer ratio effect on the inherent viscosity of the polymer

Figure 5 showed the monomer ratio effect on the inherent viscosity of the polymer, and as it can be noted from Figure 5, there was no exact relationship between the intrinsic viscosity and the ratio of the monomer, but when the ratio (PEG/BINOL) got to 60%, the polymer exhibited a higher intrinsic viscosity, that suggested it was a better matched ratio of PEG and binaphthol. Meantime, the intrinsic viscosity of the polymer didn't increase when adding lots of PEG400 as expected.

#### The solubility

The solubility of BPU in different solvents was studied (Table III). All the BPU showed good solu-

bility in amide type solvents, such as DMF, DMAC, NMP, and so on. However the BPU remained intact in some solvents, such as water, methanol, chloroform, and dichloromethane, this might have arisen from the fact that the BPU possessed a higher structural regularity, which would facilitate a closer chain packing. It also can be noted that the PBPU showed better solubility in comparison to BPU, this behavior may have resulted from the introduction of an aliphatic group in the polymer backbone, which increased chain flexibility.

#### The thermal behaviors

The thermal behaviors of the resulted BPU and PBPU were examined by TG and DSC (Figs. 6 and 7), the R-BPU and S-BPU showed one glass transition as well as melting and its significant weight loss started at 305.6 and 323.6°C. Meanwhile, the TGA traces of BPU exhibited a two-step degradation including a small weight loss of 100–150°C followed by a significant break in the range 250–400°C. On the other hand, the S-PBPU showed two glass transitions, however the R-PBPU had no obvious glass transition, and their initial weight loss occurred at 282.9 and 285.5°C respectively. TGA plot of R-BPU is similar to that of S-BPU, and the PBPU showed similar transitional trend combined the range 50–130°C and 150–300°C. Therefore, it may confirm that the BPU only contained binaphthol groups was more stable than the PBPU bearing aliphatic groups.

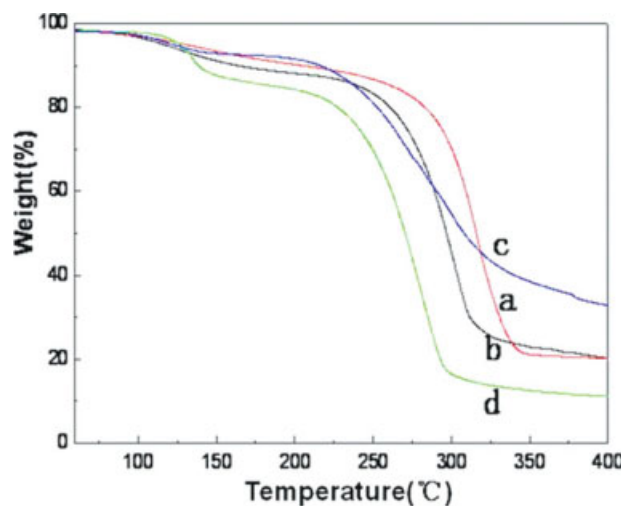
#### Circular dichroism

The CD measurement was carried out in DMF with a concentration of  $4 \times 10^{-2}$  g/dL and the CD curves of BPU and PBPU were showed in Figure 8, all the detected samples had their absorption in the range of 270–360 nm and as expected from their rotation, the cotton curves were complete mirror images, the CD spectrum of R-BPU with positive chirality exhibited two broad positive absorption peaks at 323.0 nm and 289.6 nm and the S-BPU with the negative chirality exhibited two broad negative absorption peaks at 322.6 nm and 289.4 nm, these absorption peaks were attributable to the  $n \rightarrow \pi^*$  transition of

**TABLE III**  
Solubility Behavior of BPU and PBPU

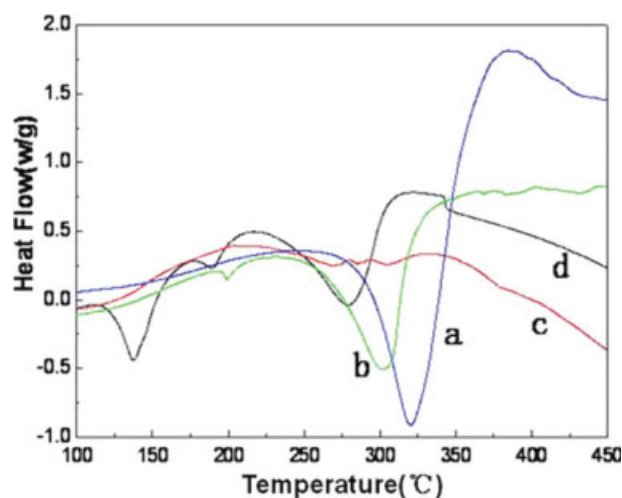
Polymer	NMP	DMF	DMAC	DMSO	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	THF	Toluene
R-BPU	+	+	+	+	–	–	–	–
S-BPU	+	+	+	+	+	+	+	+
R-PBPU	+	+	+	+	–	–	–	–
S-PBPU	+	+	+	+	+	+	+	+

“+”represents soluble “–”represents insoluble

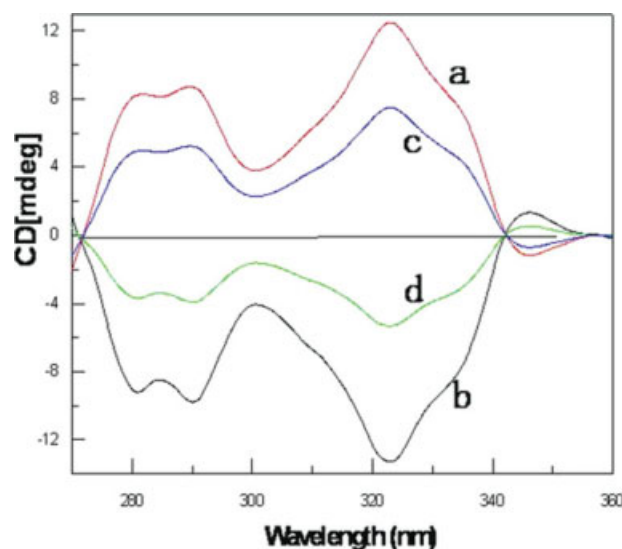


**Figure 6** TGA curves of (a) R-BPU, (b) S-BPU, (c) R-PBPU, and (d) S-PBPU. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the carbonyl groups and the  $\pi^* \rightarrow \pi^*$  transition of the aromatic groups in the binaphthol units,<sup>12,13</sup> additionally, the molecular ellipticity of R-BPU is much bigger than the polymer of S-BPU, which coincided with the optical rotation differences. As shown in Figure 8, the observations of PBPU were similar to BPUs, suggesting the same rigidity of the polymer backbone, however there were still some differences, for instance the absorption peaks of R-PBPU and S-PBPU, respectively, exhibited at 325.2 nm, 291.5 nm, and 324.7 nm, 292.6 nm, and the PBPU showed a much smaller ellipticity of PBPU compared to the BPUs.



**Figure 7** DSC curves of (a) R-BPU, (b) S-BPU, (c) R-PBPU, and (d) S-PBPU. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8** CD spectra of (a) R-BPU, (b) S-BPU, (c) R-PBPU, and (d) S-PBPU (in DMF). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Infrared emissivity

Most polymers have strong absorption in infrared band for its functional groups vibration, thus general polymers show a high infrared emissivity in thermo-infrared band. However there was some interesting facts to be found, the infrared emissivity value of the racemic BPU obtained was 0.921, but the value of the polyurethanes from optical active binaphthol reduced to 0.682 and 0.618 respectively, it was likely assumption that the chiral binaphthol groups into the polyurethanes may effect the infrared emissivity, the exact mechanism will be determined in the near future, the result was very pregnant in the composite materials for stealth field.

### CONCLUSIONS

We have described the synthesis and the properties of a novel optically active polyurethanes based on chiral binaphthol via direct hydrogen transfer addition polymerization. A better reaction conditions were selected, the specific rotation  $[\alpha]_D^{25}$  were  $-78.0^\circ$  and  $+54.6^\circ$  for the S-BPU and R-BPU, respectively, and these polymers showed better thermal stable. The CD spectra of the chiral polymers were almost identical, except that, they gave opposite signals at each wavelength, Meantime the polymers implanted with PEG group exhibit better solubility, however thermal stability reduced to some extent, and the infrared emissivity values of the S-BPU and R-BPU were 0.618 and 0.682, they displayed low infrared emissivity, which were expected to have potential application in the field of steals materials.

## References

1. Peng, C. H.; Wang, H. W.; Kan, S. W. *J Magn Magn Mater* 2004, 284, 113.
2. Fu, B. F.; Wang, L. *Dev Appl Mater* 2000, 6, 38.
3. Szycher, M. *Polyurethane Handbook*; CRC Press: Boca Raton, 1999.
4. Fabris, H. J. *Advances in Urethane Science and Technology*; Technomic: Westport, CT, 1976; p 89.
5. Hamid, Y.; Mehdi, B.; Feriedoun, N. K. *Eur Polym J* 2000, 36, 2207.
6. Ng, M. K.; Chow, H. F.; Chan, T. L.; Thomas, C. W. M. *Tetrahedron Lett* 1996, 37, 2979.
7. Yu, H. B.; Hu, Q. S.; Pu, L. *Tetrahedron Lett* 2000, 41, 1681.
8. Pu, L. *Chem Rev* 1998, 98, 2405.
9. Cheng, Y. X.; Chen, L. W.; Zou, X. W.; Song, J. F.; Wang, Z. L. *Polymer* 2006, 47, 435.
10. Cheng, Y. X.; Song, J. F.; Zou, X. W. *Polymer* 2006, 47, 6598.
11. Song, J. F.; Cheng, Y. X.; Chen, L. W. *Eur Polym J* 2006, 42, 663.
12. Gong, A. J.; Chen, Y. M.; Zhang, X. *Tetrahedron: Asymmetry* 1998, 9, 4175.
13. Gong, A. J.; Liu, W. H.; Chen, Y. M.; Zhang, X. *Tetrahedron: Asymmetry* 1999, 10, 2079.
14. Chen, C. F.; Su, Q.; Chen, Y. M.; Xi, F. *Chin J Polym Sci* 1999, 17, 371.
15. Nobuhiro, K.; Yuuji, K.; Takeshi, E. *J Polym Sci Part A: Polym Chem* 1996, 34, 2173.
16. Hiroto, K.; Atsushi, N.; Junichi, I.; Takeshi, E. *Macromolecules* 2001, 34, 5355.
17. Atsushi, N.; Junichi, I.; Hiroto, K.; Takeshi, E. *J. Polym Sci Part A: Polym Chem* 2004, 42, 1143.
18. Ding, K. L.; Wang, Y.; Zhang, L. J.; Wu, Y. J.; Matsuura, T. *Tetrahedron* 1996, 52, 1005.
19. Colonna, S.; Re, A.; Wynberg, H. J. *Chem Soc Perkin Trans1* 1981, 1, 542.
20. Hu, Q. S.; Dilrukshi, V.; Pu, L. *Tetrahedron: Asymmetry* 1995, 6, 2123.