

# Synthesis and Characterization of Aromatic/Aliphatic Co-polyureas

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**ABSTRACT:** In the present work, a series of aromatic/aliphatic co-polyureas have been synthesized from 4,4-diphenylmethane diisocyanate (MDI), *m*-phenylene diamine (*m*-PDA), and 1,6-diaminohexane (HDA) in DMAc by a two-stage solution polymerization route. Characterizations of the polyurea products have been carried out by <sup>1</sup>H-nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopic techniques. Thermal properties of the polyurea samples have been investigated by differential scanning calorimetry and thermogravimetric analysis. The mechanical properties of the polyurea samples have been measured. The results show that the polyurea samples with the expected structure have been synthesized. The results of DSC analysis

show the glass transition temperatures of the co-polyurea samples decrease with the increase of HDA content, and fit the Fox equation well. TGA data of the polyurea samples indicate that thermal stability of the aromatic polyurea is better than that of the co-polyureas. The thermal degradation activation energies of the co-polyureas are ~60–70 kJ/mol. The results of mechanical measurement show that the initial modulus and tensile strength of the co-polyurea samples decrease with the increase of HDA content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 897–902, 2008

**Key words:** polyurea; aromatic/aliphatic; synthesis; characterization

## INTRODUCTION

Polyureas have been extensively investigated for their good mechanical properties, hydrolytic stability, chemical resistance, unique nonlinear optical properties, etc.<sup>1–8</sup> Applications of polyureas in coatings and greases have been studied for many years.<sup>9,10</sup> Recently, much attention has been paid to use polyureas in films, foams, and composites in industry applications, such as vertical body panels, spray foams, microcellular foams, and liquid plastics.<sup>11,12</sup>

From the view of molecular structure, polyurea is similar to polyamide, which has a tough, high-melting point, and is suitable for fiber applications.<sup>13</sup> Applications of polyesters, polyamides, polyurethanes, and polyimides in fiber industry have been studied extensively, little work has been reported on the preparation of polyurea fibers. Although a number of methods have been used to prepare polyureas, the most common method is the step-growth addition reaction of diamine with diisocyanates. In the present work, a series of aromatic/aliphatic co-polyureas have been synthesized from *m*-phenylene diamine, 4,4-diphenylmethane diisocyanate, and 1,6-diaminohexane in DMAc by a two-stage solution polymerization route. Characterizations of the polyurea

products have been carried out using <sup>1</sup>H-nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopic techniques. Thermal properties of the polyurea samples have been also investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis. The intrinsic viscosity and the mechanical properties of the polyurea samples have been measured.

## EXPERIMENTAL

### Materials

4,4-Diphenylmethane diisocyanate (MDI) was supplied by Yantai Wanhua Co., Ltd., Shandong Province, People's Republic of China. LiCl, *m*-phenylene diamine (*m*-PDA), 1,6-diaminohexane (HDA) (AR), and dimethylacetamide (DMAc) (CR) were purchased from Shanghai Chemical Reagents, Co., Ltd., Shanghai, China. All reagents were used without further purification.

### Preparation of polyureas

The polyureas were synthesized from MDI, *m*-PDA, and 1,6-HDA by a two-step solution polymerization route. The typical reaction was as follows. A 250-mL three-necked flask equipped with a nitrogen inlet, a stir bar, and a glass stopple was charged with 5.0 g MDI; 0.7 g LiCl and 1.08 g *m*-PDA were dissolved

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completely in 30 g DMAc in a beaker. Then this solution was slowly added into the flask. After the pre-reaction was carried out for 10 min under ambient atmosphere conditions, the reaction system was heated to 40°C and continued to react for 30 min. In the second step, 1.16 g HDA was dissolved completely in 30 g DMAc in a beaker. This solution was then slowly added into the flask. The molar ratio of MDI : *m*-PDA : HDA in the system was 2 : 1 : 1. The reaction system continued to react at the temperature of 40°C for 4 h to yield a homogeneous and viscous polyurea solution. The concentration of the polyurea solution was about 12% (w/w). In the case of synthesis for other polyurea samples, different mole ratios of HDA to *m*-PDA were adopted.

### Measurements

Infrared spectra were obtained from thin films of the polyurea samples using a Nicolet NEXUS-670 FTIR. The <sup>1</sup>H-NMR spectra of samples in DMSO-d<sub>6</sub> solvent were recorded on a Bruker Advance 400 spectrometer operating at a resonance frequency of 400 MHz. DSC measurement of the samples was carried out with a METTLER TOLEDO STAR<sup>®</sup> System (Switzerland) differential scanning calorimeter at a heating rate of 10 °C/min under nitrogen atmosphere. The weight of samples was ~5 mg. The glass transition temperature, *T<sub>g</sub>*, was calculated at the intersection of the tangents to the corresponding DSC curves. The thermogravimetric analyses (TGA) of the samples

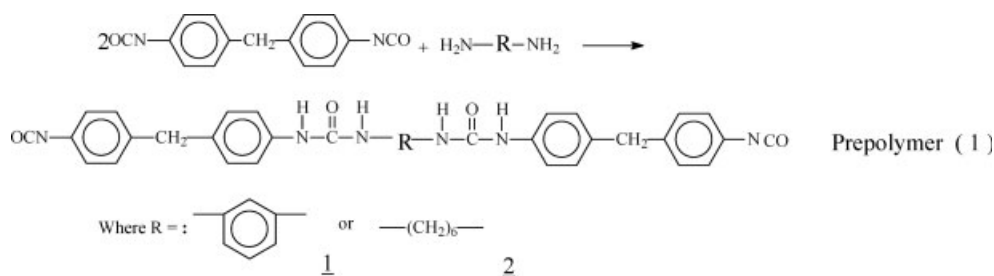
was carried out using a Perkin-Elmer TGA systems. Samples of ~10 mg were dried at 100°C for 30 min to remove moisture, and then programmed from 45 to 600°C at a rate of 20 °C/min under the nitrogen atmosphere. Intrinsic viscosity (  $\eta$  ) of the samples were determined for solution of 0.2g/dL in DMAc at 30°C using a Ubbelohde viscometer. The tensile strength and the elastic modulus of the polyureas were measured using a Shimadzu AGS-500ND forcing instrument made in Japan. The lower grip was fixed and the upper grip rose at a rate of 20 mm/min. All tests were carried out under ambient atmosphere conditions. Data from at least 10 individual tests were averaged for one sample.

## RESULTS AND DISCUSSION

### Synthesis and characterization

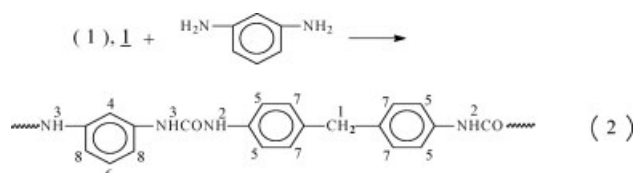
It is well known that it is essential that fiber-forming polymers should have more regular chain structures. In our work, the polyurea samples were synthesized in two stages, so that the sequence structure of the chain could be controlled more regularly. In the first step, 2 mole of MDI react with 1 mole of diamine to form NCO terminated prepolymer, as shown in (1). In the second step, different mole ratios of aromatic/aliphatic diamine were used to form pure aromatic polyurea, aliphatic polyurea and their co-polymers, as shown in (2), (3), and (4). The monomer composition of samples is listed in Table I.

Pre-polymerization.

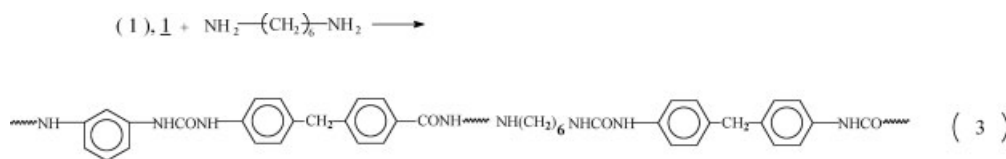


Chain extension.

(a) aromatic polyurea (sample a) synthesized from [1, (1)] and *m*-PDA:



(b) co-polyureas (samples b, c, d) synthesized from [1, ( 1 )] and 1,6-HDA:



(c) aliphatic polyurea (sample e) synthesized from [1, ( 2 )] and 1,6-HDA:

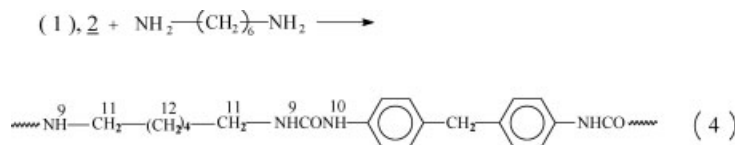


Figure 1 displays the  $^1\text{H-NMR}$  spectra of the polyurea samples. In the case of aromatic polyurea (a), the strong signal at 3.8 ppm (1) corresponds to the protons of methylene linked with a phenyl ring of MDI. The peaks at 7.0–7.6 ppm (4, 6 and 8) is associated with the protons on the phenyl ring of MDI and *m*-PDA. The peaks at 8.5 and 8.7 ppm (2 and 3) correspond to the protons associated with aromatic urea group. In the case of aliphatic polyurea (e), the resonance peaks associated with phenyl ring of MDI is still in the range of 7.0–7.6 ppm, while the resonance peaks associated with the urea group shift to 8.4 and 8.8 ppm (9 and 10). The protons of methylene on the HDA unit resonate at around 1.2–1.5 ppm (11 and 12). In the case of co-polyurea samples (b–d), there are three protons peaks at 8.3, 8.5, and 8.8 ppm, respectively. This is because the urea linkages in the co-polyurea are in three different modes. It can also be found that the proton resonance of methylene on the HDA unit become stronger as the content of HDA increases.

FTIR investigation of the polyurea samples gives the similar results. Figure 2 shows the FTIR spectrum of pure aromatic polyurea (a), pure aliphatic polyurea (e) and spectra of aromatic/aliphatic co-polyureas (b–d). The urea group shows bands at  $3340\text{ cm}^{-1}$  ( $\nu\text{NH}$ ) and  $1657\text{ cm}^{-1}$  ( $\nu\text{CO}$ ), respectively. The band at  $3031\text{ cm}^{-1}$  correspond to the CH vibra-

tion of phenyl ring, while the bands at  $\sim 2930$  and  $2857\text{ cm}^{-1}$  are the absorption of  $\text{CH}_2$  ( $\nu\text{CH}$ ) on MDI and HDA units. It can be found that with the increase of HDA content in the co-polyurea samples, the absorption at  $3031\text{ cm}^{-1}$  decreases, while the absorption at  $\sim 2930\text{ cm}^{-1}$  increases. Because the mole fraction of MDI in all samples remains invariable, and the mole concentration of the N–H group is constant, the absorption ratio  $A_{2930}/A_{3340}$  can be used to describe the concentration of HDA in samples quantitatively. It can be seen from Figure 3 that the value of  $A_{2930}/A_{3340}$  is proportional to the mole fraction of HDA in the total diamine content, which indicates that the co-polyurea samples have the expected chemical structure.

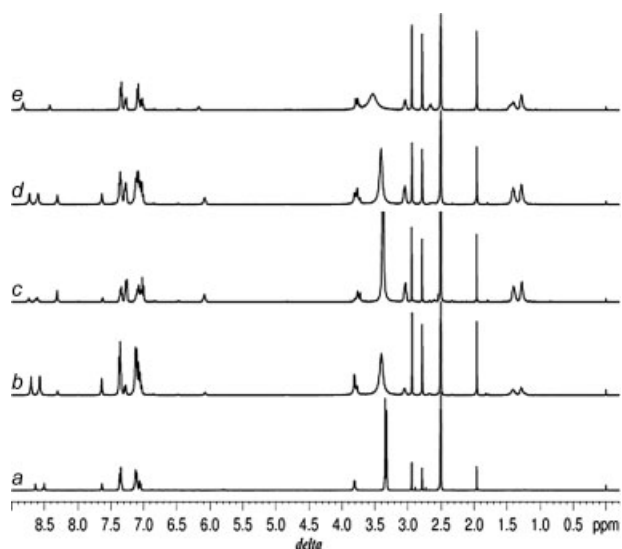
### DSC analysis

The  $T_g$  of the polyurea samples were measured by DSC. It can be seen from Figure 4 that the  $T_g$  of pure aromatic polyurea is  $132^\circ\text{C}$ , while that of pure aliphatic polyurea is  $101^\circ\text{C}$ . The glass transition temperatures of co-polyurea samples decrease with the increase of HDA content. The  $T_g$  data of co-polyurea samples can be described by the Fox equation:

$$\frac{1}{T_g} = \frac{1 - W_2}{T_{g,1}} + \frac{W_2}{T_{g,2}}, \quad (5)$$

TABLE I  
Monomer Compositions and the Intrinsic Viscosity of the Polyurea Samples

Sample	Monomer			Mole ratio of M1 : M2 : M3	[ $\eta$ ] (dL/g)
	MDI (g) (M1)	<i>m</i> -PDA (g) (M2)	1,6-HDA (g) (M3)		
a	5.0	2.16	0.00	2 : 2 : 0	0.62
b	5.0	1.62	0.58	2 : 1.5 : 0.5	0.63
c	5.0	1.08	1.16	2 : 1.0 : 1.0	0.90
d	5.0	0.54	1.74	2 : 0.5 : 1.5	0.33
e	5.0	0.00	2.32	2 : 0 : 2	0.23



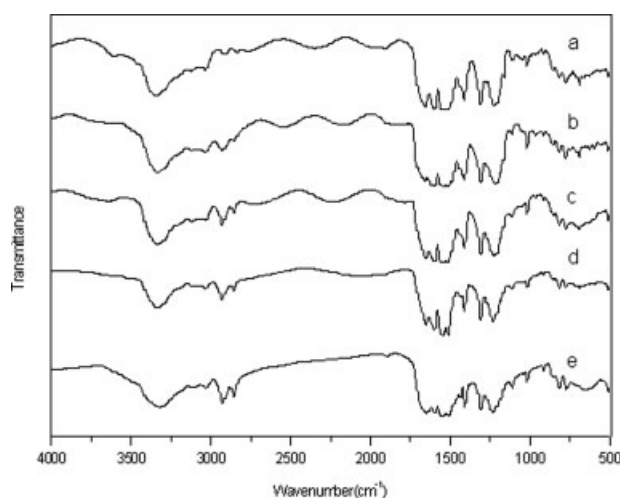
**Figure 1** H-NMR spectra of the polyurea samples.

where  $T_{g,1}$ ,  $T_{g,2}$ , and  $T_g$  are the glass transition temperatures of pure aromatic polyurea, pure aliphatic polyurea and the co-polyurea, respectively.  $W_2$  is the weight fraction of aliphatic polyurea component in the co-polymer.

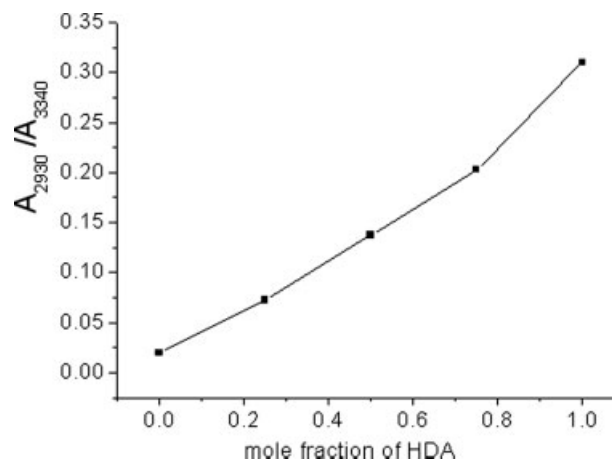
Figure 5 shows the relationship between  $1/T_g$  and  $W_2$ . It can be seen that good linear relation can be obtained. This implies that the structure of co-polyureas is random in nature.

### TGA analysis

Figure 6 shows the TGA results of the polyurea samples. In the case of pure aromatic polyurea, the thermal degradation temperature is  $\sim 290^\circ\text{C}$ . While the thermal degradation temperature of pure aromatic polyurea is  $\sim 357^\circ\text{C}$ . However, the thermal degrada-



**Figure 2** FTIR spectra of the polyurea samples.



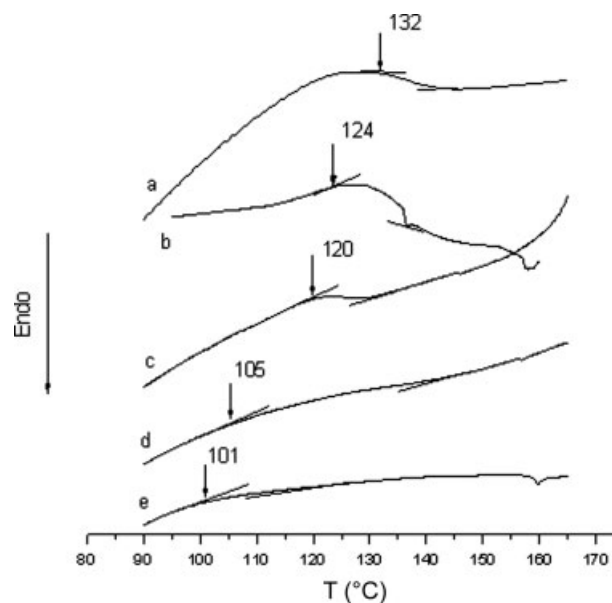
**Figure 3** Relationship between  $A_{2930}/A_{3340}$  and mole fraction of HDA in the total diamine content.

tion temperatures of the co-polyurea samples decrease significantly to  $\sim 250$ – $260^\circ\text{C}$ . This indicates that the incorporation of the HDA segment significantly reduced the thermal stability of co-polyureas.

According to the Freeman–Carroll equation, the thermal degradation activation energy of the polyurea samples can be estimated from the data of initial thermal degradation of the samples:

$$\frac{\Delta \ln(d\alpha/dt)}{\Delta \ln(1-\alpha)} = -\frac{E_d}{2.303R} \times \frac{\Delta(1/T)}{\Delta \ln(1-\alpha)} + n, \quad (6)$$

where  $E_d$  is the thermal degradation activation energy,  $\alpha$  is the weight loss fraction,  $R$  is the gas constant, and  $T$  is the absolute temperature.



**Figure 4** DSC curves of the polyurea samples.

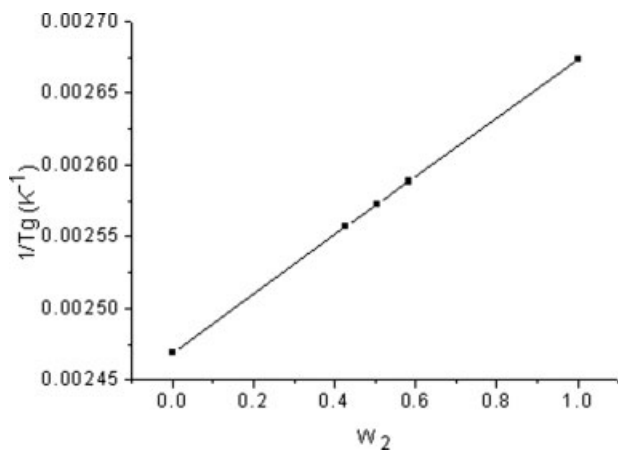


Figure 5 Relationship between  $1/T_g$  and  $W_2$ .

The relationship between  $\frac{\Delta \ln(da/dt)}{\Delta \ln(1-\alpha)}$  and  $\frac{\Delta(1/T)}{\Delta \ln(1-\alpha)}$  is shown in Figure 7. A good linear relation exists. From the slope of the lines,  $E_d$  can be calculated and are listed in Table II. As can be seen that activation energies of thermal degradation for all samples are  $\sim 60\text{--}70$  kJ/mol.

**Mechanical properties of the polyurea samples**

The results of mechanical testing are listed in Table III. It can be seen that the pure aromatic polyurea has the highest initial modulus and tensile strength. With the increase of HDA content the initial modulus of the co-polyurea samples decreases. This is ascribed to the incorporation of flexible HDA unit to

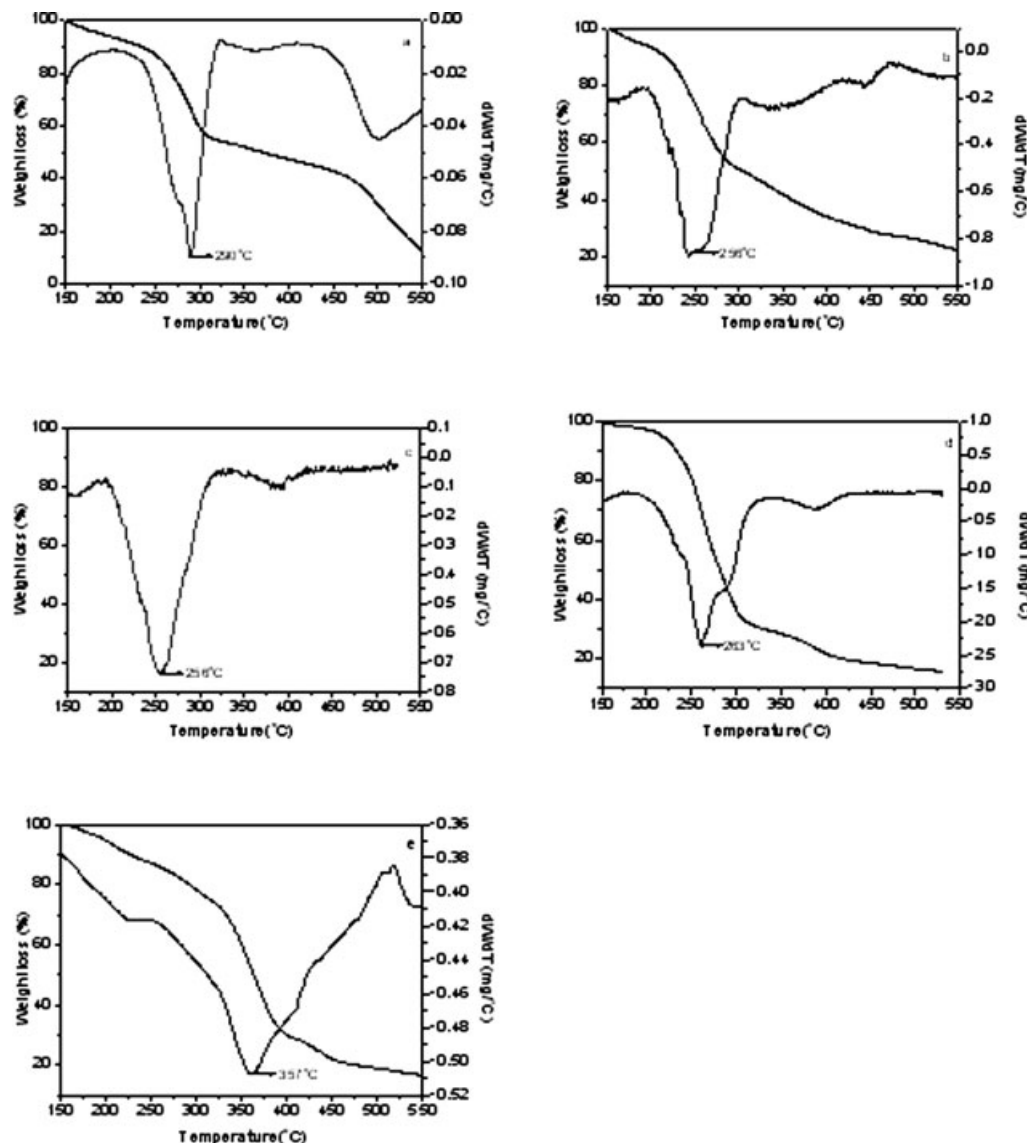
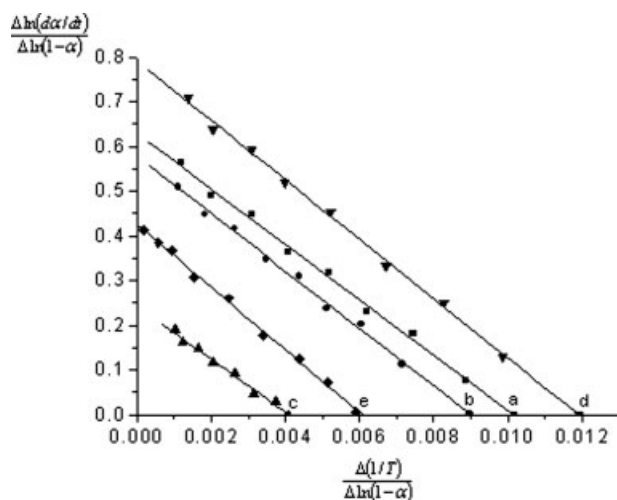


Figure 6 TGA curves of polyurea samples.



**Figure 7** Relationship between  $\frac{\Delta \ln(d\alpha/dt)}{\Delta \ln(1-\alpha)}$  and  $\frac{\Delta(1/T)}{\Delta \ln(1-\alpha)}$  of the polyurea samples.

the molecular chains. The tensile strength of the co-polyurea samples also decreases with the increase of HDA content, while the elongation at break of the samples do not change a lot.

### CONCLUSION

$^1\text{H-NMR}$  and FTIR spectroscopy confirm the polyurea samples with the expected structure. The results of DSC analysis show the glass transition temperatures of the co-polyurea samples decrease with the increase of HDA content, and fit the Fox

**TABLE II**  
Values of  $T_g$ ,  $T_d$ , and  $E_d$  of the Polyurea Samples

Samples	a	b	c	d	e
$T_g$ (°C)	132	124	120	105	101
$T_d$ (°C)	290	252	256	261	357
$E_d$ (kJ/mol)	62	65	59	66	70

**TABLE III**  
Mechanical Properties of Co-Polyurea Samples

Sample	Initial modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
a	1389	74.1	13.9
b	1040	50.2	7.4
c	301	31.0	13.7
d	397	28.7	8.7
e	371	12.0	2.9

equation well. TGA data of the polyurea samples indicate that thermal stability of the aromatic and aliphatic polyureas is better than that of the co-polyureas. The thermal degradation activation energies are  $\sim 60\text{--}70$  kJ/mol. The results of mechanical measurement show that the initial modulus and tensile strength of the co-polyurea samples decrease with the increase of HDA content.

### References

- Nalwa, H. S.; Watanabe, T.; Kakuta, A.; Miyata, S. *Mol Cryst Liq Cryst Sci Technol, Sect B: Nonlinear Opt* 1994, 82, 157.
- Sendijarevic, V.; Sendijarevic, A.; Sendijarevic, I.; Bailey, R. E.; Pemberton, D.; Reimann, K. A. *Environ Sci Technol* 2004, 38, 1066.
- Stanford, J. L.; Still, R. H.; Wilkinson, A. N. *Polym Int* 1996, 41, 283.
- Tao, X. T.; Watanabe, T.; Zou, D. C.; Shimoda, S.; Sato, H.; Miyata, S. *Macromolecules* 1995, 28, 2637.
- Wang X. S.; Takahashi Y.; Lijima M.; Fukada E. *Jpn J Appl Phys, Part 1: Reg Pap Short Notes Rev Pap* 1995, 34, 1585.
- Mahammad, I. A.; Mahadevan, V.; Srinivasan, M. *Eur Polym J* 1989, 25, 427.
- Wataru, S.; Koki, C.; Naoto, T. *J Polym Sci, Part B: Polym Phys* 2001, 39, 247.
- Hwu, J. R.; King, K. Y. *Chem Eur J* 2005, 11, 3805.
- Primeaux, D. J., II. *J Prot Coat Lin* 2001, 18, 26.
- Root, J. C.; Scruton, P. J. *NLGI Spokesman* 1995, 59, 28.
- Munstermann, M.; Buchan, T.; Von Diest, K. *Kunstst Plast Eur* 2001, 91, 11.
- Buecking, K. *Eur Coat J* 1998, 10, 730.
- Ashoosh, V.; Ambade, A. K. *J Polym Sci, Part A: Polym Chem* 2004, 42, 5134.