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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### A Preliminary Study on Preparation of the Aromatic/Aliphatic Copolyurea as Spun Fibers

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**To cite this Article** Li, Xuelian and Chen, Dajun(2006) 'A Preliminary Study on Preparation of the Aromatic/Aliphatic Copolyurea as Spun Fibers', *Journal of Macromolecular Science, Part A*, 43: 11, 1703 – 1709

**To link to this Article:** DOI: 10.1080/10601320600939049

**URL:** <http://dx.doi.org/10.1080/10601320600939049>

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# A Preliminary Study on Preparation of the Aromatic/Aliphatic Co-polyurea as Spun Fibers

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*Aromatic-aliphatic co-polyurea has been synthesized from 4,4 prime-diphenylmethane diisocyanate (MDI), m-phenylene diamine (m-PDA), and 1,6-diaminohexane (HDA) in DMAc by solution polymerization. The chemical structure of the co-polyurea has been characterized by <sup>1</sup>H-NMR. The thermal properties of the copolymers were measured by DSC and TGA. The co-polyurea solutions were spun into fibers by means of wet spinning. The effects of coagulation conditions on the morphologies and mechanical properties of the co-polyurea as spun fibers are discussed.*

**Keywords** aromatic/aliphatic co-polyurea, synthesis, characterization, as spun fiber, wet spinning

## Introduction

Polyureas have been extensively investigated for their good mechanical properties, hydrolytic stability, chemical resistance and unique nonlinear optical property etc. (1–5). Applications of polyureas in coatings and greases have been studied for many years (6, 7). Recently, much attention has been paid to utilizing polyureas in films, foams and composites in industry applications, such as vertical body panels, spray foams, microcellular foams and liquid plastics (8, 9).

From the view of molecular structure, polyurea is similar to polyamides, which are tough, have a high-melting point, and are suitable for fiber applications (10). Although applications of polyesters, polyamides, polyurethanes, and polyimides in the fiber industry have been extensively studied, little work has been reported on the preparation of polyurea fibers. The basic technology for forming synthetic fibers includes spinning and heat treatment. As is generally known, there are three major methods of spinning: melt-, dry-, and wet-spinning processes. High-performance fibers and other functional fibers usually are spun by wet technology, including wet-spinning, dry-jet wet spinning, and gel-spinning technology. For example, aromatic polyamides (Kevlar), polyimides (PI), and high-strength polyethylene are prepared by the above spinning processes.

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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 this paper, a kind of aromatic/aliphatic co-polyurea has been synthesized from *m*-phenylene diamine, 4,4-diphenylmethane diisocyanate, and 1,6-diaminohexane in DMAc by a two-step solution polymerization route. Characterization of the polyurea products was carried out using  $^1\text{H-NMR}$  spectroscopic techniques. Thermal properties of the polyurea samples were also investigated using differential scanning calorimetry and thermogravimetric analysis. The co-polyurea solutions were spun into fibers by means of wet spinning. The effects of coagulation conditions on the morphologies of the co-polyurea fibers were observed by SEM. The mechanical properties of the co-polyurea as-spun fibers have been tested.

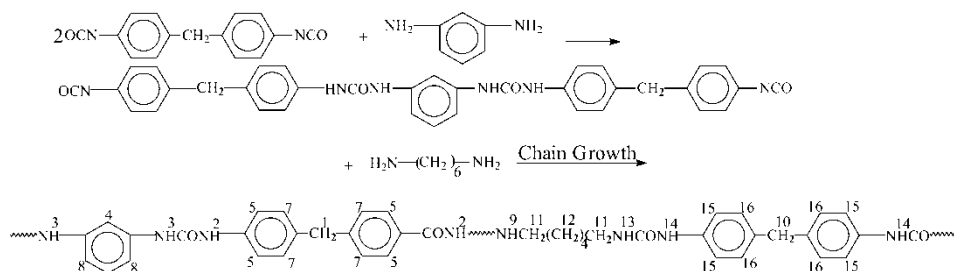
## Experimental

### Materials and Reagents

4,4-Diphenylmethane diisocyanate (MDI) was supplied by Yantai Wanhua Co. Ltd. of Shandong Province, China. LiCl, *m*-phenylene diamine (*m*-PDA), 1,6-diaminohexane (HDA) (A.R.) and dimethylacetamide (DMAc) (C.R.) were purchased from Shanghai Chemical Reagents Co., China.

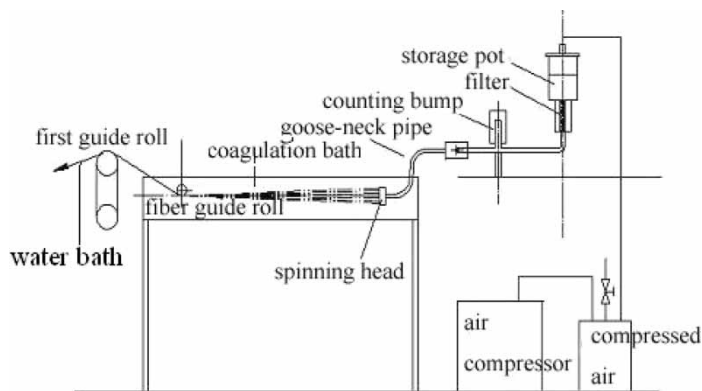
### Synthesis of Co-polyurea Sample

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 stopper was charged with 5.0 g MDI. 0.7 g LiCl and 1.08 g *m*-PDA were dissolved quickly and completely in 20 g DMAc in a beaker. This solution was then 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 20 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 homogenous and viscous polyurea solution. The concentration of the polyurea solution was about 16.6% (w/w).



### Preparation of Co-polyurea Fibers

The co-polyurea solution was filtered and degassed at 25°C. Fiber formation was conducted on a spinning machine, which was home designed, as shown in Scheme 1.



**Scheme 1.** Flow process diagram of spinning co-polyurea fibers.

The conditions of spinning were as flows: air pressure 0.5 MPa; 16% (w/w) co-polyurea solution in the storage pot; 12 holes spinneret with 0.8 mm diameter of each hole. The dopes at 25°C were spun into a coagulation bath by a wet-spinning process with no gas gap. The composition of the bath was a mixture of water and DMAc with different weight ratios (DMAc weight percent: 0, 10, 20, 30, 40%). The as-spun fibers entered directly into the heated water bath at 55°C.

### Measurements

<sup>1</sup>H-NMR spectra of samples in DMSO-d<sub>6</sub> solvent were recorded on a Bruker Avance 400 spectrometer operating at a resonance frequency of 400 MHz.

DSC measurements of the co-polyurea were carried out using a METTLER TOLEDO 822e System differential scanning calorimeter at a heating rate of 10°C/min under nitrogen atmosphere from 25°C to 350°C. Thermogravimetric analyses were carried out using a Perkin-Elmer TGA system. Samples of about 10 mg were dried at 100°C in an oven to remove moisture for 30 min, and then programmed from 45 to 600°C at a rate of 20°C/min under a nitrogen atmosphere.

The morphology of the surfaces of the co-polyurea fibers was observed using a JSM-5600LV scanning electron microscopy at an accelerating voltage of 10 KV.

The mechanical properties of the co-polyurea fibers were measured using a Shimadzu AGS-500ND instrument. All tests were carried out under ambient atmosphere conditions. Data from at least 10 individual tests for each sample were averaged.

## Results and Discussion

### Characterization of the Aliphatic-Aromatic Co-polyurea

Figure 1 is the <sup>1</sup>H-NMR spectrum of the co-polyurea sample. The strong signals at 3.0–3.8 ppm (1, 10, 11 and 12) correspond to the protons of methylene linked with the phenyl ring of MDI and HDA. The peaks at 7.0–7.8 ppm (a, b and c) are associated with the protons on phenyl ring of MDI and m-PDA. The peaks at 8.3, 8.6 and 8.7 ppm (2, 3 and 14) correspond to the protons associated with aromatic urea groups. The protons of methylene on the HDA unit resonate at around 1.2–1.5 ppm (9 and 13). The analysis of

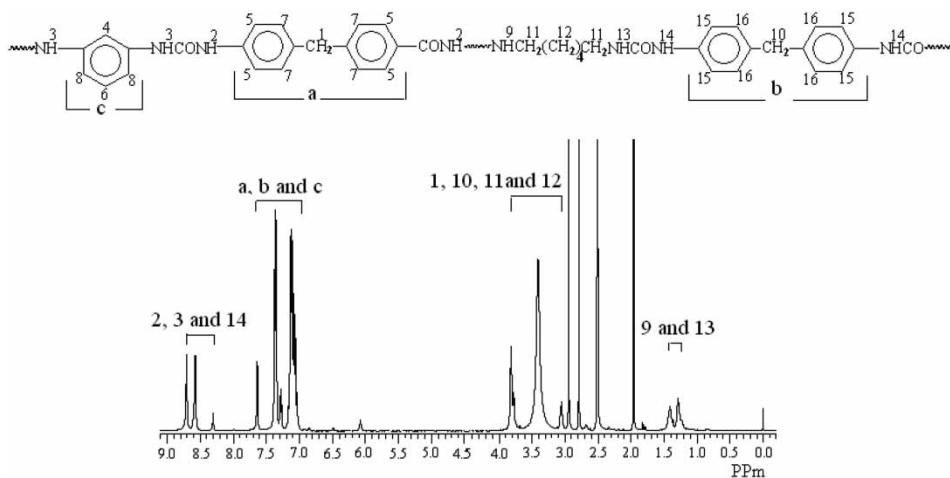


Figure 1.  $^1\text{H-NMR}$  spectrum of co-polyurea sample.

the  $^1\text{H-NMR}$  spectrum of the sample confirmed the co-polyurea with the expected chemical structure.

#### Thermal Analysis of the Co-polyurea Sample

The glass transition temperatures ( $T_g$ ) of the co-polyurea sample were measured by DSC, (Figure 2). The  $T_g$  of the co-polyurea is about  $120^\circ\text{C}$ , which indicates that the co-polyurea has a relatively rigid chain conformation. Figure 3 shows the TGA results of the polyurea sample. The thermal degradation temperature of the co-polyurea sample is about  $256^\circ\text{C}$ . This indicates that the thermal stability of the co-polyurea is poorer than that of polyamides. This is why wet spinning had to be adopted for the formation of the co-polyurea fibers.

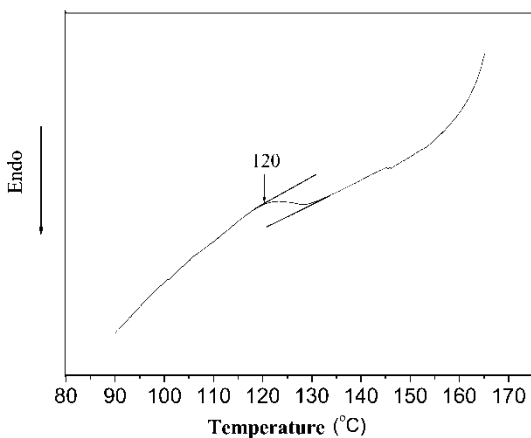
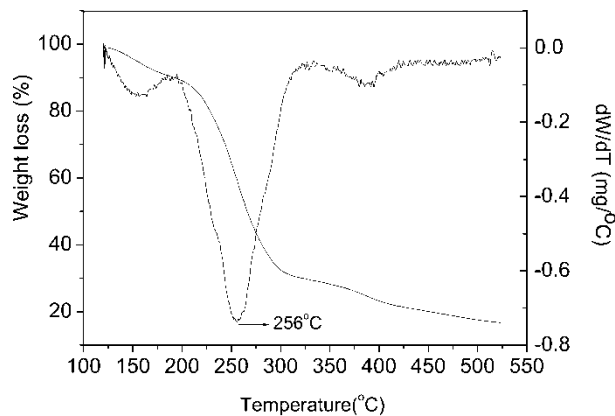


Figure 2. DSC curve of the co-polyurea sample.

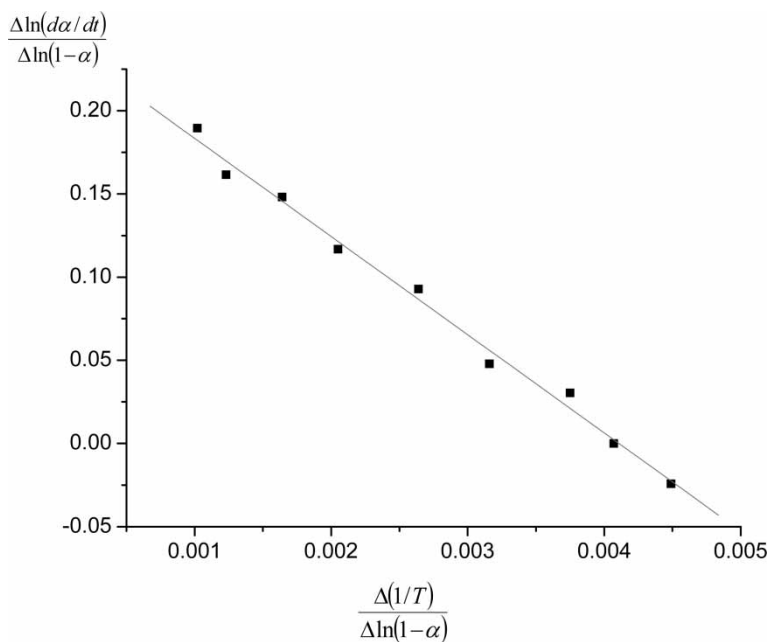


**Figure 3.** TG-DTG curves of the co-polyurea sample.

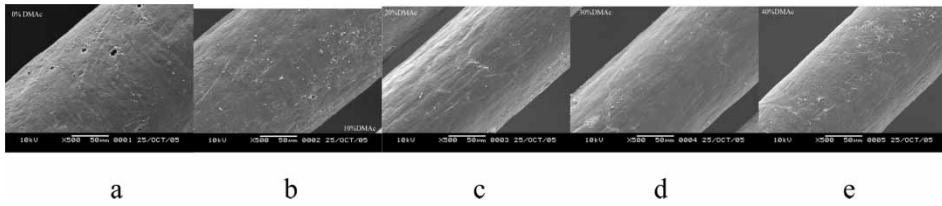
According to the Freeman-Carroll equation, the thermal degradation activation energy of the polyurea samples can be estimated from the data of initial thermal degradation of the samples.

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

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



**Figure 4.** The relationship between  $\Delta \ln(d\alpha/dt)/\Delta \ln(1-\alpha)$  and  $\Delta(1/T)/\Delta \ln(1-\alpha)$ .

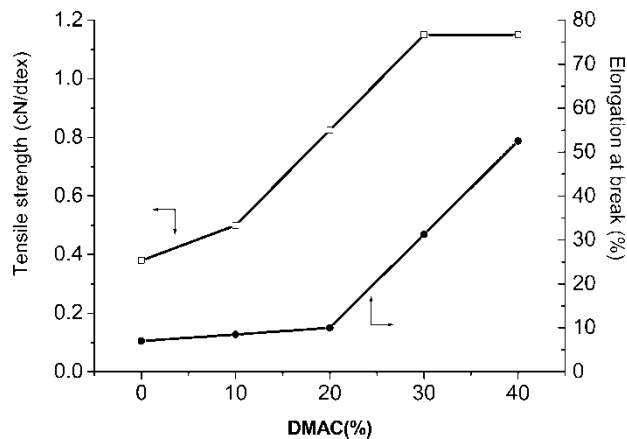


**Figure 5.** SEM pictures of the as-spun fibers prepared in the different coagulation conditions (DMAC content in coagulation bath: a: 0%; b: 10%; c: 20%; d: 30%; e: 40%).

The relationship between  $\Delta \ln(d\alpha/dt)/\Delta \ln(1 - \alpha)$  and  $\Delta(1/T)/\Delta \ln(1 - \alpha)$  is shown in Figure 4. A good linear relation exists. From the slope of the lines  $E_a$  can be calculated. The activation energy of thermal degradation for the sample is about 60 kJ/mol.

#### *The Effect of Coagulation Conditions on the Mechanical Properties of the As-Spun Fiber*

Figure 5 shows the SEM micrographs of the as-spun co-polyurea fibers prepared with different coagulation conditions. The fiber coagulated in pure water has a rough surface and the diameter of the fiber is the largest. This is because pure water is a nonsolvent for the co-polyurea solution. When the spinning solution was extruded into the coagulation bath, the surface of the fiber coagulated rapidly and the skin layer formed, which prevents the solvent diffusing from the inner part of the fiber. This may result in large pores in the fiber. As shown in Figure 6, the tensile strength and elongation at break of the fiber coagulated in pure water are lowest. With an increase of DMAC content in the coagulation bath, the tensile strength and elongation at break of the fibers increase. As shown in Figure 5, the surface of the as-spun fibers become smooth and the diameter of the fibers become smaller with increase of the solvent content in the coagulation bath. This proved that the formation of more dense nascent fibers benefits from slower coagulation.



**Figure 6.** Mechanical properties of the as-spun fibers prepared in the different coagulation conditions.

## Conclusions

<sup>1</sup>H-NMR spectroscopy confirms the structure of the polymers. From DSC curves, the glass transition temperatures (T<sub>g</sub>) of co-polyureas was about 120°C. The thermal degradation temperature of the co-polyurea is above 250°C. The apparent activation energy of thermal degradation is about 60 kJ/mol. The coagulation conditions have a significant effect on the fiber forming ability of co-polyureas solution and the mechanical properties of the fibers. With an increase of DMAc content in the coagulation bath, the tensile strength and elongation at break of the fibers increase.

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