

# Thermal oligomerization of *N,N'*-(1,6-hexanediyl)bisurea

Robert F. Harris\* and Jason E. Kinney

Central Research and Development, Materials Science and Development Laboratory,  
The Dow Chemical Company, Midland, MI 48674, USA

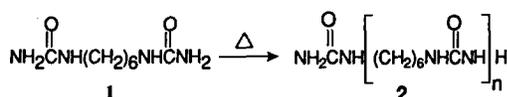
(Received 19 August 1993; revised 20 February 1994)

*N,N'*-(1,6-Hexanediyl)bisurea oligomerizes thermally in the melt (>190°C) to urea-terminated poly(1,6-hexamethyleneurea) with the volatilization of ammonia and isocyanic acid. At higher temperatures (225–250°C) in the liquid phase, the trimerization of isocyanic acid to cyanuric acid also occurs.

(Keywords: polyureas; oligomerization; thermolysis)

## INTRODUCTION

Recently, we have been studying the synthesis and characterization of urea-terminated poly(1,6-hexamethyleneurea) particles in polyols as reinforcing fillers in polyurethanes<sup>1,2</sup>. As synthesized, these particles are 2–5 μm in length and have a unique spiral fibre bundle morphology with aspect ratios of 10–20. During the course of this study, an unusual thermal effect was observed by heating *N,N'*-(1,6-hexanediyl)bisurea (**1**) above its melting point. This communication describes the thermal oligomerization of **1** to urea-terminated poly(1,6-hexamethyleneurea) (**2**); when *n* = 1, compounds **1** and **2** are one and the same.



## EXPERIMENTAL

### Materials and equipment

Urea, 1,6-hexanediamine, and methanesulfonic acid were purchased from Aldrich Chemical Co. Differential scanning calorimetry (d.s.c.) was done on a DuPont 910 instrument at a rate of 10°C min<sup>-1</sup> under nitrogen. Carbon-13 n.m.r. spectra (in methanesulfonic acid) were obtained on a Varian Gemini-300 Spectrometer (75 MHz for carbon) using methanesulfonic acid as the internal reference line (40.0 ppm). Thermolysis samples were analysed by thermogravimetry/mass spectrometry (t.g.a./m.s.) and thermogravimetry/gas chromatography/mass spectrometry (t.g.a./g.c./m.s.) during heating to 280°C in a helium atmosphere using a Cahn 131 TGA and a Trio-1 GC/MS controlled by a Camille™ 2000. High-temperature visual observations were made using a Bausch & Lomb hot-stage microscope. Scanning

electron microscopy (SEM) was done on a Hitachi S-570 SEM. The FTi.r. spectra were obtained on a Nicolet 5PC FT-IR spectrophotometer in KBr pellets.

### Preparation of *N,N'*-(1,6-hexanediyl)bisurea (**1**)

Urea (180.2 g, 3.0 mol) was placed in a 500 ml flask under nitrogen containing a condenser, thermometer and mechanical stirrer and heated to 145°C (m.p. = 135°C). 1,6-Hexanediamine (58.1 g, 0.50 mol) was added in small portions over a 4 h period, while maintaining the temperature at 145°C. Thirty minutes after the final addition, the crude reaction product was poured into water (700 ml) and the resultant slurry was neutralized with H<sub>2</sub>SO<sub>4</sub> (1 N) to pH ~4 and filtered. The solid white product was washed several times with water, recrystallized from water, and dried in a vacuum oven at 120°C, m.p. 188–192°C (structure consistent with carbon-13 n.m.r. and FTi.r. of authentic sample).

## RESULTS AND DISCUSSION

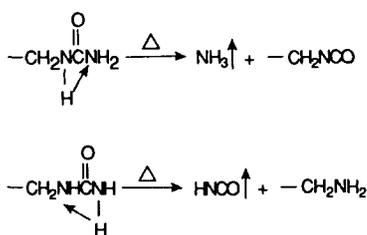
*N,N'*-(1,6-Hexanediyl)bisurea (**1**) is a well known material that can be synthesized by several methods<sup>3–7</sup>. However, this communication is the first known report of its synthesis directly from urea and 1,6-hexanediamine in molten urea and its subsequent oligomerization to urea-terminated poly(1,6-hexamethyleneurea) under thermolysis conditions.

When a well characterized sample of **1** was heated on a hot-stage microscope, its melting range was observed from 188 to 192°C. However, when heating was continued, the melt solidified at about 202°C. Further heating led to the melting of this second solid at 250°C. This observation suggested that **1** was reacting in the melt to produce a higher-melting material. This experiment was scaled up by heating a 3 g sample of **1** in a vacuum oven at 203–204°C, where any physical changes could be observed. The sample began melting in 15 min and was completely melted in 20 min. Some gas was evolved. By 24 min some solid was observed and by 40 min only solid

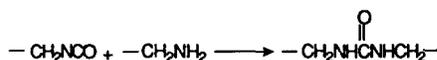
\* To whom correspondence should be addressed

was present. After 45 min, the sample was cooled under nitrogen. The resultant white solid (**2a**) represented 88.5% of the initial sample weight.

The melt and subsequent reactions were studied further by the simultaneous technique of t.g.a./m.s. and t.g.a./g.c./m.s. A sample of **1** was heated from ambient to 280°C and real-time mass spectra were taken of the vapour. A small amount of water was detected at about 100°C. Between 190 and 215°C, ammonia and isocyanic acid (HCNO) were detected as major volatiles. Trace amounts of cyanuric acid were detected between 250 and 280°C. Total weight loss was about 19%. A portion of the volatiles was trapped throughout the experiment and analysed by g.c./m.s. Urea was the major component, as well as smaller amounts of ammonia, water and cyanuric acid. Urea is presumably a secondary product formed by the reaction between ammonia and isocyanic acid. From these data it is clear that the predominant reactions occurring when **1** is heated above its melting point involve the release of ammonia and isocyanic acid. Both of these materials are reasonable thermal decomposition products of ureas<sup>8,9</sup>.



The non-volatile isocyanate and amine components can react further to form internal urea moieties.



This thermolysis sequence was further characterized by the carbon-13 n.m.r. spectra of **1** and **2a** in methanesulfonic acid. Structure **1** had a four-line pattern. The terminal urea carbonyl carbon atoms were present at 161.2 ppm (Figure 1). The six-carbon-atom segment between the terminal urea moieties had a three-line pattern, due to symmetry, at 42.6, 28.9 and 26.5 ppm for the methylene carbon atoms  $\alpha$ ,  $\beta$  and  $\gamma$  to the terminal urea carbonyl atoms, respectively. The thermolysis product **2a** had a five-line pattern indicative of urea-terminated poly(1,6-hexamethyleneurea)<sup>2</sup>. Terminal urea carbonyl carbon atoms and internal urea carbonyl carbon atoms were present at 161.2 and 159.6 ppm, respectively (Figure 1). The six-carbon-atom segment between the urea moieties had a three-line pattern at 42.6, 28.9 and 26.5 ppm for the methylene carbon atoms  $\alpha$ ,  $\beta$  and  $\gamma$  to the urea carbonyl atoms, respectively<sup>2</sup>.

Two additional, but smaller, carbonyl lines at 161.9 and 163.0 ppm have not yet been identified. However, the 163.0 ppm line is consistent with urea. This thermolysis sequence resulted in the polymerization of **1** to **2**. Quantitative carbon-13 n.m.r. (based on the relative heights of the terminal and internal urea carbonyl carbon atoms<sup>2</sup>) indicated that  $M_n$  had increased from 202 (**1**) to 538 g mol<sup>-1</sup> (**2a**) (Table 1).

When characterized by d.s.c., **1** had a melt endotherm centred at 190°C. However, an additional broad, multiple endotherm was observed between about 210 and 270°C (Figure 2). This multiple endotherm was a consequence of the oligomers formed by molecular-weight advancement during further heating, since the carbon-13 n.m.r. spectrum of **1** indicated no higher-molecular-weight

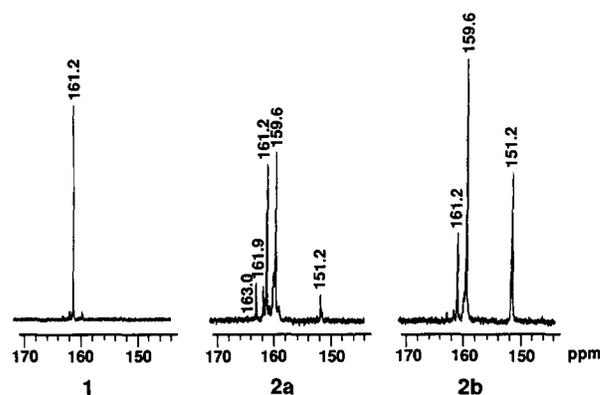


Figure 1 Carbon-13 n.m.r. spectra of carbonyl region

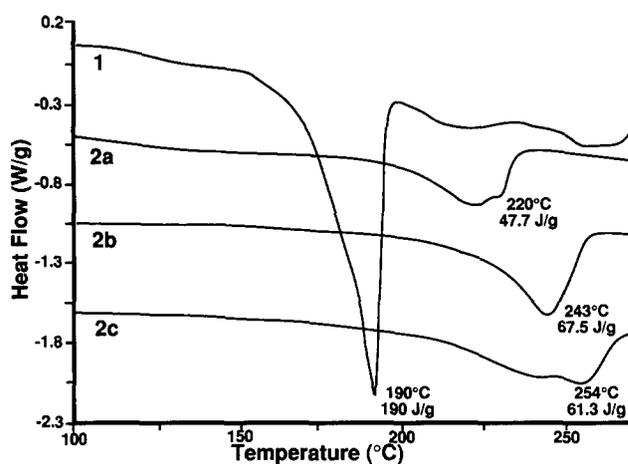


Figure 2 D.s.c. traces of *N,N'*-(1,6-hexanediy)bisurea and its thermolysis products

Table 1 Thermolysis conditions of *N,N'*-(1,6-hexanediy)bisurea and product characterization

Sample	Vacuum oven		D.s.c. data		Carbon-13 n.m.r. data	
	Temperature (°C)	Weight loss (%)	Melting point (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$M_n$ (g mol <sup>-1</sup> )	Polymer/cyanuric acid (wt ratio)
<b>1</b>	—	—	190	190.0	202	—
<b>2a</b>	203–204	11.5	220	47.7	538	97.6/2.4
<b>2b</b>	225–228	19.0	243	67.5	1283	85.3/14.7
<b>2c</b>	249–250	22.5	254	61.3	3500	80.1/19.9

oligomers (lack of line at 159.6 ppm). Thermolysis product **2a** gave a d.s.c. trace with a multiple endotherm observed between about 210 and 230°C (consistent with oligomer formation); **1** was absent. A small amount of a higher-melting impurity was detected as a melt endotherm centred at 372°C (consistent with cyanuric acid). Unfortunately, SEM results indicate the **2** made by the above process does not possess the spiral fibre bundle morphology useful in polyurethane reinforcement<sup>1,2</sup>.

This reaction sequence was studied further by heating **1** at 225–228°C (**2b**) and at 249–250°C (**2c**) in a vacuum oven (Table 1). The semicrystalline, urea-terminated poly(1,6-hexamethyleneurea) oligomers were formed at increasingly higher  $M_n$  (**2b**,  $M_n = 1283$ ; **2c**,  $M_n = 3500$  g mol<sup>-1</sup>) and had increasingly higher melting points as melt reaction temperatures were increased. When the reaction proceeded to an oligomer composition with a melting point above the reaction temperature, oligomerization rates were reduced considerably. However, cyanuric acid was present in larger quantities as reaction temperatures were increased. Cyanuric acid was indicated by an additional line in the carbon-13 n.m.r. spectrum (methanesulfonic acid) at 151.2 ppm (Figure 1), identical to the known material. No other significant lines were present. Thermolysis products **2b** and **2c** were confirmed to contain cyanuric acid by the FTi.r. spectra and by d.s.c. melt endotherms at 377°C. Cyanuric acid was formed by the high-temperature trimerization of isocyanic acid. This is similar to the commercial process where urea is heated (200–300°C) to produce isocyanic acid, which trimerizes to cyanuric acid<sup>10</sup>.

Poly(1,6-hexamethyleneurea) is reported to have a melting range from 270 to 300°C<sup>11–13</sup> and to be thermally stable to about 350°C<sup>14</sup>. However, urea-terminated poly(1,6-hexamethyleneurea) decomposes slowly at its melting point (about 270°C)<sup>15</sup>.

The urea cleavage method is an important phosgene-free isocyanate synthesis<sup>16</sup>. These thermal decomposition reactions are typically carried out on trisubstituted ureas in the vapour phase at temperatures between 135 and 500°C in the presence of acidic materials to produce the corresponding amines and isocyanates<sup>17</sup>. The liquid-phase decomposition of di- and trisubstituted ureas to isocyanates has been carried out in the presence of acidic materials to interact with amine by-products<sup>6,18–20</sup>. In one report, a solvent was used at 230°C<sup>21</sup>. It has been reported that compound **1** has been heated in a sealed tube at 206°C both neat and in toluene for 17 h to yield

an unidentified material that was not poly(1,6-hexamethyleneurea)<sup>22</sup>. As shown in this communication, oligomerization of **1** and **2** is driven by loss of ammonia and isocyanic acid under thermolysis conditions, a process that is negated in a sealed tube.

## ACKNOWLEDGEMENT

The authors acknowledge D. R. Miller for obtaining the t.g.a./m.s. and t.g.a./g.c./m.s. results

## REFERENCES

- 1 Harris, R. F. and Savina, M. R. *US Pat.* 4 994 503, 1991
- 2 Harris, R. F., Savina, M. R., Kinney, J. E. and St Jeor, V. L. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1992, **33**(1), 1002
- 3 Ishikawa, N., Okawara, M. and Imoto, E. *Kogyo Kagaku Zasshi* 1960, **63**, 2152
- 4 Kaneyuki, H., Ota, M. and Matsui, K. *Nippon Kagaku Zasshi* 1961, **82**, 940
- 5 Yoneda, F., Tanaka, K., Yamato, H., Moriyama, K. and Nagamatsu, T. *J. Am. Chem. Soc.* 1989, **111**, 9199
- 6 Shawl, E. T., Zajacek, J. G. and Kesling, H. S. *Eur. Pat. Appl.* 408 277, 1991
- 7 Roessler, M., Stern, G. and Muellner, M. *Eur. Pat. Appl.* 495 218, 1992
- 8 Caruso, S., Foti, S., Maravigna, P. and Montaudo, G. *J. Polym. Sci.* 1982, **20**, 1685
- 9 'Encyclopedia of Polymer Science and Engineering', 2nd Edn, Wiley, New York, 1979, Vol. 13, p. 229
- 10 'Kirk-Othmer Encyclopedia of Chemical Technology', 3rd Edn, Wiley, New York, 1979, Vol. 7, p. 403
- 11 Boenig, H. V., Walker, N. and Myers, E. H. *J. Appl. Polym. Sci.* 1961, **5**, 384
- 12 Borner, V. P., Gugel, W. and Pasedag, R. *Makromol. Chem.* 1967, **101**, 1
- 13 Sandler, S. R. and Karo, W. 'Polymer Synthesis', Academic Press, New York, 1992, Vol. 1, p. 220
- 14 Montaudo, G., Scamporrino, E. and Vitalini, D. *J. Polym. Sci.* 1983, **21**, 3321
- 15 Harris, R. F., Kinney, J. E., St Jeor, V. L., Bicerano, J. and Landes, B. unpublished results
- 16 'Kirk-Othmer Encyclopedia of Chemical Technology', 3rd Edn, Wiley, New York, 1981, Vol. 13, p. 800
- 17 Muller, E. 'Houben-Weyl Methoden der Organischen Chemie', Thieme-Verlag, Stuttgart, 1963, Vol. 8, p. 119
- 18 Hearsey, C. J. *US Pat.* 3 898 259, 1975
- 19 Hentschel, P., Zengel, H. and Bergfeld, M. *US Pat.* 4 223 145, 1980
- 20 Merger, F., Towae, F., Hellbach, H., Isbarn, G. and Koehler, W. *US Pat.* 4 596 678, 1986
- 21 Rosenthal, R. and Zajacek, G. *US Pat.* 3 936 484, 1976
- 22 DiSalvo, A. L. and Cornell, J. H. *J. Polym. Sci.* 1975, **13**, 97