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Synthesis and characterization of urea-based polyureas: 1. Urea-terminated poly(1,6-hexamethyleneurea) polyol dispersions

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The reactions of urea with 1,6-hexanediamine at 150°C in a polyol continuous phase in the presence of a stabilizer for the resultant particles, produce low-molecular-weight oligomers of urea-terminated poly(1,6-hexamethyleneurea) having a M_n in the range of 500–700 g mol^{-1}. This is thought to involve a polymerization/precipitation mechanism in which the molecular units are held together by hydrogen bonding into a macrostructure which separates as a stable dispersed phase. This macrostructure has a spiral fibre bundle morphology, a particle size distribution of about 1 to 10 μm, and aspect ratios from about 6 to 20. The urea-terminated poly(1,6-hexamethyleneurea) particles are highly crystalline thermoplastics with a melting point of $\sim$270°C and are only soluble in strong acids, where the macroparticles dissociate into their molecular units. High-molecular-weight poly(1,6-hexamethyleneurea) has been synthesized in bulk by other methods and is reported to have a melting point in the range 270–300°C. Urea-terminated poly(1,6-hexamethyleneurea) oligomers having a spiral fibre bundle morphology have not been previously reported. These materials are useful as filled polyols for polyurethanes.

(Keywords: polyureas; polyols; fillers)

INTRODUCTION

Polyurethanes are generally synthesized by reacting polyether polyols or polyester polyols with isocyanates[1]. Other organic polymers are sometimes incorporated into the polyether polyols as fillers (typically via *in situ* polymerization of the monomers[2]) to provide additional reinforcement (i.e. greater stiffness and hardness) to the polyurethanes, beyond the reinforcement provided by their hard segments. The industrial use of such reinforced polyurethanes is quite common, both in foam and elastomer applications. Polyols containing polymeric fillers are called *copolymer polyols*. Some examples of copolymer polyols are: (a) very commonly used *conventional copolymer polyols* where the filler particles are copolymers of styrene and acrylonitrile[3–6], (b) *PHD polyols* where the filler particles are polyureas[6–10], (c) *PIPA polyols* where the filler particles are polyurethanes[10,11], and (d) *epoxy dispersion polyols* where the filler particles are cured epoxy resins[12,13].

In all of the examples of copolymer polyols given above, the filler particles typically have an aspect ratio (A_f) close to one, where the A_f of a particle of regular shape (such as an ellipsoid) is defined as the ratio of the lengths of the longest and shortest dimensions. Therefore, $A_f \sim 1$ characterizes a particle of nearly spherical shape, including both spheres ($A_f = 1$) and irregular shapes with no major shape anisotropy. It is well known, from observations on many types of filled polymers, that a filler where $A_f \sim 1$ provides the least effective type of reinforcement[14], where the magnitude of the reinforcement is quantified by the ratio of the tensile (Young's) moduli of the filled and unfilled polymers. The reinforcing efficiency of filler particles possessing a given set of mechanical properties, when incorporated in a matrix material at a given volume fraction, rapidly increases with the increasing shape anisotropy of the particles, and eventually asymptotically approaches the continuous fibre limit for prolate

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particles (fibres), and the infinitesimally thin disk limit for oblate particles (platelets)[14].

Our work was started as an attempt to synthesize new copolymer polyols where the filler particles would: (a) be polyureas made from the reaction of an aliphatic diamine with urea (which have the advantages of being inexpensive and much less toxic than polyisocyanates), (b) have fibrous shapes with a significant amount of shape anisotropy ($A_f \gg 1$), and (c) be synthesized *in situ* in a polyol and form a stable dispersion of reasonable viscosity (thus being readily mixed with the polyisocyanate and incorporated into the polyurethane as a result of the polyol–isocyanate reaction). (The dispersion viscosity is an important consideration, since it increases with increasing A_f of the solid particles[15]. The relative increase of the viscosity, and the resulting undesirable increase in the difficulty of processing, are usually even greater than the desirable increase of the reinforcing efficiency in the filled polymer.) These goals have been achieved by synthesizing certain aliphatic polyurea copolymer polyol dispersions.

The synthesis (at 150°C) and characterization of urea terminated poly(1,6-hexamethyleneurea) copolymer polyols, which are one of the systems we have studied most extensively so far, will be discussed in this paper[16,17]. The properties of both the dispersions and the polyurea solids isolated from these dispersions will be considered. Subsequent papers in this series will discuss effects of reaction parameters on morphology control, effects of variations in amine structure and carbonyl source, and the properties of polyurethanes containing these particles.

EXPERIMENTAL

Starting materials

Urea, n-butylurea, 1,3-diethylurea, 1,6-hexanediamine, 1,6-hexanediisocyanate, n-hexylamine, and methanesulfonic acid were purchased from Aldrich Chemical Company. Voranol™ 4702 (a glycerol-initiated poly(propylene oxide), end-capped with poly(ethylene oxide); $MW = 5000$) was manufactured by The Dow Chemical Company. Partially aminated Voranol™ 4701 was prepared by the reductive amination of Voranol™ 4701 (a glycerol-initiated poly(propylene oxide), end-capped with poly(ethylene oxide); $MW = 5000$; manufactured by The Dow Chemical Company) to 30.6% conversion of the hydroxyl moieties to amino moieties[18]. Jeffamine™ M-2005 (an ethylene oxide/propylene oxide adduct of 2-methoxyethanol; $MW = 2000$; aminated so that its hydroxyl groups are converted to amino moieties) was obtained from Texaco.

Preparation of an internal urea prepared from urea and excess n-hexylamine

n-Hexylamine (101.2 g, 1.0 mol) was placed in a 250 ml flask under nitrogen and heated at reflux with stirring. Urea (20.0 g, 0.333 mol) was added in small batches over a 30 min period. The reactor was heated at reflux for an additional 4 h; the reactor temperature increased from 133 to 150°C. The crude reaction product was poured into water (1000 ml), and the resultant slurry was neutralized with H_2SO_4 (1 N) to pH ~ 4 and filtered. The solid white product was washed several times with water and then dried in a vacuum oven at 120°C.

Preparation of an extended internal urea prepared from n-hexylamine and 1,6-hexanediisocyanate

n-Hexylamine (76.34 g, 0.754 mol) was placed in a 500 ml flask, under nitrogen, containing a dropping funnel, condenser, thermometer and mechanical stirrer. 1,6-Hexanediisocyanate (31.7 g, 0.189 mol) was added to the dropping funnel. The diisocyanate was added dropwise, while maintaining a temperature of 30–35°C (ice bath cooling) over a 45 min period. The cooling was removed and stirring was continued for an additional 1 h. Water (300 ml) was added to the crude reaction product and the resultant slurry was neutralized with H_2SO_4 (1 N) to pH ~ 4 and filtered. The solid white product was washed several times with water and dried in a vacuum oven at 120°C.

Preparation of a terminal urea prepared from 1,6-hexanediamine and excess urea

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 a temperature of 145°C. Then, 30 min after the final addition, the crude reaction product was poured into water (700 ml) and the resultant slurry was neutralized with H_2SO_4 (1 N) to pH ~ 4 and filtered. The solid white product was washed several times with water and dried in a vacuum oven at 120°C.

Preparation of a polyurea polyol dispersion

Voranol™ 4702 (800 g), urea (1.0 g), 1,6-hexanediamine (1.12 g) and a partially (30.6%) aminated Voranol™ 4701 (16.0 g) were combined in a 1000 ml resin kettle, under nitrogen, equipped with a mechanical stirrer, condenser and a port for solids addition. The mixture was heated at 150°C for 22 h to form the stabilizer solution. Additional urea (34.0 g) and 1,6-hexanediamine (65.6 g) were ground together and added to the reactor in small portions over 8 h; the stirring speed was 1200 rev min^{-1}. The reactor was continually heated until titrometric analysis indicated no change in amine concentration. Additional urea (4.0 g) was added to react with any residual amine and the reactor was stirred for an additional 20 h at 150°C. The stirring rate was slowed to 500 rev min^{-1} and vacuum (10 mmHg) was applied to the system for 2 h. After cooling, the product was filtered through an 80 mesh screen. The finished particulate polymer was a stable dispersion having a viscosity of 2.2 Pa s at 25°C and a solids content of 9.1 wt%.

Isolation of particulate polymer

A sample of the polyurea polyol dispersion prepared above (10 g) was placed in a 200 ml jar. Methanol was added (150 ml) and the jar was shaken vigorously in order to wash the Voranol™ 4702 off the surface of the particles. The resultant slurry was filtered through a fine sintered glass filter to remove the methanol and Voranol™ 4702. The polymer on the filter was washed with additional methanol (200 ml) to be sure that all of the Voranol™ 4702 was removed from the polymer surface. The resultant white solid polymer was then placed in a vacuum oven at 150°C for ~ 1 h to remove any residual methanol. The polymer had a melting point of ~270°C by optical microscopy and by differential scanning calorimetry (d.s.c.).

Isolation of stabilizer solids

A sample of the stabilizer prepared above was placed in a 200 ml jar. Methanol was added (150 ml) and the jar was shaken vigorously in order to wash the Voranol™ 4702 off the surface of the particles. The resultant slurry was filtered through a fine sintered glass filter to remove the methanol and Voranol™ 4702. The stabilizer on the filter was washed with additional methanol (200 ml) to be sure that all of the Voranol™ 4702 was removed from the stabilizer surface. The resultant tan paste was then placed in an oven at 150°C for ~1 h to remove any residual methanol.

Characterization procedures

Dispersion basicities were determined by potentiometric titration of samples dispersed in methanol with HCl (0.1 N) using a Brinkmann 636 Titroprocessor. ^{13}C 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). Scanning electron microscopy (SEM) was carried out on a Hitachi S-570 scanning electron microscope; the samples had 15–20 nm of sputter coating (50/50 mixture of an Au–Pd blend), carried out on a Hummer X. Transmission electron microscopy (TEM) grids were coated with a thin film of Formvar. Particles were sprinkled on to the film and the grids, with film and particles, were stabilized with an evaporated carbon film and examined directly using a JEOL TEM 100CX at 80–100 kV. Environmental scanning electron microscopy (ESEM) was carried out on an Electroscan ESEM. A thin layer of dispersion was applied to a polished carbon specimen stub and examined at a pressure of 4 torr at 25°C. Particle size distributions were determined by using a Horiba (Model LA-500) laser light scattering instrument with the polyurea particles suspended in methanol.

Thermal analysis

Melting temperatures were measured on a Du Pont Instrument 910 differential scanning calorimeter scanning from ambient to 350°C at a rate of 10°C min^{-1} under nitrogen. Samples (~10 mg) were encased in crimped aluminium pans. The chromel–alumel thermocouple was calibrated using indium and lead standards. Elevated-temperature weight loss data were measured on a Du Pont Instrument 951 Thermogravimetric Analyzer with an Omnitherm brand hot quartz beam and disposable aluminium pans, from ambient temperature to 600°C under nitrogen. The chromel–alumel thermocouple was calibrated using indium and lead standards. Both modules were interfaced with a Du Pont 9900 Thermal Analyzer/Computer for data reduction and analysis.

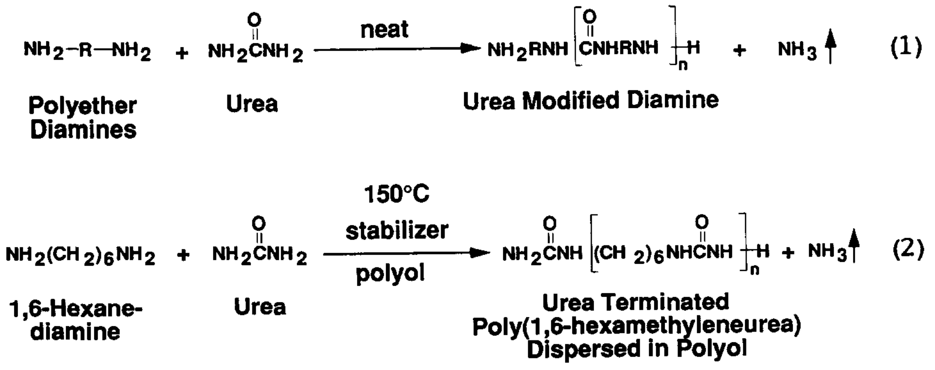
RESULTS AND DISCUSSION

Synthesis

Polyurea polyol dispersion synthesis. The neat reactions of polyamines with urea provide a convenient method for making oligomers which contain internal urea moieties in their backbone and end groups which are either amino-functional[19–25] or urea-functional[26–31], depending on the stoichiometry of the reactants. *Figure 1* (equation (1)) illustrates this synthesis for urea-modified diamines.

The polyurea polyol dispersions described in this paper were made by reacting 1,6-hexanediamine and urea in a polyether polyol at 150°C in the presence of a stabilizing agent[16]. In the first step of the reaction sequence, the stabilizing agent was prepared *in situ* by reacting a partially aminated (30.6%) Voranol 4701, in Voranol 4702, with a small amount of urea and 1,6-hexanediamine. In the second step, the majority (97–98%) of the urea and 1,6-hexanediamine was added to the reactor, as solid, in small batches in equal molar amounts at 150°C using a stirring rate of about 1200 rev min^{-1}. Amine conversion was 93–95% at the end of the second step. In the third step, additional urea was added in amounts sufficient to convert the residual amine end groups to terminal urea groups. Amine conversion was ~99% after this third step. As a finishing step, vacuum was applied to the reactor at 150°C to remove any volatile components. The product was a stable dispersion of about 10-wt%-urea-terminated poly(1,6-hexamethyleneurea) in Voranol. *Figure 1* (equation (2)) gives the overall equation.

The stabilizer can also be made separately as a concentrate and added as needed for polyurea polyol dispersion preparation. Details of the effects of reaction parameters on polyurea polyol dispersion synthesis and properties will be the subject of the second paper in this series.



$$NH_2{-}R{-}NH_2 + NH_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{\text{neat}} NH_2RNH\left[\overset{O}{\overset{\|}{C}}NHRNH\right]_nH + NH_3\uparrow \quad (1)$$

$$NH_2(CH_2)_6NH_2 + NH_2\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[\text{polyol}]{\text{150°C stabilizer}} NH_2\overset{O}{\overset{\|}{C}}NH\left[(CH_2)_6NH\overset{O}{\overset{\|}{C}}NH\right]_nH + NH_3\uparrow \quad (2)$$

Figure 1 Selected reactions of diamines with urea

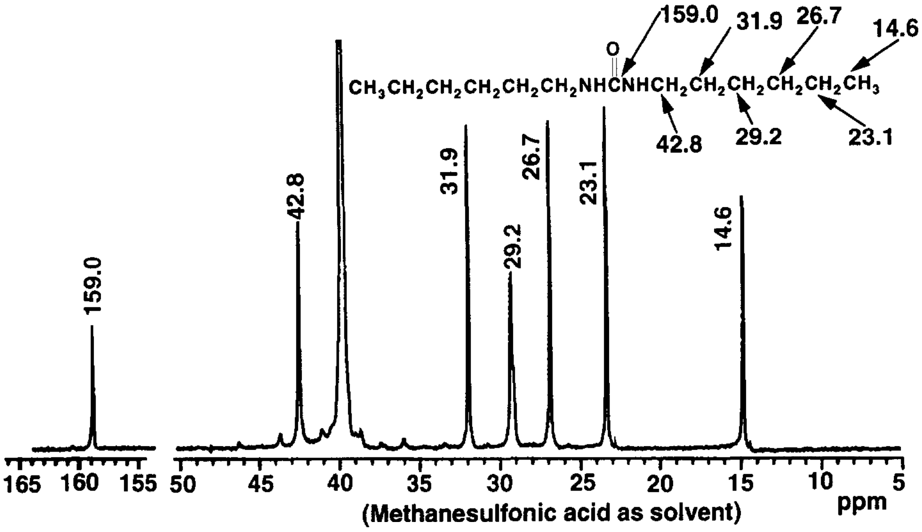


Figure 2 ^{13}C n.m.r. spectrum of an internal urea prepared from urea and excess n-hexylamine

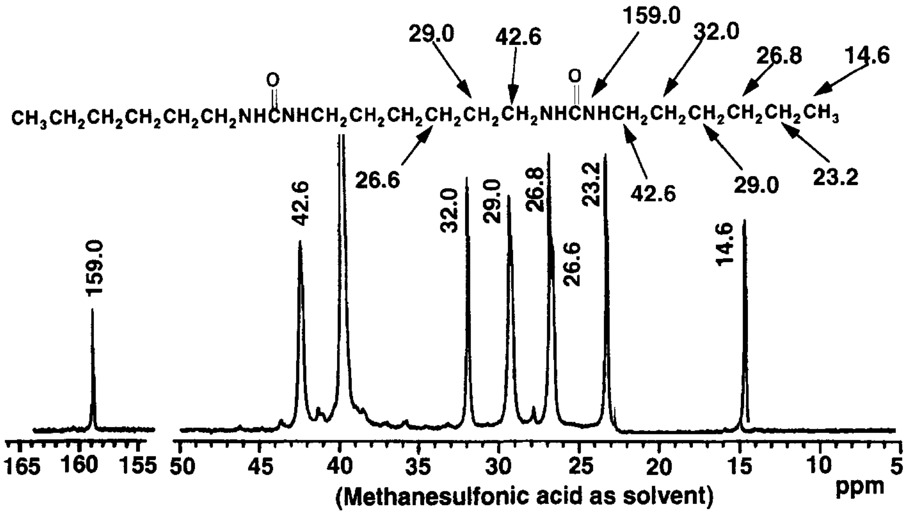


Figure 3 ^{13}C n.m.r. spectrum of an extended internal urea prepared from n-hexylamine and 1,6-hexanediisocyanate

Particulate particle isolation and solubility. The particulate particles were separated from the Voranol 4702 continuous phase by treatment with methanol. The particles were insoluble in methanol, while the Voranol 4702 was soluble. The particles were separated by filtration and residual Voranol 4702 was removed by additional washing with methanol. After drying, the particles were obtained as a free-flowing white solid.

The particles were insoluble in all common organic solvents. It had previously been shown that aliphatic polyurea structures react with strong acids and can be titrated by perchloric acid in glacial acetic acid[25]. These particles were found to be highly soluble in strong acids such as sulfuric and methanesulfonic acid. Methanesulfonic acid was a good solvent for ^{13}C n.m.r. analysis.

Model systems for ^{13}C n.m.r. spectroscopic study. A series of model urea-containing materials was analysed by ^{13}C n.m.r. spectroscopy in order to develop a spectral data base to verify the structure of the particles isolated from the 1,6-hexanediamine/urea polyurea polyol dispersions. The ^{13}C n.m.r. spectral results for urea, n-butylurea, and diethylurea in methanesulfonic acid indicated that the unsubstituted urea, terminal aliphatic urea, and internal aliphatic urea carbonyl carbon atoms were clearly resolved at 163.2, 160.6, and 159.2 ppm, respectively (relative to methanesulfonic acid at 40.0 ppm). The aliphatic methyl and methylene carbon atoms also gave important structural information. There was a systematic increase in chemical shift as the carbon atoms were located closer to the urea moiety (42.2, 31.3, and 20.3 for the methylene carbon atoms α, β, and γ to the urea moiety in n-butylurea). Di-n-hexylurea was used as a model of a linear six-carbon-atom internal urea (*Figure 2*). The internal urea carbonyl carbon atoms were present at 159.0 ppm; the methyl and methylene carbon atom line patterns were identified.

A larger-molecular-unit model was prepared from n-hexylamine and 1,6-hexanediisocyanate. This molecule had linear, six-carbon-atom end groups, two internal, aliphatic urea moieties, and a linear six-carbon-atom segment between the internal urea moieties (*Figure 3*). The internal urea carbonyl carbon atoms were present at 159.0 ppm. The linear, six-carbon-atom segment between the internal urea moieties had a three-line pattern, due to symmetry, at 42.6, 29.0, and 26.6 ppm for the methylene

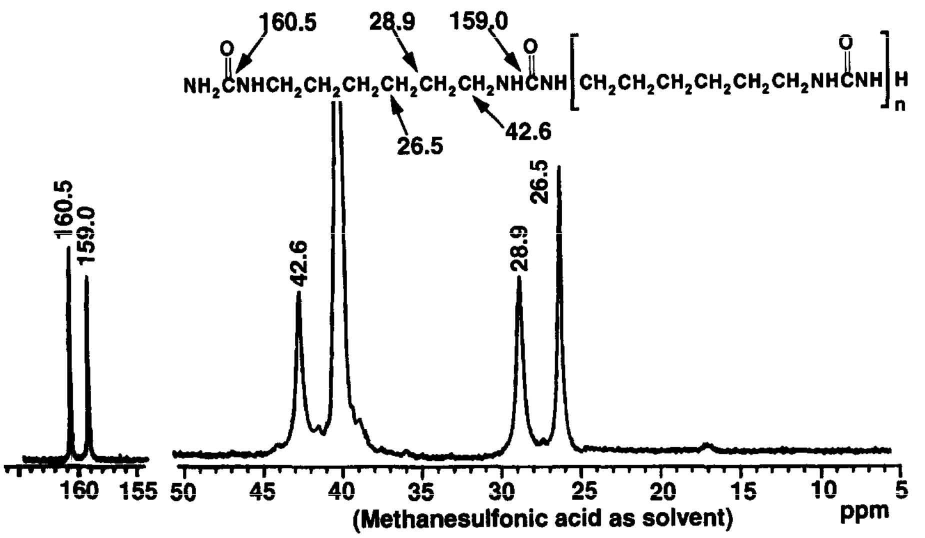


Figure 4 ^{13}C n.m.r. spectrum of a terminal urea prepared from 1,6-hexanediamine and excess urea

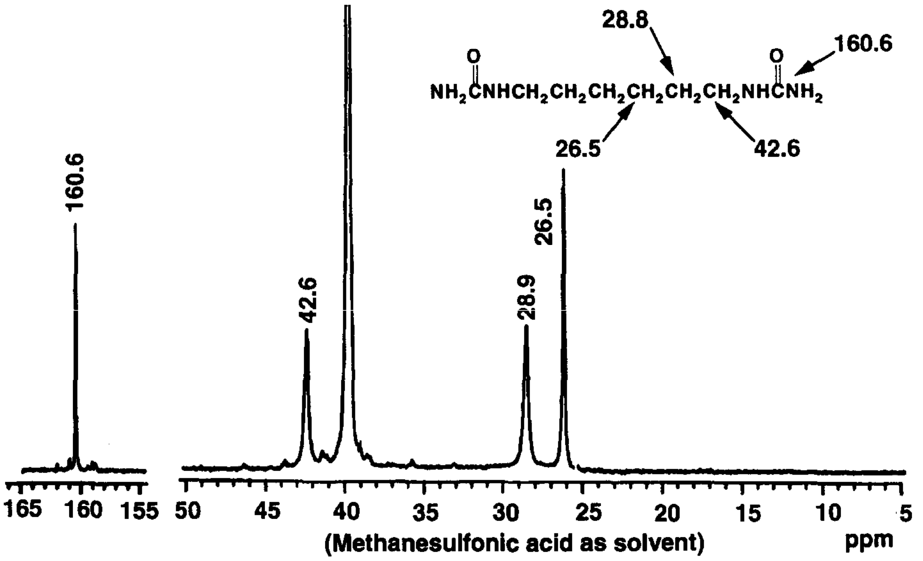
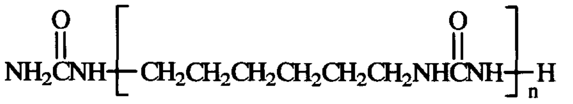


Figure 5 ^{13}C n.m.r. spectrum of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion

carbon atoms α, β, and γ to the internal urea carbonyl atoms, respectively. The six-carbon-atom end groups had the same line spectrum as di-n-hexyl urea.

An additional model compound was prepared by the reaction of 1,6-hexanediamine with a large excess of urea. This molecule has a linear, six-carbon-atom segment between the terminal urea moieties (*Figure 4*), and had a four-line pattern. The terminal urea carbonyl carbon atoms were present at 160.6 ppm. 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 α, β, and γ to the terminal urea carbonyl atoms, respectively.

^{13}C n.m.r. of 1,6-hexanediamine/urea polyurea polyol dispersion solids. The ^{13}C n.m.r. spectrum of the solids isolated from the polyurea polyol dispersion based on 1,6-hexanediamine/urea is given in *Figure 5*. It has a simple, five-line pattern. Terminal urea carbonyl carbon atoms and internal urea carbonyl carbon atoms were present at 160.5 and 159.0 ppm, respectively. 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 α, β, and γ to the urea carbonyl atoms, respectively. These results strongly suggest that the structure of the dispersed solids was that of a urea-terminated poly(1,6-hexamethyleneurea) as indicated below:



$$NH_2\overset{O}{\overset{\|}{C}}NH\left[CH_2CH_2CH_2CH_2CH_2CH_2NH\overset{O}{\overset{\|}{C}}NH\right]_nH$$

Solids were also isolated from polyurea polyol dispersions based on 1,6-hexanediamine/urea where other modifications were made in the dispersion preparation. In one case, Jeffamine M-2005 was used in place of partially aminated Voranol 4701. In a second case, Voranol 5287 (a diol with $MW = 2000$) was used as the continuous phase in place of Voranol 4702. In each

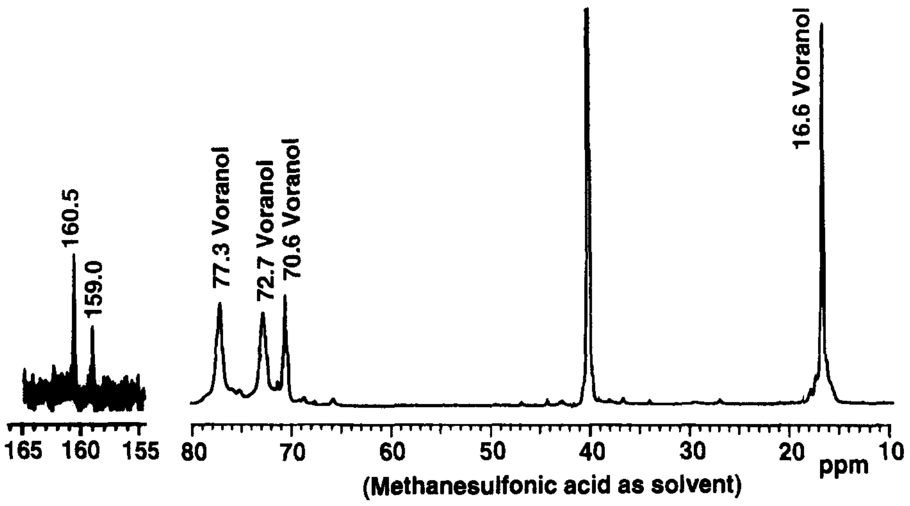


Figure 6 ^{13}C n.m.r. spectrum of stabilizer concentrate based on partially aminated Voranol™ 4701/1,6-hexanediamine/urea

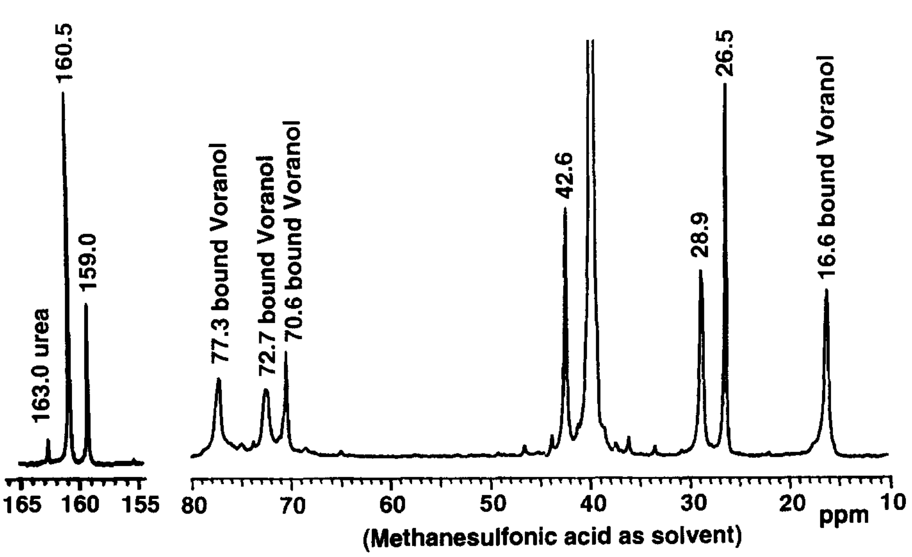


Figure 7 ^{13}C n.m.r. spectrum of stabilizer solids based on partially aminated Voranol™ 4701/1,6-hexanediamine/urea

case the solids isolated from the dispersion had the same n.m.r. spectra as that shown in *Figure 5*.

Isolation and ^{13}C n.m.r. spectrum of stabilizer. The stabilizer concentrate based on partially aminated Voranol 4701, urea, and 1,6-hexanediamine in Voranol 4702 was dissolved in methanesulfonic acid and its spectrum obtained (*Figure 6*). At normal amplification, only Voranol 4702 was detected. However, when the carbonyl carbon atom region of the spectrum was expanded considerably, lines were detected at 160.5 and 159.0 ppm, corresponding to terminal urea and internal urea, respectively.

The stabilizer was separated from the Voranol 4702 continuous phase by treatment with methanol. The stabilizer had limited solubility in methanol while the Voranol 4702 was soluble. The stabilizer was separated by filtration and residual Voranol 4702 was removed by additional washing with methanol. After drying, the particles were obtained as a white pasty solid.

The stabilizer was dissolved in methanesulfonic acid and its spectrum obtained (*Figure 7*). Urea carbonyl carbon atoms, terminal urea carbonyl carbon atoms, and internal urea carbonyl carbon atoms were present at 163.0, 160.5, and 159.0 ppm, respectively. 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 α, β, and γ to the urea carbonyl atoms, respectively. Lines at 16.6, 70.6, 72.7, and 77.3 ppm represent Voranol 4701 that was chemically part of the stabilizer structure. These results are consistent with the structure of the stabilizer given in *Figure 8*.

This stabilizer was effective since one end of the molecule was similar to the urea-terminated poly(1,6-hexamethyleneurea) solids, while the other end of the molecule was structurally similar to the Voranol 4702 continuous phase.This is similar to stabilizer strategies used in other filled polyols: PHD and PIPA polyol dispersions utilize polyisocyanate–polyol reactions for stability, while copolymer polyol dispersions use a vinylized polyol graft for stability.

Materials characterization: fluids

Polyurea polyol dispersion viscosity characterization. Viscosity measurements (*Figure 9*) indicated

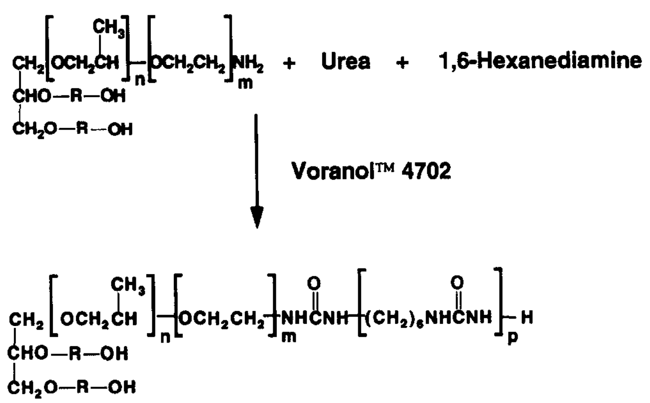


Figure 8 Reaction sequence for stabilizer preparation

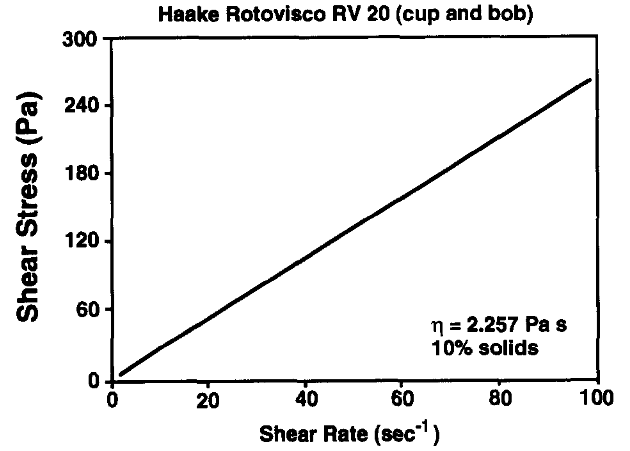


Figure 9 Shear stress vs. shear rate for polyurea polyol dispersion at 25°C

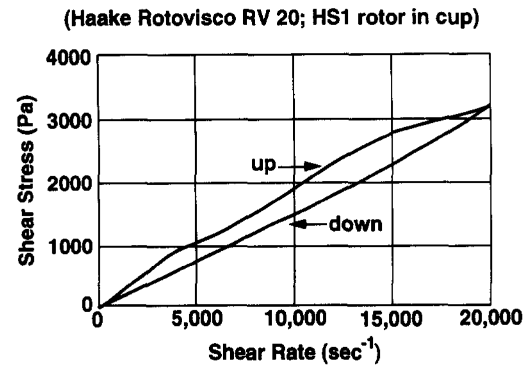


Figure 10 Shear stress vs. shear rate for polyurea polyol dispersion at 75°C

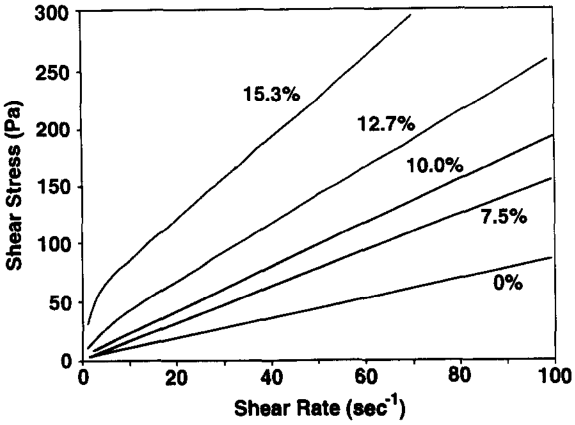


Figure 11 Effects of loading on shear stress vs. shear rate for urea-terminated poly(1,6-hexamethyleneurea) solids redispersed in Voranol™ 4702

Table 1 Viscosities of urea-terminated poly(1,6-hexamethyleneurea) solids redispersed in Voranol 4702[a]

Redispersed solids (wt%)	Viscosity (Pas)
15.3	4.212
12.7	2.803
10.0	1.955
7.5	1.531
0	0.846

[a] Measured at 25°C at a shear rate of 70 s^{-1}

that polyurea polyol dispersions with 10 wt% solids were Newtonian fluids (from 1 to 100 s^{-1} shear rate) with viscosities of $\sim$2.2 Pa s at 25°C. When the shear rate was scanned from 1 to 20 000 s^{-1} at 75°C, some curvature was experienced; some hysteresis was experienced on the reverse scan (*Figure 10*). Viscosities at 10% solids were low enough to be useful under a broad range of polyurethane fabrication conditions.

Viscosities as a function of solids loading were determined by separating the solids from the polyol continuous phase, followed by redispersion at various solid levels. A 10 wt% polyurea polyol dispersion (160 g) was added to a mixture (500 g) of isooctane (70 vol%) and toluene (30 vol%). The resultant slurry was stirred, filtered, washed (with the same solvent mixture), and dried (16 h, 120°C/< 1 mmHg) to give a white powder[16]. After solids removal, nothing was detected in the serum phase (after solvent stripping) by viscosity, i.r. spectroscopy, or size exclusion chromatography (s.e.c.). When a portion of the isolated solids was redispersed in fresh Voranol 4702 at 10 wt%, no change in viscosity profile was experienced. Portions of the solids were redispersed in Voranol 4702 at selected concentrations. *Figure 11* shows both an increase in viscosity and a deviation from Newtonian behaviour with increased loading levels (from 1–100 s^{-1}). Viscosities are given in *Table 1* and plotted vs. solids content in *Figure 12*. Since the behaviour of some of the samples was non-Newtonian at low shear rates, the viscosities were taken at a shear rate of 70 s^{-1}, a region where the viscosity profiles were all relatively flat.

Polyurea polyol dispersion particle size characterization. In one series of experiments, the particle size and distribution of the dispersion solids were measured by laser light scattering. Jeffamine M-2005 was used as the stabilizer precursor and a stabilizer concentrate (22.6 wt% stabilizer in Voranol 4703) was made using a molar ratio of Jeffamine 2005/1,6-hexanediamine/urea of 1.0/4.0/5.0. This stabilizer concentrate was used

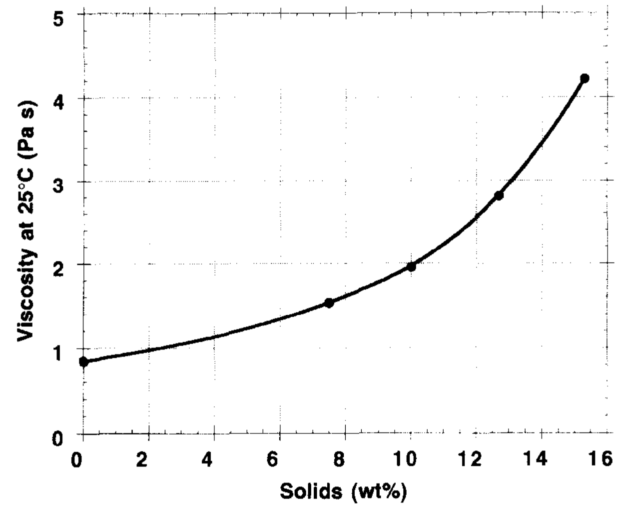


Figure 12 Viscosities of urea-terminated poly(1,6-hexamethyleneurea) solids redispersed in Voranol™ 4702, measured at 25°C

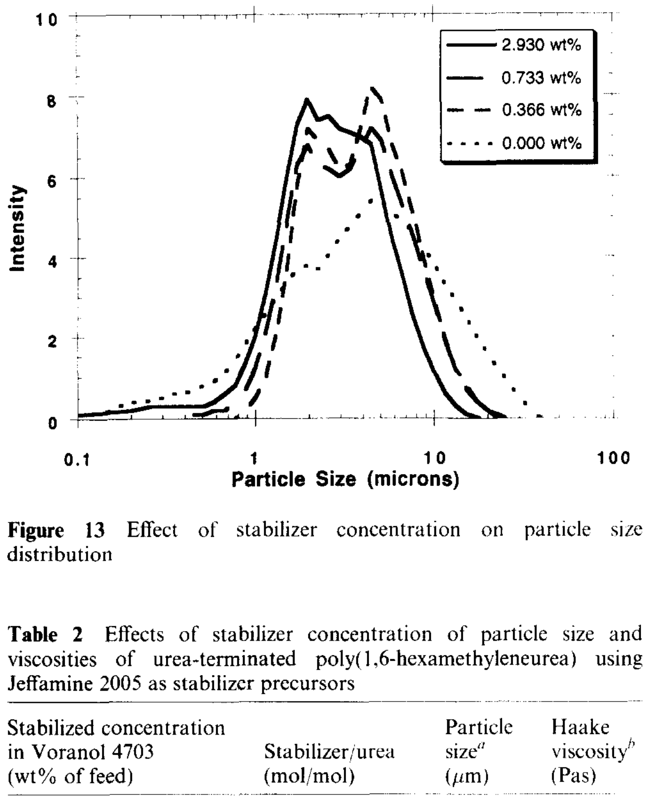


Figure 13 Effect of stabilizer concentration on particle size distribution

Table 2 Effects of stabilizer concentration of particle size and viscosities of urea-terminated poly(1,6-hexamethyleneurea) using Jeffamine 2005 as stabilizer precursors

Stabilized concentration in Voranol 4703 (wt% of feed)	Stabilizer/urea (mol/mol)	Particle size[a] (μm)	Haake viscosity[b] (Pas)
2.930	0.0160	2.48	0.2350
1.465	0.0080	2.51	0.2355
0.733	0.0040	3.22	0.2347
0.366	0.0020	3.60	0.2358
0.000	0.0000	3.76	0.1257

[a] Particle sizes are median values
[b] Measured at 25°C

to make a series of polyurea polyol dispersions in which the stabilizer concentration was varied systematically from 2.930 to 0 wt%. The results are given in *Table 2* and plotted in *Figure 13*. The curves indicate little change in particle size and distribution between stabilizer concentrations of 2.930 and 0.366 wt%; median particle sizes increase with decreasing stabilizer concentration. A bimodal particle size distribution is evident. When the stabilizer is absent during dispersion synthesis, the distribution of dispersed particles becomes much broader. In addition, only ~50% of the solids are dispersed in the absence of stabilizer. The remainder of the solids drop out and are not dispersible. The viscosity remains constant as the stabilizer concentration is reduced (constant solids loading). However, the viscosity drops sharply in the absence of stabilizer due to the 50% reduction in solids loading.

Figure 14 Environmental scanning electron microscopy of urea-terminated poly(1,6-hexamethyleneurea) particles contained in a polyurea polyol dispersion

Polyurea polyol dispersion particle morphology in Voranol. When the polyurea polyol dispersions were studied by optical microscopy, it was clear that the particles had significant aspect ratios. The polyurea polyol dispersions were then studied by environmental scanning electron microscopy (ESEM) in order to visualize the particles without removing them from the polyol continuous phase. *Figure 14* clearly shows that the particles have significant aspect ratios and appear as bundles of fibres approximately 5 μm in length. This is a unique morphology for a filled polyol dispersion. All previously described filled polyol dispersions are spherical or nearly spherical.

Materials characterization: solids

Thermal analysis of urea-terminated poly(1,6-hexamethyleneurea) solids. When the solids isolated from the polyurea polyol dispersion based on 1,6-hexanediamine/urea were analysed by thermogravimetric analysis (t.g.a.) in nitrogen the trace given in *Figure 15* was obtained. A differential scanning calorimetry (d.s.c.) trace in nitrogen of the same sample showed endotherms centred at 202 and 262°C (*Figure 16*); the cooling curve indicated a crystallization exotherm centred at 205°C. The endotherm at 202°C was identified as N,N'-(1,6-hexanediyl)bisurea, **1**, by t.g.a./gas chromatography/mass spectroscopy[32]. This is the lowest-molecular-weight species in the molecular-weight distribution of **2** (**2** = **1**, when $n = 1$).

A portion of the same solids isolated from the polyurea polyol dispersion based on 1,6-hexanediamine/urea was treated in a vacuum oven (240°C/1 mmHg) for 1 h. A d.s.c. trace of the residue showed no endotherm at around 200°C (*Figure 17*), but a

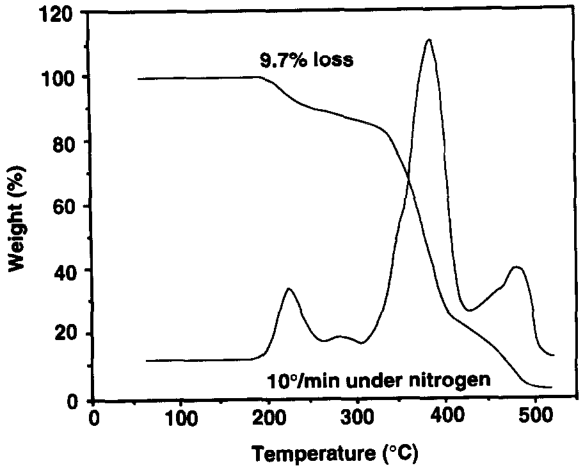


Figure 15 Thermogravimetric analysis of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion

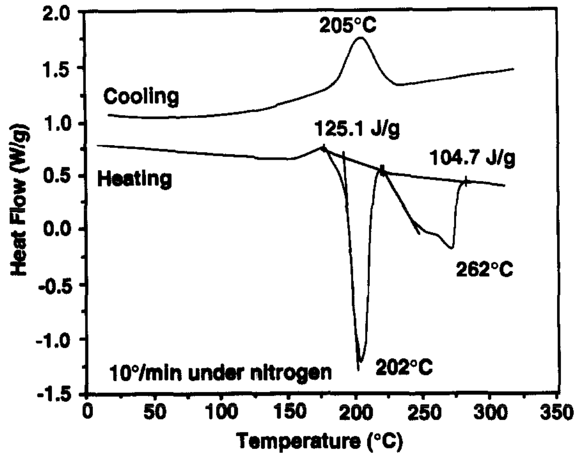


Figure 16 Differential scanning calorimetry of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion

multiple endotherm centred at 269°C, indicating molecular-weight advancement. Some crystallinity was lost during the thermal annealing procedure. This endotherm was shown to be the melting point of the urea-terminated poly(1,6-hexamethyleneurea), **2**. A thermally annealed sample was also heated on a hot-stage microscope and the melting point was observed at 270°C. More details of the thermal behaviour of **2** will be presented in the second paper of this series; this material is an interesting thermoplastic in its own right.

Molecular weight by quantitative ^{13}C n.m.r. spectroscopy. Since the terminal and internal urea carbonyl carbon atoms are clearly resolved, the ratio of these resonance lines in a quantitative ^{13}C n.m.r. spectrum can be used to calculate the number-average molecular weight (M_n). In ^{13}C n.m.r. spectroscopy the nuclei are allowed to relax to equilibrium (D1), inverted with a 180° pulse (P1), then given a variable time to return to equilibrium (D2), and finally are given a monitoring pulse (PW) to measure their peak heights as a function of D2. The behaviour of the peak heights as a function of D2 will be exponential, and this exponential time is the T1 value. The 180° pulse width needed to give zero intensity was determined to be 30 μs. By taking half of this value, the 90° pulse width was determined to be 15 μs. The T1 values for the external and internal carbonyl carbons were determined to be 0.83 and 1.48 s, respectively. A minimum delay time (D1) would be $5 \times$ (the largest T1), which would be $\sim$7.5 s. In our case, a D1 of 20 s was used; with the correct delay times, quantitative spectra were obtained.

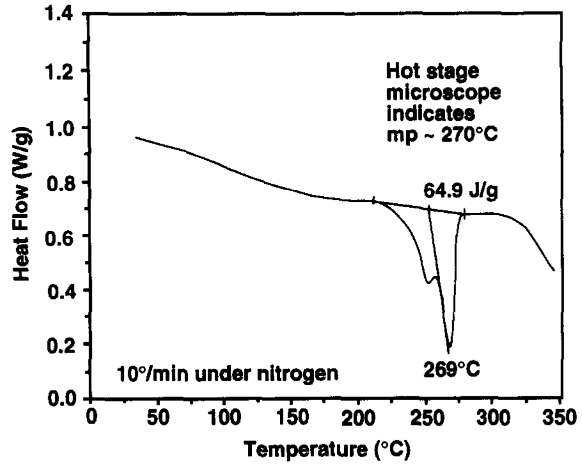
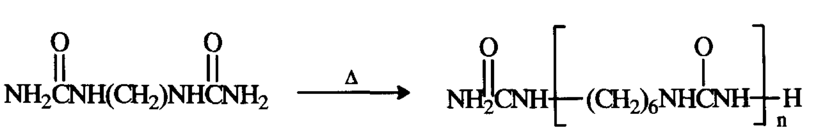


Figure 17 Differential scanning calorimetry of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion (after heating at 240°C/1 mmHg for 1 h)



$$NH_2\overset{\overset{O}{\|}}{C}NH(CH_2)NH\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow{\Delta} NH_2\overset{\overset{O}{\|}}{C}NH\left[(CH_2)_6NH\overset{\overset{O}{|}}{C}NH\right]_n H$$

The ratios of the internal (159.0 ppm) and terminal (160.5 ppm) carbonyl carbon peaks of the urea-terminated poly(1,6-hexamethyleneurea) were determined by examination of the lines between 158–161 ppm. This region was expanded and the two peaks were integrated. A representative quantitative ^{13}C n.m.r. spectral trace is given in *Figure 18*. The number-average molecular weight (M_n) was calculated to be $\sim$666 g mol^{-1}; $n = \sim 4.3$, on average. The M_n values ranged from $\sim$500 to 700 g mol^{-1} for the samples studied, indicating that the urea-terminated poly(1,6-hexamethyleneurea) particles were composed of oligomeric molecular units.

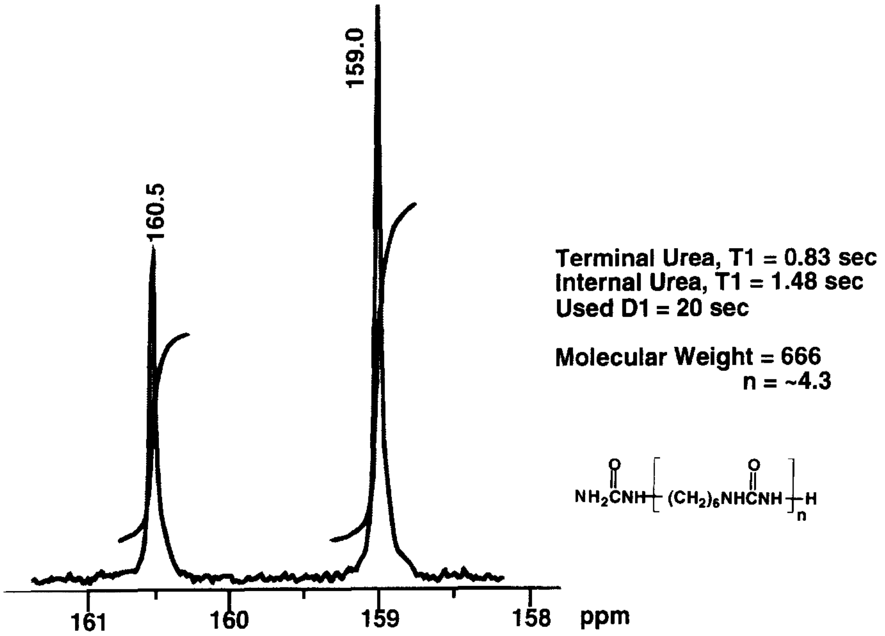


Figure 18 Number-average molecular weight of urea-terminated poly(1,6-hexamethyleneurea) by quantitative ^{13}C n.m.r. spectroscopy

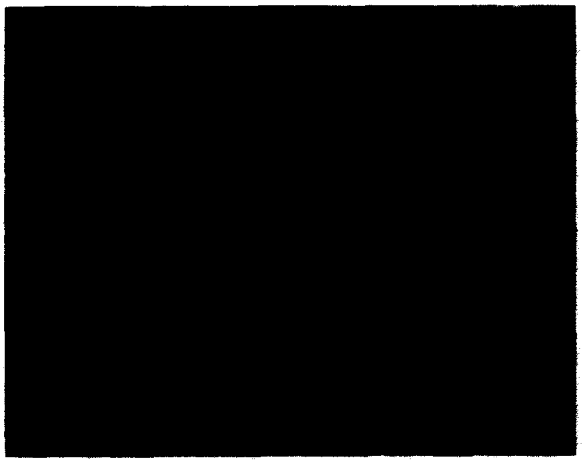


Figure 19 Scanning electron microscopy of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion

Figure 20 Scanning electron microscopy of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion (expanded scale)

Morphology of urea-terminated poly(1,6-hexamethyleneurea particles. The isolated polyurea polyol dispersion particles based on 1,6-hexanediamine and urea in Voranol 4702, prepared at 150°C using a partially aminated Voranol 4701 based stabilizer were shown by scanning electron microscopy to have a spiral fibre bundle morphology (*Figure 19*). These urea-terminated poly(1,6-hexamethyleneurea) fibre bundle particles range from 3 to 10 μm in length and have aspect ratios of ~6 to 20. At higher magnifications, the fibres making up the bundles all appear to twist in the same direction for all bundles in a given batch and appear to be rather tightly wrapped (*Figure 20*). These results are consistent with the ESEM visualizations, indicating that this morphology is present in the dispersion and is not an artifact of solids isolation.

Transmission electron microscopy indicated an openness to the spiral fibre bundles (*Figure 21*). The bundles appeared as small swatches of fabric. This open structure should enhance their effectiveness as reinforcing particles in a resin matrix because of increased surface area, thus allowing penetration of the resin.

Much more detailed morphological studies (SEM, wide-angle X-ray scattering (WAXS), Fourier transform infra-red (*FT*i.r.) spectroscopy, etc.) to indicate the extent of morphology control by adjusting reaction parameters will be presented in the next paper in this series.

CONCLUSIONS

The reactions of urea with 1,6-hexanediamine at 150°C in a polyol continuous phase in the presence of a stabilizer for the resultant particles, produce low-molecular-weight oligomers of urea-terminated poly(1,6-

Figure 21 Transmission electron microscopy of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion

hexamethyleneurea) having an M_n in the range 500–700 g mol^{-1}. This is thought to involve a polymerization/precipitation mechanism in which the molecular units are held together by hydrogen bonding into a macrostructure which separates as a stable dispersed phase. This macrostructure has a spiral fibre bundle morphology, a particle size distribution of ~1 to 10 μm, and aspect ratios from ~6 to 20. The urea-terminated poly(1,6-hexamethyleneurea) particles are highly crystalline thermoplastics with a melting point of ~270°C and are only soluble in strong acids, where the macroparticles dissociate into their molecular units.

High-molecular-weight poly(1,6-hexamethyleneurea) has been synthesized in bulk by other methods[33–37] and is reported to have a melting point in the range 270–300°C[33,35,37]. However, urea-terminated poly(1,6-hexamethyleneurea) oligomers having a spiral fibre bundle morphology have not been previously reported[38].

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