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Synthesis and characterization of urea-based polyureas: 2. Morphology control in urea-terminated poly(1,6-hexamethyleneurea) particles

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The effects of reaction parameters on the synthesis of urea-terminated poly(1,6-hexamethyleneurea) particles dispersed in a polyol continuous phase have been studied. Oligomeric units are held together by hydrogen bonding into a macrostructure which separates as a stable dispersed phase during synthesis. Monomer addition rate, synthesis temperature and stirring rate are important factors in morphology control of the particles. High aspect ratio (10–20) particles having a spiral fibre bundle morphology (by scanning electron microscopy) are produced at synthesis temperature between 140 and 175°C; spherical particles are produced at 185°C. Particles produced at 140°C have a different crystalline structure from particles produced at higher temperatures. Molecular weight, particle size and the extent of hydrogen bonding increase with increasing synthesis temperature. The structure of these highly crystalline particles is established at an early stage in the reaction. Annealing up to 185°C has little effect on particle morphology. Annealing near the melting point (270°C) results in loss of crystallinity; particle macrostructure is destroyed by melting or dissolution.

(Keywords: polyureas; poly(1,6-hexamethyleneurea); morphology)

INTRODUCTION

The reactions of urea with 1,6-hexanediamine 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)[1-4]. The reactions are 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. When the polyurea polyol dispersions are synthesized at 150°C, this macrostructure has a spiral fibre bundle morphology, a particle size distribution of ~ 1–10 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 macrostructure dissociates into the molecular units. Urea-terminated poly(1,6-hexamethyleneurea) oligomers having a spiral fibre bundle morphology have not been previously reported by groups other than ours[3,4].

The synthesis (at 150°C) and characterization of urea-terminated poly(1,6-hexamethyleneurea) copolymer polyol dispersions were reported in the first paper in this series[3]. This paper will discuss dispersion synthesis in more detail and delineate the effects of reaction parameters on morphology control. Subsequent papers will present initial results of modelling these unique particles, address the effects of variations in amine structure and carbonyl source and discuss the properties of polyurethanes containing these particles.

EXPERIMENTAL

Starting materials

Urea and 1,6-hexanediamine were purchased from Aldrich. Voranol 4703 (a glycerol-initiated poly(propylene oxide) end capped with poly(ethylene oxide); 5000 g mol^{-1} molecular weight) was manufactured by Dow. 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); 5000 g mol^{-1} molecular weight; manufactured by Dow) to 30.6% conversion of the hydroxy moieties to amino moieties[5]. Jeffamine M-2005 (an

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aminated 2-methoxyethanol-initiated poly(propylene oxide) adduct of nominally 2000 g mol^{-1} molecular weight containing 5% randomly incorporated ethylene oxide) was obtained from Texaco.

Stabilizer concentrate based on 1,6-hexanediamine, urea and Jeffamine M-2005

Voranol 4703 (668.4 g), urea (21.12 g, 0.3516 mol), 1,6-hexanediamine (32.48 g, 0.2795 mol) and Jeffamine M-2005 (152.1 g, 0.0703 mol) were combined in a 1000 ml resin kettle equipped with a mechanical stirrer, thermometer, condenser and temperature controller, and maintained under a nitrogen atmosphere. The mixture was heated at 150°C for 20 h. The resultant stabilizer concentrate was calculated to be 22.6 wt% active.

Preparation of a polyurea polyol dispersion

A portion of the stabilizer concentrate (108 g) and Voranol 4703 (750.0 g) were combined in the same reaction kettle used above and heated to 150°C (2.93 wt% stabilizer). Urea (33.0 g, 0.5495 mol) and 1,6-hexanediamine (62.0 g, 0.5335 mol) were ground together under nitrogen and added to the reactor in small (~13.5 g every 45 min) portions over ~5 h. The stirring rate was 1200 rev min^{-1} unless otherwise noted. The reactor was heated until titrometric analysis indicated no change in amine concentration (20 h). Additional urea (4.0 g) was added to react with residual amine and the mixture was stirred for 20 h at 150°C. The stirring was slowed to 500 rev min^{-1} and vacuum (2 mmHg) was applied to the system for 2 h. After cooling, the product was filtered through an 80 mesh screen. The finished product was a stable polyurea polyol dispersion having a viscosity of 2.20 Pa s at 25°C and a solids content of 9.1 wt%. If desired, the solid polymer could be isolated from the dispersion by treatment with methanol[3].

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 (40.0 ppm). Scanning electron microscopy (SEM) was done with either a Hitachi S-570 or a Hitachi S-4000 field emission scanning electron microscope; the samples had 15–20 nm of sputter coating (50 : 50 mixture of an Au–Pd blend) done on a Hummer X. Particle size distributions were determined using a Horiba Capa 700 disc centrifuge. The dispersions were diluted to ~2% in tripropylene glycol and accelerated from rest to 5000 rev min^{-1} over 1 h. Reported data represent the average of five determinations. Additional particle size distributions were determined using a Horiba LA-500 laser light scattering instrument with the polyurea particles suspended in methanol. Fourier transform infra-red (*FT*i.r.) spectra were obtained on a Nicolet 5PC spectrophotometer in KBr pellets. The particle density was measured in a Micromeritics AccuPyc-1330 by hydrogen displacement of a known mass.

Wide angle X-ray scattering (WAXS)

Dried dispersion solids were loaded onto zero background (off-axis cut quartz) sample holders and analysed using a Siemens D500 automated diffractometer equipped with a position sensitive proportional counter (PSPC). A cobalt X-ray tube (operating at 35 kV and 30 mA) and a quartz crystal monochromator were used to provide CoKα_1 radiation ($\lambda = 1.78897$ Å). Scattering intensities were collected in the range $2\theta = 2$–92° using a scan rate of 0.2° min^{-1}. For simultaneous differential scanning calorimetry (d.s.c.)–X-ray diffraction (X.r.d.) studies, the instrument design consisted of an X.r.d. system utilizing Guinier transmission–subtraction optics and a PSPC. A second component of the system was a d.s.c. cell with both computerized temperature control and data acquisition. (Samples ~20 mg) were loaded into ultrathin aluminium d.s.c. pans; the PSPC was held in a fixed position and collected, simultaneously, a $2\theta = 20$–25° range of diffracted radiation. A copper X-ray tube (operating at 40 kV and 30 mA) and a germanium crystal monochromator were used to provide CuKα_1 radiation ($\lambda = 1.54059$ Å). The d.s.c. cell was heated at a rate of 1°C min^{-1} from 80 to 290°C. Each X-ray pattern spanned a 5°C temperature range. The temperature reported for each diffraction pattern represents the average temperature during the 5 min data collection time.

RESULTS AND DISCUSSION: MORPHOLOGY CONTROL

Effects of monomer addition rate on particle morphology

The monomer addition rate was found to have a major effect on the stability of polyurea polyol dispersions. Early attempts in which all of the monomers were charged in one shot to a continuous phase containing the dispersant at 150°C resulted in dispersions of poor quality. Large quantities of polymer solids (30–50%) were not well dispersed[3]. In addition, the dispersed polymer solids had a bimodal particle size distribution. *Figure 1* gives particle distribution data obtained using a disc centrifuge and indicates (1) particles from ~1 to 7 μm and (2) particles from ~7 to 25 μm. *Figure 2* gives a representative SEM micrograph of the isolated polymer solids. The smaller particle size solids have a spiral fibre bundle morphology with a significant aspect ratio, as previously reported[2–4]. The larger particles are spherical but have a fibrous appearance, at least at their surfaces.

In order to help develop an understanding of the

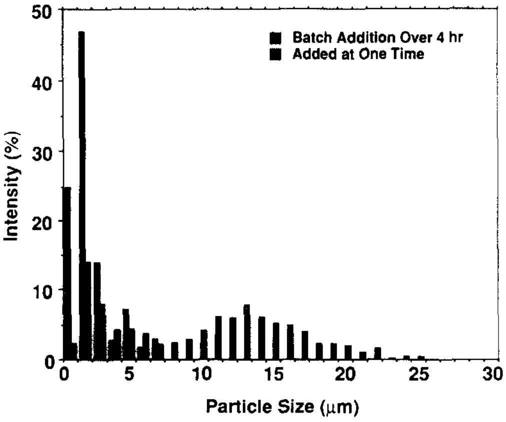


Figure 1 Effect of mode of addition on particle size distribution of polyurea polyol dispersions synthesized at 150°C (disc centrifuge data)

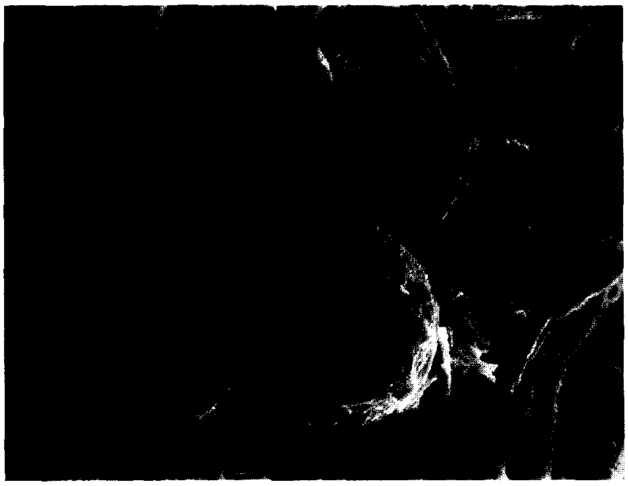


Figure 2 SEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) particles isolated from a polyurea polyol dispersion; all urea and 1,6-hexanediamine added at one time

Figure 3 FESEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) synthesized at 120°C

Figure 4 FESEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) synthesized at 140°C

reaction mechanisms which can be responsible for these results, the solubilities of the monomers in Voranol 4702 were determined. The solubility of urea in Voranol 4702 is very low, less than 0.5wt%, even at 150°C. Above 0.5wt%, droplets of molten urea (melting point 134°C) are observed in the reaction vessel. 1,6-Hexanediamine is soluble in both Voranol 4702 and molten urea. Thus, under single-shot addition, it is possible to have bulk and/or interfacial polymerization occurring in and on the urea droplets, producing spheres, and solution polymerization occurring in the continuous phase, followed by precipitation of the spiral fibre bundle macrostructure. The majority of the bulk polymerization appears to lead to larger, unstable polymer solids.

This dispersion stability problem was circumvented by using a batchwise addition mode. Equal molar quantities of 1,6-hexanediamine and urea were ground together under nitrogen (both are hygroscopic) so that equal molar quantities were added during each addition. The solids were added to the continuous phase containing the dispersant at 150°C in small batches under conditions where reaction was rapid. By using this batchwise mode of addition, stable dispersions were obtained without larger, spherical particles. *Figure 1* shows the particle size distribution obtained by disc centrifuge using this addition mode and compares it to the particle size distribution obtained using a one-shot addition.

Effects of dispersion synthesis temperature on particle morphology

The effects of dispersion synthesis temperature on particle morphology were studied from 120 to 185°C. When the polyurea polyol dispersions were synthesized at 120°C, spherical particles were obtained with particle diameters up to ~50 μm. *Figure 3*, a field emission scanning electron microscopy (FESEM) micrograph of some of the smaller particles, shows a fibrous surface structure. These spherical particles were probably unmelted urea particles which had slowly undergone a small amount of reaction at the solid urea surface. ^{13}C n.m.r. spectra of particles isolated using chloroform (to minimize urea solubility) indicated that the solids were, for the most part, a mixture of urea and *N,N'*-(1,6-hexanediyl)bisurea. Urea was indicated by the carbonyl carbon line at 163.0ppm, while *N,N'*-(1,6-hexandiyl)-bisurea was indicated by a line at 160.6ppm for the terminal carbonyl carbons and lines at 42.6, 28.6 and 26.5ppm for the methylene carbon atoms α, β and γ to urea moieties[3,6]. A small amount of higher oligomers was indicated[3] by the internal carbonyl carbon line at 159.0ppm.

When the dispersion synthesis temperature was increased to 140°C, the particle morphology was very similar to that obtained[3] at a synthesis temperature of 150°C. *Figure 4* gives an FESEM micrograph of these spiral fibre bundles. Each intact particle has the appearance of having grown (crystallized) into its established morphology. The particles have one tapering end and a broader end which appears to have partially opened. The particles are 3–7 μm in length and have aspect ratios of ~10. Even though the urea is liquid at this synthesis temperature, the reaction rate is quite low (*Table 1*). Amine conversion was 87–90% 24h after monomer addition at 140°C and was <93% after several days at 140°C. By way of contrast, amine conversions >98%

Table 1 Effects of synthesis temperature of polyurea polyol dispersions on amine conversion

Time after addition (h)	Amine conversion (%) at synthesis temperature			
	140°C	150°C	160°C	175°C
1	65.5	86.8	90.1	93.2
3		87.5	92.8	95.0
5		91.1	92.7	96.5
17	87.0	92.7	94.7	97.7
21[a]	[b]	98.2	99.6	98.9

[a] Additional urea added as a finishing step

[b] Conversion of 97.5% four days after urea added as a finishing step

Figure 5 FESEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) synthesized at 160°C

were obtained at 150°C in under 24 h after monomer addition.

When the dispersion synthesis temperature was increased to 160°C, the particle morphology changed somewhat (*Figure 5*). The particles were very similar to the particles synthesized at 140–150°C in size and shape[3]. However, they had a more open morphology. Aspect ratios were about the same, although aspect ratio does not adequately describe such an open morphology. It should be easy for a matrix resin to penetrate these fibres to form composite structures. Reaction rates increased and amine conversions >99% were obtained at 160°C in under 24 h after amine addition (*Table 1*). In fact, amine conversions >90% were obtained 1 h after monomer addition.

When the dispersion synthesis temperature was increased to 175°C, the particle morphology took on additional changes (*Figure 6*). The fibrous substructure was much less pronounced; the particles were open in appearance with no twisting or braiding and appeared to be internally fused. However, the particle sizes and shapes were similar to those synthesized at 140–160°C. Dispersions synthesized at 165 and 170°C showed a systematic transition from the 160°C-synthesized to the 175°C-synthesized particles. Reaction rates were much faster and both addition times and total reaction times could be shortened significantly (*Table 2*).

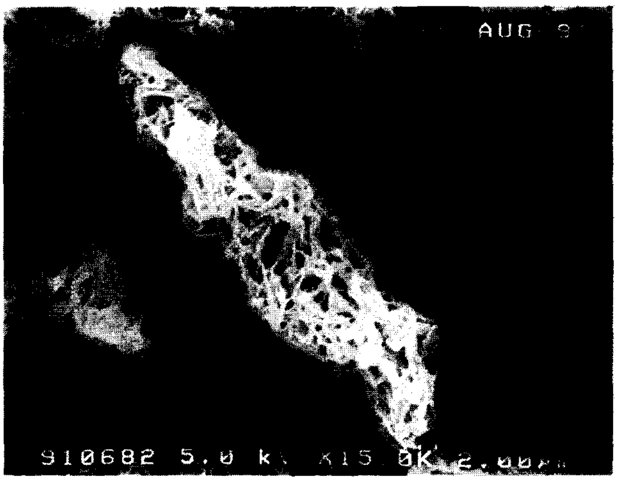


Figure 6 FESEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) synthesized at 175°C

Table 2 Effects of reduced cycle time at 175°C on amine conversion

Addition time (h)	Time after addition (h)	Vacuum time (h)	Total time (h)	Amine conversion (%)
5.0	17	2.0	24	98.9
4.5	1	1.5	7	97.5
1.5	1	1.5	4	96.0

Figure 7 FESEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) synthesized at 185°C

When the dispersion synthesis temperature was increased to 185°C, the particle morphology changed completely (*Figure 7*). The particles were spherical and much larger. They appeared to be aggregates of smaller, fibrous structures. These particles should be much less effective as reinforcing fillers.

Effects of stirring rate on particle morphology

The effects of stirring rate during polyurea polyol dispersion synthesis were studied at 300, 700 and 1200 rev min^{-1} at 150°C. At 300 rev min^{-1} the stirring rate was too low. There was a heavy paste build-up owing to insufficient stirring and a significant quantity of the solids was not well dispersed. The dispersed particles had a loosely bound structure and appeared to have a high aspect ratio by FESEM (*Figure 8*). However, the

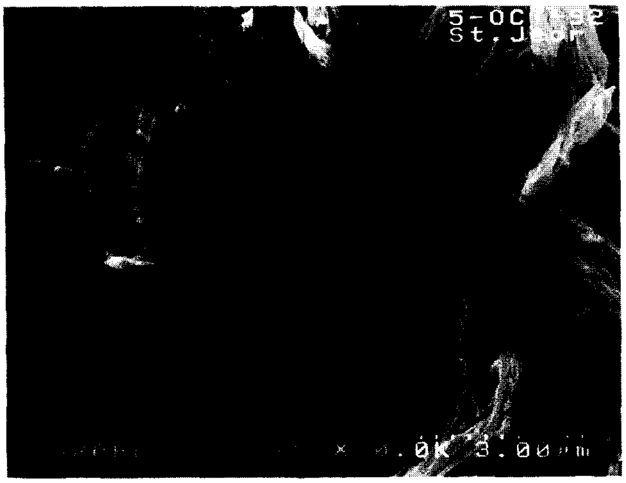


Figure 8 FESEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) synthesized at 150°C with a stirring rate of 300 rev min^{-1}

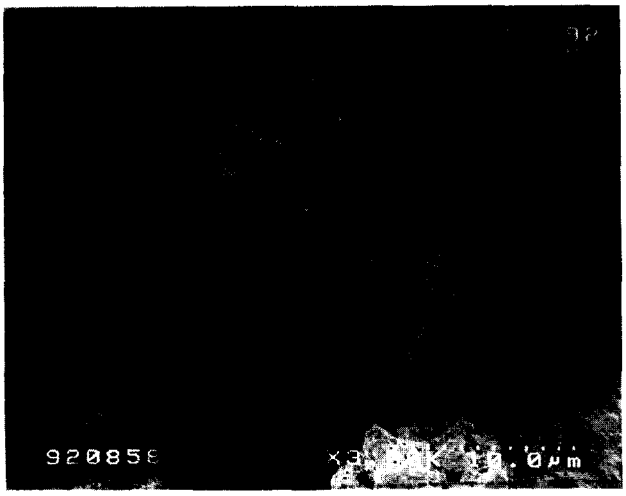


Figure 9 FESEM micrograph of urea-terminated poly(1,6-hexamethyleneurea) synthesized at 175°C with a stirring rate of 300 rev min^{-1}

aspect ratio loses some of its meaning with this morphology. The particles made at 700 and 1200 rev min^{-1} had similar morphologies. However, the particles made at 700 rev min^{-1} were slightly bent or bowed, while the particles made at 1200 rev min^{-1} were straight. The SEM micrograph of these particles made at 150°C using a 1200 rev min^{-1} stirring rate has been previously reported[3].

The effects of stirring rate during polyurea polyol dispersion synthesis were also studied at 300, 700 and 1200 rev min^{-1} at a 175°C synthesis temperature. The size of the particles made at 300 rev min^{-1} was very large (>25 μm) and the aspect ratio approached 1 (*Figure 9*). These particles appeared somewhat porous and had many globular protrusions. Particles synthesized at 700 rev min^{-1} had aspect ratios of $\sim$4, were somewhat porous and had many globular protrusions. Particles synthesized at 1200 rev min^{-1} have been previously described (*Figure 6*). The aspect ratios increased with increasing stirring rates for particles synthesized at 175°C. A stirring rate of 1200 rev min^{-1} was used in this work during polyurea polyol dispersion synthesis unless otherwise noted.

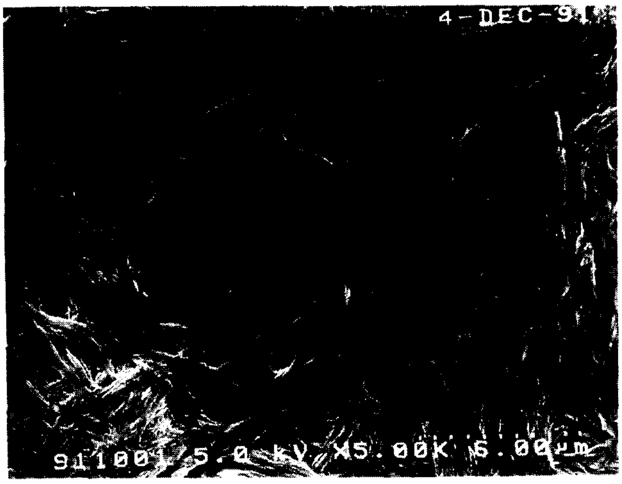


Figure 10 Effect of extent of conversion at 140°C on the morphology of urea-terminated poly(1,6-hexamethyleneurea); FESEM micrograph after fifth monomer addition

Effect of the extent of reaction on particle morphology

The above results indicate the control of the morphology of polyurea polyol dispersion particles by synthesis temperature and stirring rate. All results showed the final particle morphology. A series of studies was undertaken to observe particle morphology as a function of conversion. Experiments were run at 140°C (where reaction is relatively slow and spiral fibre bundle particles are produced). The partially aminated Voranol 4701 stabilizer precursor was used. Samples were taken prior to each monomer addition and at selected times after monomer addition up to final conversion. Each example was titrated to determine the extent of conversion and visualized by SEM.

At a very early stage in the reaction, the particles were present as a very fine mat of small fibres. Although fibres were evident, they were shorter (up to $\sim$3 μm) and had much smaller diameters (<1.0 μm) than in the final product. Aspect ratios were of the order of 30 or greater. *Figure 10*, an FESEM micrograph of the solids present after the fifth (of seven) monomer addition, is representative of the particle morphology during the early stages of the reaction. Conversion has little meaning during monomer addition.

After complete monomer addition, there was a gradual transition from these small fibre-like structures to a larger spiral fibre bundle morphology. *Figure 11* shows the morphology, by FESEM, 1 h after complete monomer addition (66.1% amine conversion). The fibre-like structures were beginning to increase in diameter and showed increased twisting. As conversion increased, the particles took on the spiral fibre bundle morphology previously described (*Figure 4*).

Effects of particle annealing on morphology

A series of studies was undertaken to observe particle morphology as a function of annealing at higher temperatures. A portion of a polyurea polyol dispersion synthesized at 150°C (spiral fibre bundle particles) was heated at 175°C for 8 h. After cooling to ambient temperature, the particles were isolated and examined by FESEM (*Figure 12a*). There was essentially no change in the size or shape of the particles. The particles did

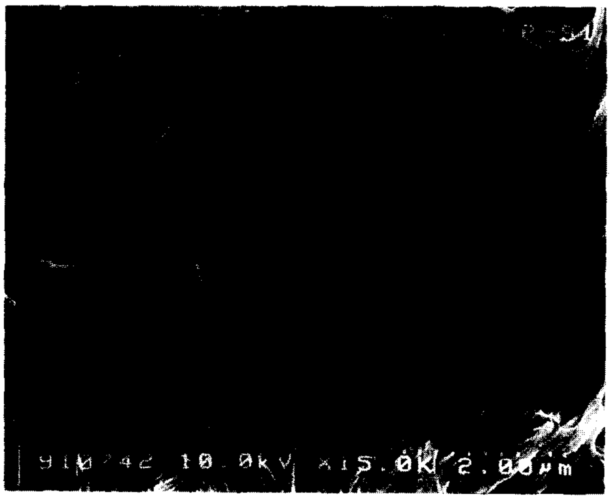
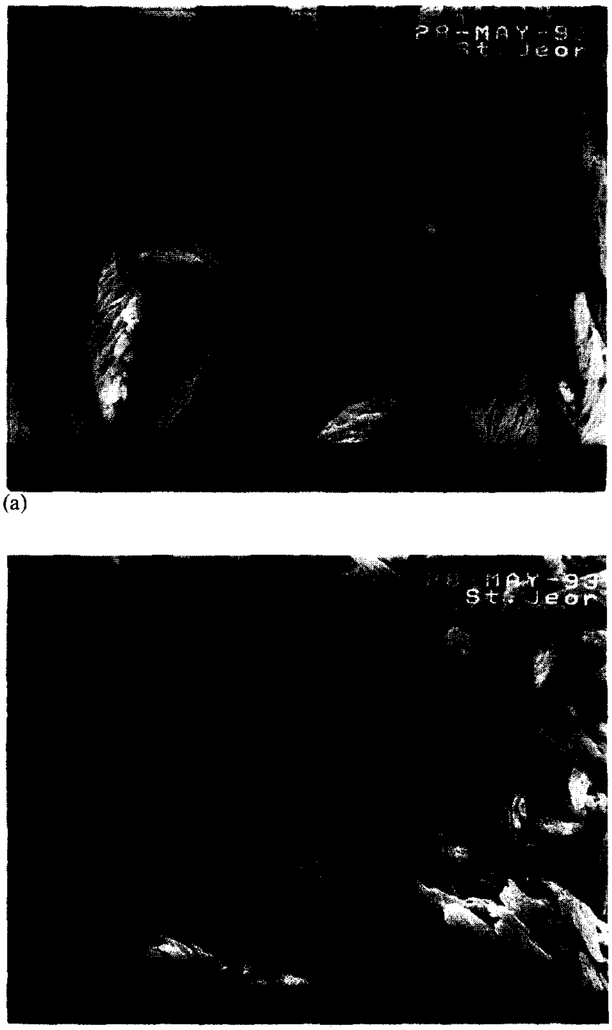


Figure 11 Effect of extent of conversion at 140°C on the morphology of urea-terminated poly(1,6-hexamethyleneurea); FESEM micrograph 1 h after monomer addition



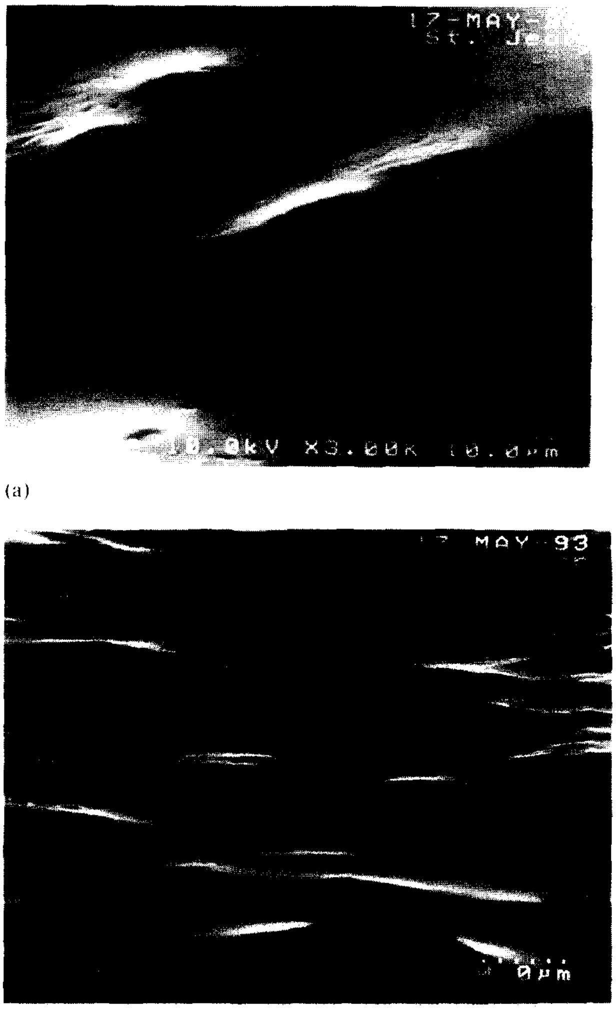
(a)

(b)

Figure 12 Effect of annealing at (a) 175°C and (b) 185°C on the morphology of urea-terminated poly(1,6-hexamethyleneurea) particles

not convert to the morphology of particles synthesized at 175°C.

Another portion of the same polyurea polyol dispersion synthesized at 150°C was heated to 185°C for 16 h to subject the particles to even harsher conditions. After cooling to ambient temperature, the particles were isolated and examined by FESEM (*Figure 12b*). The particles retained their initial morphology, for the most part. However, some of the particles were reduced in size, but appeared to be miniatures of themselves. They retained the spiral fibre bundle morphology, but they were reduced in length and diameter. The aspect ratios of the smaller particles appeared to be as high or higher than those of the original larger particles. The particles did not convert to the morphology of particles synthesized at 185°C. The polyol darkened considerably (black) during this experiment, indicating that the particles have a higher thermal stability than the polyol.



(a)

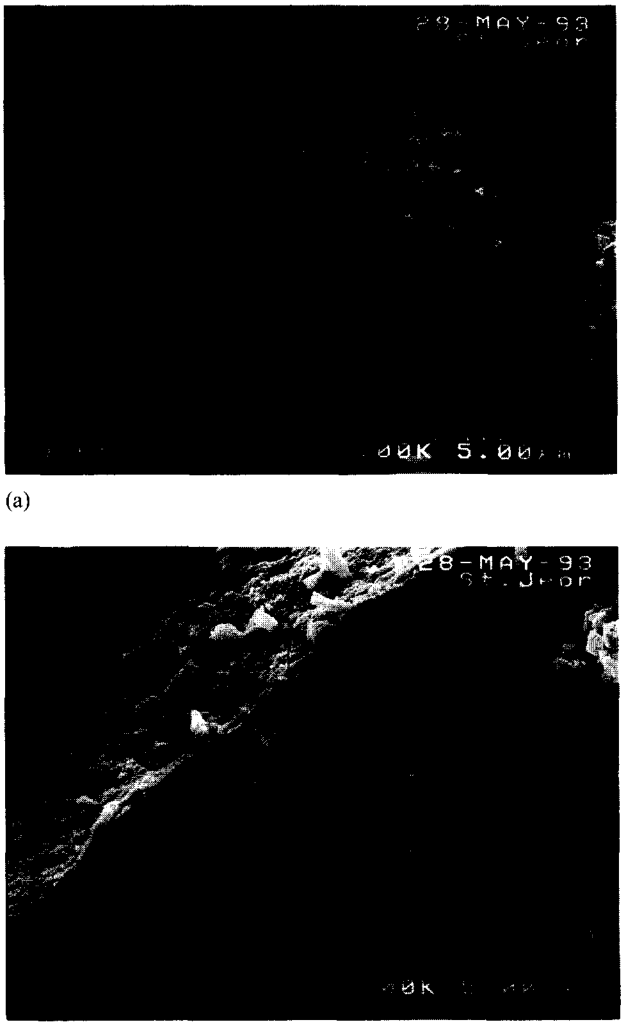
(b)

Figure 13 Effects of particle melting on morphology. FESEM micrographs of particles synthesized at 150°C, melted to 285°C then solidified: (a) surface; (b) fracture face

It appears that the morphology of the urea-terminated poly(1,6-hexamethyleneurea) particles is established during their synthesis. Once formed, the morphology of the particles is relatively stable to annealing at higher temperatures. Some reduction in particle size occurs after annealing at 185°C for extended periods of time.

Effects of particle melting on morphology

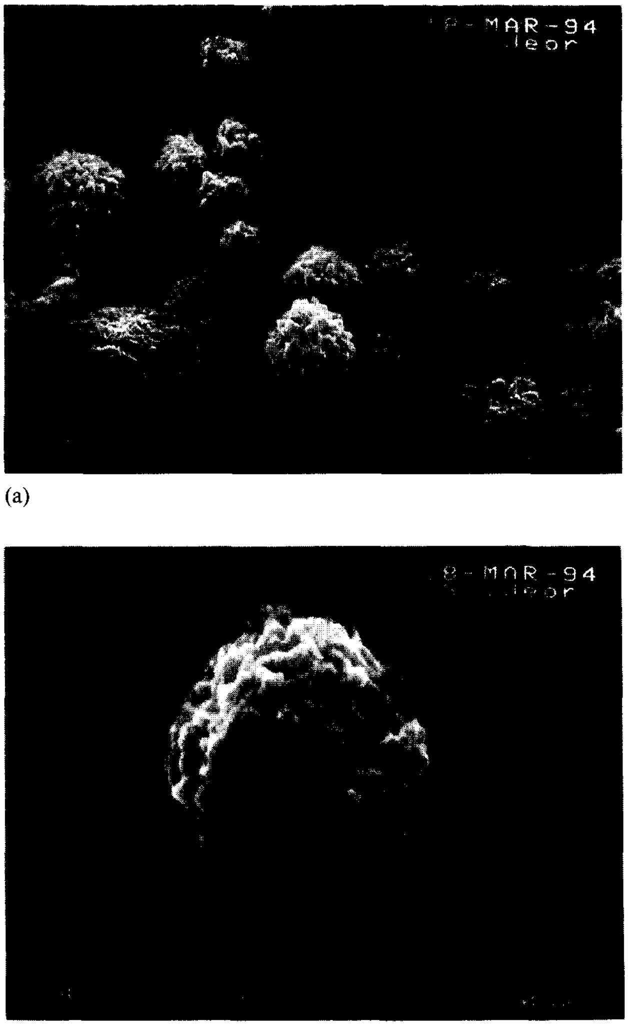
The effects of particle melting on morphology were studied by heating isolated urea-terminated poly(1,6-hexamethyleneurea) particles that had been synthesized



(a)

(b)

Figure 14 Effects of particle melting on morphology. FESEM micrographs of particles synthesized at 150°C, ~90% melted then solidified: (a) surface; (b) fracture face



(a)

(b)

Figure 15 Effects of particle solution–precipitation on morphology. FESEM micrograph of particles synthesized at 150°C, dissolved in methanesulfonic acid and precipitated in methanol

at 150°C (spiral fibre bundle morphology) to 285°C (melting point 270°C) under nitrogen on a differential scanning calorimeter, followed by controlled cooling at 3°C min^{-1}. FESEM micrographs of the surface (*Figure 13a*) and fracture face (*Figure 13b*) of the resultant recrystallized solid indicated that the individual particle morphology no longer existed as it was in the parent material. The resulting resolidified structure appeared to be a continuous phase with occasional lumps of various sizes indicating inclusions within the continuous phase. Most of the lumps apparent in the surface structure had a ring at the top of the protrusion indicating the possible presence of isolated structures within these lumps. Also, within this ring there was a slight increase in texture, indicative of a second phase. Lumps were also visible in the fracture face, where a similar morphology existed. These lumps were of the order of 3–12 μm across and perhaps 3–6 μm tall. The continuous phase appeared amorphous in both the surface structure and in the fracture face, though shallow, irregularly shaped pits were seen scattered across the sample surface. These pits were of the order of 1–8 μm across and less than 0.1 μm deep. The crystallinity that existed (indicated by a crystallization exotherm on the d.s.c. trace and a WAXS peak) must be accounted for in terms of the inclusions and/or pits, or it was at a level not structurally recognized in the FESEM analysis.

In a second experiment, particles that had been synthesized at 150°C were heated in a calorimeter as above, but the temperature scan was terminated ~90% of the way through the melting endotherm. Controlled cooling at 3°C min^{-1} was carried out as above. FESEM micrographs of the surface (*Figure 14a*) and fracture face (*Figure 14b*) of the resultant recrystallized solid indicated that the individual particle morphology no longer existed as it was in the parent material. Most of the resolidified structure appeared to be a continuous phase similar to that produced in the experiment above. However, there were clusters of small crystals at the surface. The clusters appeared to be composed of submicrometre crystals possessing an aspect ratio greater than 1.

Apparently, the initial spiral fibre bundle morphology was destroyed during the melting process. Even the unmelted portion of the sample underwent a morphology change at the higher temperature of the melt. The effects of temperature on morphology were also studied by d.s.c.–WAXS and the results will be presented later in this paper.

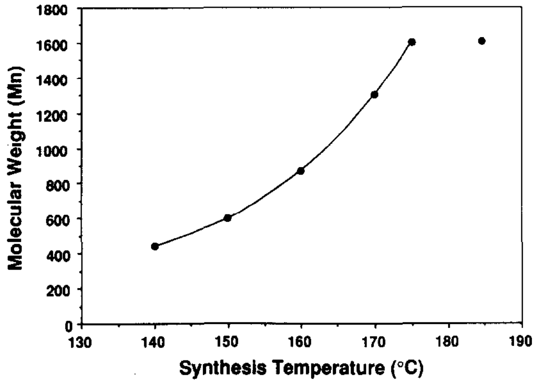


Figure 16 Effect of synthesis temperature on the number average molecular weight as measured by quantitative ^{13}C n.m.r.

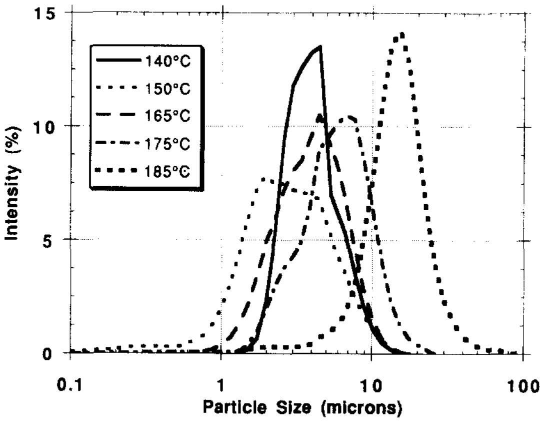


Figure 17 Effect of synthesis temperature on particle size distribution

Effects of particle solution–precipitation on morphology

The effects of particle solution–precipitation on morphology were studied for urea-terminated poly(1,6-hexamethyleneurea) particles that had been synthesized at 150°C (spiral fibre bundle morphology). Particles were dissolved in methanesulfonic acid (17 wt%) and precipitated by slowly adding the methanesulfonic acid solution to methanol (1 : 20 dilution). FESEM indicated that the precipitated particles were spherical with a textured surface and diameters ranging from 1 to 5 μm (*Figure 15*). Clearly, the particle macrostructure is destroyed by solution. The high aspect ratios of the initial particles are a consequence of their synthesis process.

RESULTS AND DISCUSSION: MATERIALS CHARACTERIZATION

Molecular weight by quantitative ^{13}C n.m.r.

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 $(M_n)^3$. This method was used to calculate M_n for particles prepared at synthesis temperatures from 140 to 185°C (*Figure 16*). There is a systematic increase in M_n with increasing synthesis temperature from 140 to 175°C. This is probably a consequence of the precipitation–polymerization mechanism thought to be operative in the synthesis process. At a given concentration, the urea-terminated poly(1,6-hexamethyleneurea) oligomers form a macrostructure and precipitate from the continuous phase to give stable dispersed particles. It is reasonable to presume that this precipitation occurs with higher molecular weight oligomers at increasing synthesis temperatures owing to higher solubility. The morphology of the particles synthesized at 185°C indicates aggregate formation, with about the same M_n as 175°C-synthesized particles.

Particle size distributions

The particle size and distribution of the dispersed solids made at different synthesis temperatures 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 4702) was made using a molar ratio of Jeffamine M-2005 to 1,6-hexanediamine to urea of 1.0 : 4.0 : 5.0. The results are plotted in *Figure 17*. There is a systematic increase in median particle size with increasing synthesis temperature from 150 to 185°C (*Table 3*). The particle size distribution also changes from bimodal to unimodal with increasing temperature.

Table 3 Effects of synthesis temperature on median particle size and viscosity

Synthesis temperature (°C)	Median particle size (μm)	Viscosity[a] (Pa s)
140	3.69	2.300
150	2.56	2.350
160	3.20	2.700
165	3.69	3.030
170	4.54	3.236
175	5.45	3.158
185	13.56	1.904

[a] At 10 wt% solids content

The particle size of the dispersed solids made at 140°C appears to be out of sequence (3.69 μm) with the particle sizes made at higher temperatures. However, the solids made at 140°C have a different crystalline structure from solids made at higher temperatures, as will be shown by WAXS studies later in this paper.

Polyol dispersion viscosities (10 wt% solids in Voranol 4702) increase with increasing synthesis temperature. This is probably a consequence of increasing oligomer molecular weight and changes in macrostructure morphology. However, viscosity decreases considerably for polyol dispersions synthesized at 185°C, where the particle morphology becomes spherical.

Infra-red spectroscopy

The effects of synthesis temperature (140, 150, 160 and 175°C, respectively) on the N–H (*Figure 18*) and C=O (*Figure 19*) portions (between 3200 and 3500 cm^{-1} and ~1600 cm^{-1}, respectively) of the i.r. spectra of urea-terminated poly(1,6-hexamethyleneurea) were studied (*Table 4*). For the particles synthesized at 140°C, two bands were present in the N–H portion of the spectrum at 3431 (not hydrogen bonded) and 3343 cm^{-1} (hydrogen bonded)[7–13]. The non-hydrogen-bonding band decreased systematically with increasing synthesis temperature; it was only present as a shoulder at 160°C and was absent at 175°C.

Table 4 Infra-red spectra results of N-H and C=O stretching regions as a function of synthesis temperature

	Wavenumber (cm^{-1}) at synthesis temperature			
Band assignment	140°C	150°C	160°C	175°C
N-H stretch (not hydrogen bonded)	3431	3434	3437 (shoulder)	
N-H stretch (hydrogen bonded)	3343	3336	3333	3331
C=O stretch (not hydrogen bonded)	1650	1650		
C=O stretch (hydrogen bonded)	1615	1615	1615	1618
Unassigned	1600	1598		
N-H bend and C-N stretch (combination)	1565	1572	1575	1573

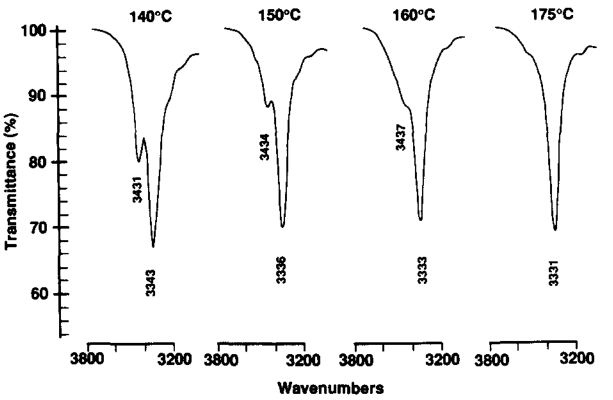


Figure 18 Infra-red spectra of the N-H stretching region as a function of synthesis temperature

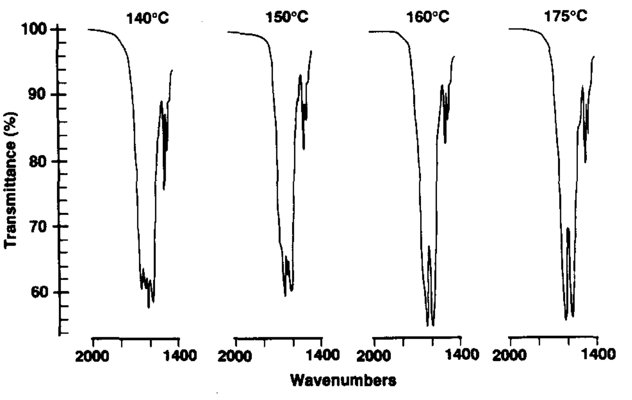


Figure 19 Infra-red spectra of the C=O stretching region as a function of synthesis temperature

A similar effect was observed in the carbonyl region of the spectra (*Table 4*). For the particles synthesized at 140°C, bands were present at 1650 (not hydrogen bonded) and 1615 cm^{-1} (hydrogen bonded)[7-11,13] The non-hydrogen-bonding band decreased systematically with increasing synthesis temperature; it was absent at 160 and 175°C. The band centred at 1565-1575 cm^{-1} was present in all samples and is thought to represent mixed vibrational modes of N-H bending and C-N stretching[10,11].

The largest qualitative change in the i.r. spectrum occurs when going from a synthesis temperature of 150°C to a synthesis temperature of 160°C. On the other hand, 160-175°C is the synthesis temperature range where the largest increase occurs in the average degree of polymerization, as determined by quantitative ^{13}C n.m.r. measurements of the number average molecular weight (M_n). It can therefore be deduced that an increasing degree of hydrogen bonding (rather than a reduction in the number of terminal NH_2 groups through the increased degree of polymerization) is the main cause of the observed changes in the i.r. spectra.

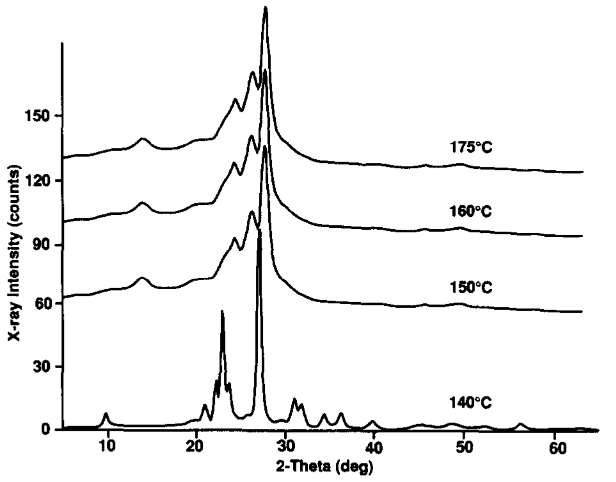


Figure 20 WAXS patterns as a function of dispersion synthesis temperature

WAXS variations with synthesis temperature

The WAXS patterns are shown as a function of the synthesis temperature of the polymer in *Figure 20*. It can be seen that the scattering pattern for the polymer synthesized at 140°C is different from the patterns for the polymers synthesized at higher temperatures. This indicates that the crystal structure for this material is different from that for materials polymerized at higher temperatures. In addition, the presence of many sharp, discrete diffraction peaks indicates an appreciable degree of order. The density of 1.2244 ± 0.0005 $g\,ml^{-1}$, measured by helium pycnometry (*Figure 23*), also suggests the presence of a significant amount of crystallinity. On the other hand, the polymers synthesized at 150-175°C all show diffraction patterns with fewer discrete peaks than shown by the material synthesized at 140°C. This indicates that these materials possess smaller, less perfect crystalline domains and a lower level of crystallinity. These results make the polymer synthesized at 140°C an ideal candidate for structure elucidation by molecular modelling. The results of the molecular modelling effort will be presented in a forthcoming paper.

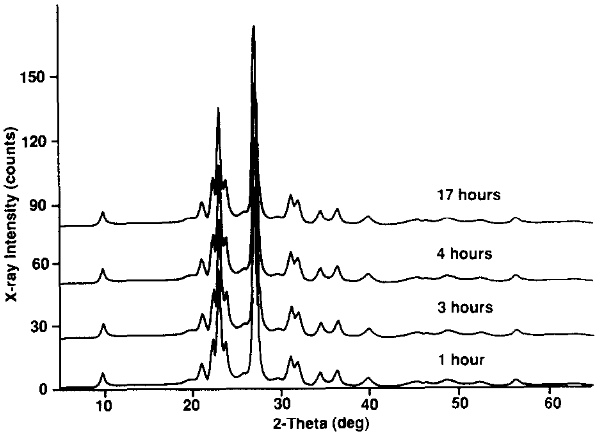


Figure 21 WAXS patterns as a function of amine conversion at 140°C

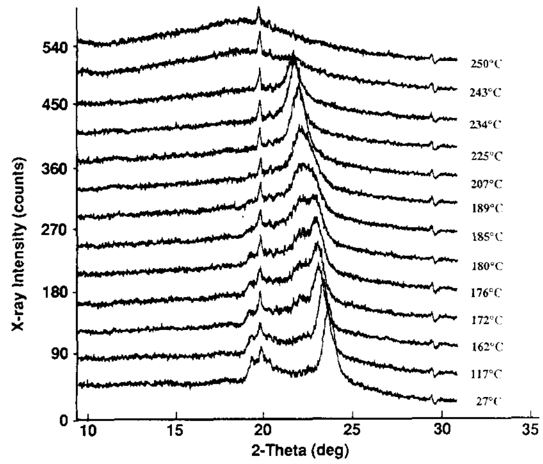


Figure 22 WAXS patterns as a function of sample heating temperature

WAXS variations with extent of conversion

It is shown in *Figure 21* that the polymer synthesized at 140°C does not change structurally in any discernible manner as a function of the reaction time from 1 h after addition (65.5% amine conversion) to 17 h (87.0% amine conversion). These WAXS patterns are identical to the pattern of the final product at 140°C shown in *Figure 20* (97.5% amine conversion). Crystalline order is therefore established early in the reaction, and it is not altered significantly by the subsequent incremental polymerization and major changes in the macrostructure morphology uncovered by SEM.

WAXS variations during heating

The effects of heating urea-terminated poly(1,6-hexamethyleneurea) particles synthesized at 150°C on their WAXS patterns are shown in *Figure 22*. Gradual changes are seen with increasing temperature until the melting temperature is reached. No significant change in crystallinity or average crystallite size was observed after annealing this material below the melting temperature for various periods of time. A reasonable representation of the amorphous phase scattering pattern is observed from the d.s.c.–X.r.d. scans collected for this sample above 240°C. The diffuse peak, however, is dramatically shifted to lower angles because of the effects of thermal expansion at these elevated temperatures.

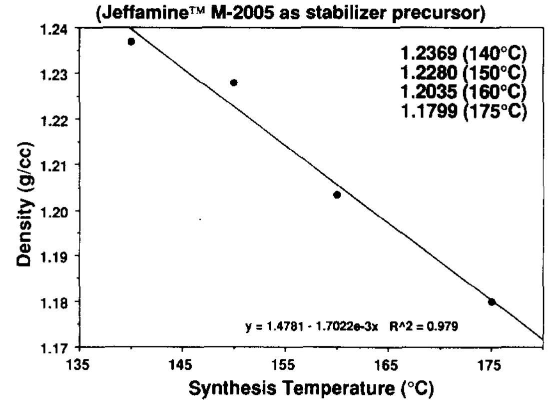


Figure 23 Effect of synthesis temperature on the density of urea-terminated poly(1,6-hexamethyleneurea) particles (25°C)

Density

The measured density of the urea-terminated poly(1,6-hexamethyleneurea) is listed and graphically depicted in *Figure 23* as a function of the synthesis temperature. Note that the density decreases monotonically with increasing synthesis temperature. The most likely explanation for this observation is the decreasing crystalline fraction of the polyurea particles with increasing temperature. The validity of this explanation could not be examined more quantitatively since it proved to be impossible to obtain specimens of different percentages of crystallinity by means of annealing studies.

Observations on effects of morphological scale

Note from the results discussed above that each quantifier of morphology at different size scales shows its largest change as a function of the synthesis temperature over a different range of synthesis temperatures. The WAXS pattern (presence and nature of short range and long range periodic order) changes most between synthesis temperatures of 140 and 150°C. The i.r. spectrum (hydrogen bonding at the local atomic environment scale) changes most between synthesis temperatures of 150 and 160°C. Finally, the SEM pattern (gross overall morphology) changes most between synthesis temperature of 160 and 175°C, which is also the synthesis temperature range where the largest increase occurs in the average degree of polymerization.

These observations provide fundamental insights into the mechanisms at work in determining the morphology at different scales. Crystallinity is better developed at the lower synthesis temperature (140°C), where the reaction is slowest and the crystallinity therefore has the largest amount of time to develop. The development of the optimum interchain alignments for hydrogen bonding requires a somewhat higher synthesis temperature (in the range 150–160°C), at which the long range crystalline order does not develop as effectively. On the other hand, the gross morphological changes observed by SEM parallel the large increase in M_n between 160 and 175°C, perhaps indicating that both of these characteristics are affected by the rapid rate of reaction.

CONCLUSIONS

The effects of reaction parameters on the synthesis of urea-terminated poly(1,6-hexamethyleneurea) particles dispersed in a polyol continuous phase have been studied. Oligomeric units are held together by hydrogen bonding into a macrostructure which separates as a stable dispersed phase during synthesis. Batchwise monomer addition is required for optimal results, since low monomer concentrations at proper stoichiometry can force solution polymerization. Agitation is extremely important in multiphase systems; effective stirring was achieved in the range 700–1200 rev $\min^{-1}$. Monomer addition rate, synthesis temperature and stirring rate are important factors in morphology control of the particles. High aspect ratio (10–20) particles having a spiral fibre bundle morphology (by SEM) are produced at synthesis temperatures between 140 and 175°C; spherical particles are produced at 185°C. The reaction rate is too slow below the melting point of urea. Particles produced at 140°C have a different crystalline structure from particles produced at higher temperatures. Molecular weight, particle size and the extent of hydrogen bonding increase with increasing synthesis temperature. The structure of these highly crystalline particles is established at an early stage in the reaction. Annealing up to 185°C has little effect on particle morphology. Annealing near the melting point (270°C) results in loss of crystallinity; particle macrostructure is destroyed by melting or solution.

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