In Situ Polymerization of Nylon–Polyurea Block Copolymers. I. Synthesis and Characterization

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Synopsis

The synthesis of a carbamyl caprolactam terminated polyurea and a series of nylon–polyurea block copolymers has been accomplished. In addition to reaction profiles and thermal properties, proof of block copolymer formation is described.

INTRODUCTION

During the past ten years there has been much interest in the modification of the semi-crystalline polymer, nylon 6. Several investigators[1-8] have incorporated a variety of short block segments with low glass transition temperatures into the nylon polymer chain. We have developed a sodium caprolactamate initiated and carbamyl caprolactam activated copolymerization to yield nylon-polyurea block copolymers. In this paper we report the synthesis and characterization of the polyurea prepolymer and a series of block copolymers.

EXPERIMENTAL

Chemicals

Inhibitor-free tetrahydrofuran (THF) was dried over 4 Å molecular sieves and stored under argon. Caprolactam was dried at 55°C and 0.01 Torr. Sodium hydride powder was stored in a vacuum desiccator and 1,6-hexamethylene diisocyanate was used as received. The amine terminated poly(propylene oxide) (Jeffamine D-2000, Texaco Chemical Co.) was dried overnight at 100°C and 0.05 Torr.

Spectroscopy

Proton nuclear magnetic resonance (PNMR) spectroscopy was done with an IBM Instruments NR 270 AF NMR at room temperature in hexafluoro-acetone-deuterate. Infrared spectra (IR) were determined with a Perkin-Elmer 283B infrared spectrophotometer.

Thermal Analysis

Differential scanning calorimetry (DSC) was carried out with an Omni-therm thermal analysis system. The heat of fusion of nylon 6 was taken to be 230 J/g.[9]

Synthesis of Hexamethylene Dicarbamyl Dicaprolactam

Caprolactam (2.0 mol, 226 g) and 1,6-hexamethylene diisocyanate (1.0 mol, 168 g) were dissolved in THF (1000 mL) contained in a 2 L Morton flask fitted with mechanical stirrer, reflux condenser, argon purge, and thermometer. The reaction solution was heated at reflux with monitoring of the reaction by IR. When no further changes in the spectra were observed, the solvent was removed by means of a rotary evaporator and the product was purified by crystallization from 50/50 THF/diethyl ether. Melting point: 84–85°C (lit.[10] mp 78–80°C). IR maxima (HCCl$_3$): 1710, 1650 cm^{-1}. PNMR maxima (DCCl$_3$): 9.25 δ (s), 4.0 δ (m), 3.3 δ (q), 2.7 δ (m), 1.75 δ (s), 1.45 δ (m).

Synthesis of Carbamyl Caprolactam Terminated Polyurea (I)

In a typical synthesis, caprolactam (0.048 mol, 5.4 g) and 1,6-hexamethylene diisocyanate (0.71 mol, 120 g) were dissolved in THF (4 L) contained in a 10 L Morton flask fitted with argon purge, mechanical stirrer, reflux condenser, and pressure equalizing dropping funnel. The solution was refluxed with monitoring of the reaction by IR. When reaction was complete, as indicated by no further changes in the IR spectrum, a previously prepared solution of amine terminated poly(propylene oxide) (0.60 mol, 1200 g) in THF (1200 g) was added during 2 h. Reaction was continued with heating and stirring until the isocyanate maximum in the IR was small (approx. 24 h). Additional caprolactam was added to insure capping of all polyurea chains. A transparent light yellow polymer was obtained by flash evaporation of the solvent followed by heating at 100°C and 0.05 Torr for several hours. Dialysis with toluene removed unreacted caprolactam and other by-products. IR(THF): 1690 cm^{-1}, GPC(THF): 15,000 M_n, PNMR(CDCl$_3$): 1.1 δ (d), 1.3 δ (m), 1.7 δ (s), 3.0–3.3 δ (m), 3.25–3.6 δ (m). Expanded PNMR baseline from 2.25 δ to 4.25 δ: 2.7 δ (m), 4.0 δ (m).

Synthesis of Nylon–Polyurea Block Copolymer (II)

The appropriate, preweighed portion of dry polyurea (Table I) along with all but 30 g of the required caprolactam and the preweighed hexamethylene dicarbamyl dicaprolactam were placed in an oven dried 500 mL capacity glass jar. The jar was fitted with an argon inlet tube and placed in an equilibrated oil bath. Once the polyurea had dissolved to form reactant A, the remaining 30 g of caprolactam were placed in an oven dried 75 mL capacity test tube fitted with an argon inlet tube. This test tube was also placed in the oil bath. The sodium hydride was added in small potions to the test tube while stirring with the argon inlet tube. When the sodium hydride reaction with caprolactam was complete (reactant B) and both solutions had reached 140°C, the contents of the test tube were poured into the jar. Mixing was accomplished by high speed mechanical stirring for about a three second duration. The resultant liquid was poured into a preheated steel mold with a 0.3 × 20 × 20 cm cavity and placed in an air circulating oven at 140°C for 15 min. The steel mold was fitted with thermocouples attached to an IBM-XT-Keithly Series 500 data acquisition system. Data acquisition was begun when A and B were combined. The phase changes were observed by using molds made with glass plates and having a cavity with the same depth (0.3 cm) as the steel molds. After removal from

TABLE I
Synthesis of Nylon–Polyurea Block Copolymers at 140°C

Block[a] copolymer	Reactant A[b]			
	Polyurea (g)	HMDC (g)	Total[b] activator $(10^{-2}$ mol)	Caprolactam (g)
100/0	0	3.6	1.8	170
90/10	20	3.2	1.9	150
80/20	40	2.4	1.7	130
75/25	50	2.4	1.8	120
70/30	60	2.4	1.9	110
65/35	70	2.4	2.0	100
60/40	80	2.4	2.1	90
50/50	100	1.2	1.8	70

[a] Copolymer designation: weight percent nylon/weight percent polyurea.

[b] Reactant B consisted of NaH (0.75 g, 0.031 mol) and caprolactam (30 g, 0.26 mol) except in the case of the 50/50 copolymer where 0.38 g NaH and 1.2 g HMDC were used. Total activator = concentration of hexamethylene carbamyl caprolactam moieties from HMDC and polyurea end groups.

the oven, the plaques were allowed to attain room temperature before demolding. The plaques were stored under anhydrous conditions. PNMR($C_3F_6O–H_2O$): 1.25 δ (s), 1.4 δ (s), 1.55–1.7 δ (m), 2.3 δ (t), 2.5 δ (s), 3.3 δ (t), 3.65 δ (m), 3.85 δ (m), 5.1 δ (s).

Molecular Weight Analysis

Polyurea samples were dissolved in THF and injected into a Waters 150-C ALC/BPC chromatograph at 25°C. Nylon–polyurea samples were dissolved in freshly distilled m-cresol containing tetramethyl ammonium bromide and injected at 110°C. The M_n and weight average molecular weight (M_w) were calculated with a universal calibration curve based on polystyrene standards. The intrinsic viscosity of the nylon homopolymer (100/0) was obtained at 30°C in concentrated sulfuric acid. The molecular weight was calculated by the Mark–Houwink–Sakurada relationship, using $\alpha = 0.76$ and $K = 0.00063$.[11]

RESULTS AND DISCUSSION

The synthesis of nylon–polyurea block copolymers required the initial preparation of polyurea polymers with the necessary end groups to take part in the polymerization as activators. The hexamethylene carbamyl caprolactam moiety was chosen as this is a very efficient activator in the anionic polymerization of caprolactam. In order to control the ultimate molecular weight of the polyurea and to insure the nature of the end groups,

$x \simeq 33, \quad y \simeq 8$
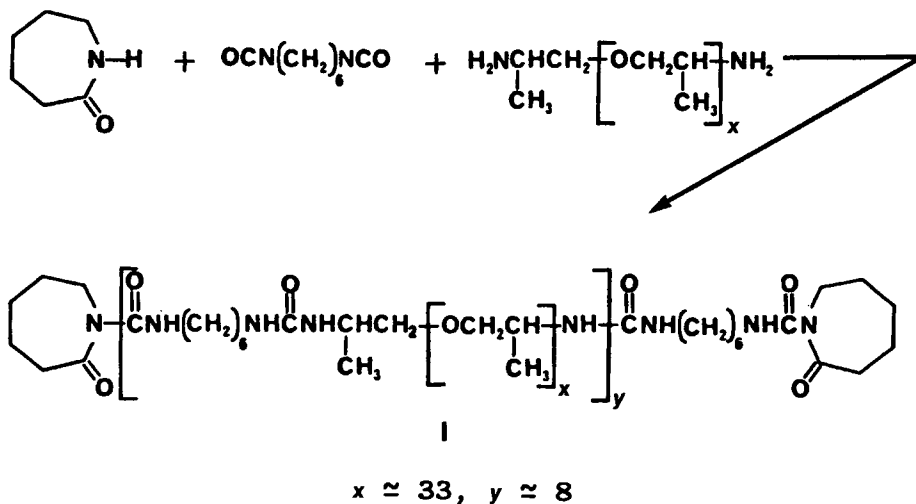
caprolactam was first reacted with a 30-fold molar excess 1,6-hexamethylene diisocyanate to form a mixture of the unisolated monoadduct and unreacted diisocyanate in the correct proportions so that reaction with sequentially added amine terminated poly(propylene oxide) would yield the desired molecular weight prepolymer (I). At the start of the reaction the IR maximum (1680 cm^{-1}) due to the caprolactam carbonyl was readily observed. As the reaction progressed, the 1710 cm^{-1} maximum resulting from formation of the adduct, caprolactam carbamyl, increased. When all caprolactam had been consumed, the amine-terminated poly(propylene oxide) was added and reaction continued. When the isocyanate peak was very small, a small amount of caprolactam was added to terminate the reaction. The polyurea was isolated and dried. After dialysis to remove any unreacted caprolactam or monoadduct and other possible side products, the PNMR spectrum (Fig. 1) contained the peaks expected for the carbamyl caprolactam terminated polyurea. Of particular importance was the region from 2.25 to 4.25 δ (Fig. 1 inset). Peaks due to the α hydrogens (2.7 δ) and ϵ hydrogens (4.0 δ) of the carbamyl caprolactam end groups were observed. The efficiency of the dialysis procedure for the removal of low molecular weight materials was corroborated by the absence of any peak (2.4 δ) due to the α hydrogens of any residual unreacted caprolactam. An M_n of 15,000 was obtained by GPC.

A series of block copolymers (II) containing 0, 10, 20, 25, 30, 35, 40, and 50 wt % polyurea were prepared by the anionic polymerization of caprolactam in the presence of the caprolactam terminated polyurea. In this polymerization the activator, an N-substituted caprolactam, undergoes a nucleophilic
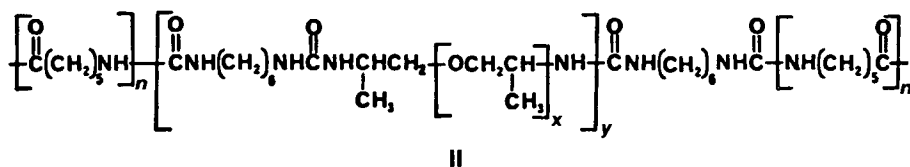
attack by the initiator, sodium caprolactamate. The activator becomes the chain growth site and initiator is regenerated by proton extraction from the monomer,
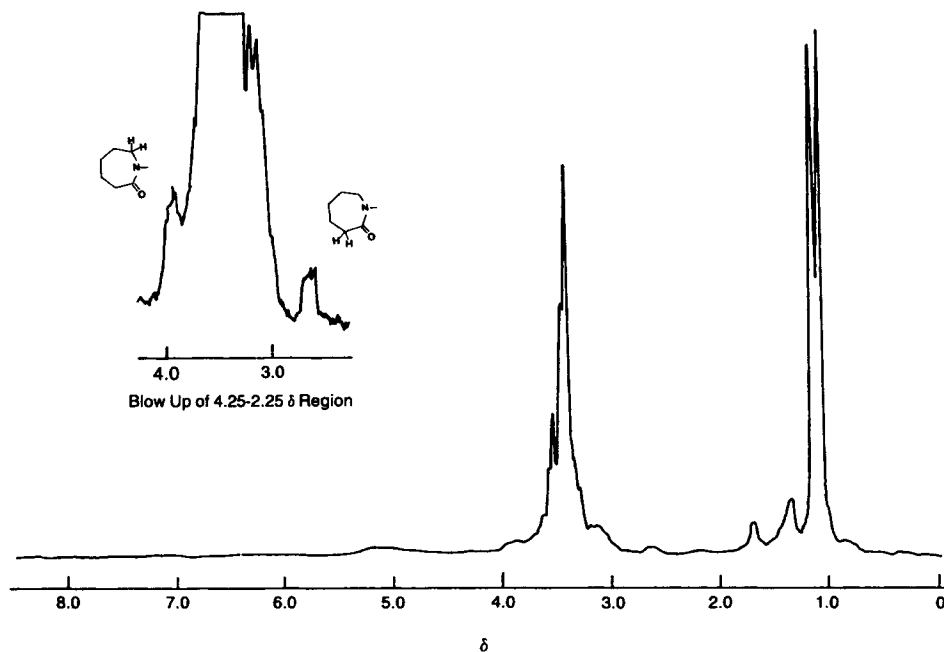
Fig. 1.   Proton nuclear magnetic resonance spectrum of carbamyl-caprolactam-terminated polyurea (I).

caprolactam. In the case of the caprolactam-terminated polyurea activator (I), a nylon–polyurea block copolymer (II) results. When the activator is a low molecular weight compound like hexamethylene dicarbamyl dicaprolactam, the product is nylon 6. The following notation has been used. For example, the block copolymer containing 70 wt% nylon and 30 wt % polyurea is designated as the 70/30 copolymer. The composition of the copolymer was controlled by the reactants A and B (Table I). Reactant B was held constant, except for the 50/50 copolymer, while the polyurea content of reactant A was varied. The viscosity of reactant A increased with increasing polyurea content until pouring into the mold was not possible after reactant B was added. Decreasing the amount of initiator and activator for the 50/50 copolymer made mold filling possible. All these *in situ* polymerized block copolymers, which are essentially composites of nylon–polyurea and nylon 6, were given the same thermal histories by monitoring the heating and cooling cycles with embedded thermocouples.

Number average molecular weights in the range of 80,000–90,000 were obtained. These M_n's were artificially high and the results are included here only to show that high molecular weight copolymers were obtained. The viscosity molecular weight of the 100/0 polymer was 47,000.

The PNMR spectrum of the 70/30 copolymer is shown in Figure 2. The incorporation of the carbamyl caprolactam terminated polyurea in the nylon polymer backbone by participation of the carbamyl caprolactam end groups in the caprolactam polymerization gave rise to several PNMR maxima. The peak at 1.25 δ was due to the methyl group and the unresolved multiplet at 3.65 δ was a result of the methylene groups in the propylene oxide repeat unit. The methine proton alpha to the oxygen in the polypropylene oxide repeat unit appeared as an unresolved multiplet at 3.85 δ. Maxima due to the nylon portion
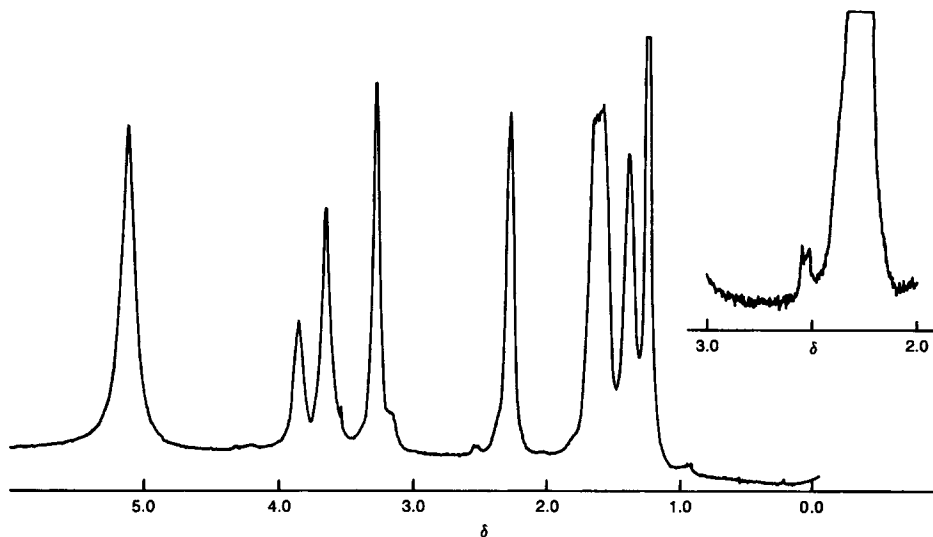
Fig. 2.   Proton nuclear magnetic resonance spectrum of 70/30 nylon–polyurea block copolymer (II).

of the block copolymer are observed at 1.4 δ, 1.55–1.7 δ, 2.3 δ, and 3.3 δ. This "as-polymerized" nylon–polyurea block copolymer had all the peaks requisite for the proposed structure (II). Residual caprolactam was observed at 2.5 δ. This amounted to approximately 2%. The maximum at 5.0 δ was due to impurities in the PNMR solvent. No unreacted, substituted caprolactam was observed at 2.7 δ in Figure 2 nor in the expanded view of this region (Fig. 2 insert). Therefore, all the polyurea was incorporated into the nylon–polyurea block copolymer.

Reaction Profiles

The polymerization of caprolactam at 140°C in the presence of sodium caprolactamate and the very efficient activator, hexamethylene dicarbamyl dicaprolactam, is very fast. The time–temperature responses at 140°C were established under identical conditions for all nylon–polyurea copolymers. Under these conditions exotherms for both polymerization and crystallization were observed. At low polyurea concentrations, i.e., copolymers 100/0, 90/10, 80/20, the polymerization exotherms appeared as shoulders on the much larger crystallization exotherms. At higher polyurea compositions, two distinct exotherms were observed; the first larger exotherm due to polymerization and the second smaller exotherm due to crystallization. The change from predominantly one exotherm to two distinct exotherms could be due to phase separation beginning early in the polymerization when the polyurea concentration reached 25 wt %.

For purposes of comparison, the time to peak polymerization exotherm and peak crystallization exotherm have been tabulated in Table II. Zero time was taken when the components were added to the same container for mixing. In the 100/0, 90/10, and 80/20 copolymers only an approximate time to polymerization exotherm peak time could be reported since the exotherm appeared

TABLE II
Time to Peak Polymerization, Phase Change, and Crystallization Exotherms

Copolymer	Polymerization time (s)	Phase change time (s)	Crystallization time (s)
100/0	50	55–70	85
90/10	70	75–85	125
80/20	60	85–120	140
75/25	50	15–30	110
70/30	55	10–15	110
65/35	55	15–20	145
60/40	60	10	125
50/50	NA[a]	NA[a]	NA[a]

[a] NA = data not available.

as a shoulder on the crystallization exotherm. The 50–60 s polymerization time was constant for the remaining copolymers. A very definite increase in crystallization time was seen as the polyurea concentration was increased from 0 to 10 wt %, a difference of 40 s. The broad crystallization exotherm peaked in the range of 110–140 s for the 90/10 to 60/40 copolymers. Although plaques of the 50/50 copolymer could be obtained, the viscosity of the reacting solution made filling of the mold cavity very difficult and reproducible polymerization and crystallization times could not be recorded.

Reactions were also run in glass molds so that the phase change, as indicated by a change in optical transmission from transparent to opaque, could be observed. The heat transfer characteristics of steel and glass are different but the results are comparable. In the polymerization of caprolactam to nylon 6 the low viscosity solution at the beginning is transparent. There is first an increase in viscosity due to polymerization, followed by an opacity with subsequent crystallization of the nylon. Both polymerization and crystallization are exothermic whereas the phase transition is not. This change from transparent to opaque, due to crystallization, began at 55 s and was complete at 70 s for the 100/0 copolymer (Table II). This was consistent with the thermal traces which showed a peak exotherm due to polymerization at 50 s followed by a crystallization exotherm at 85 s. In both the 90/10 and 80/20 copolymers, the change in light transmission also occurred at times between the exotherm peaks. With the 75/25 copolymer the development of opacity was seen beginning at 15 s and being complete at 30 s. This change resulted from the phasing out of the polyurea portion of the block copolymer early in the polymerization process. Any optical observation of the crystallization was obscured. The 70/30, 65/35, and 60/40 copolymers also showed the early phase transition (Table II) as observed with the 75/25 copolymer.

Thermal Properties

The samples used in the determination of thermal properties all had identical thermal histories. The temperatures and duration of the copolymers in the mold were monitored both in the oven and during the cool down to room temperature before demolding. The results as obtained by DSC are summarized in Table III. A general decrease in peak melting temperature from 216 to 196°C

TABLE III
Thermal Properties of Block Copolymers

	Melting temperature			Crystallinity[b]	
Copolymer	Onset (°C)	Peak (°C)	ΔH_f[a] (J/g)	NY/PU (%)	NYLON (%)
100/0	208	216	111.1	48	48
90/10	202	208	96.0	41	46
80/20	200	211	83.7	36	45
75/25	195	207	71.8	31	42
70/30	200	211	77.4	33	48
65/35	192	204	68.2	31	46
60/40	189	203	58.0	25	42
50/50	179	196	46.2	20	40

[a] ΔH_f = heat of fusion.
[b] NY/PU = crystallinity of nylon–polyurea copolymer; NYLON = crystallinity of nylon portion only; ΔHf of crystalline nylon = 230 J/g.[10]

was observed as the composition changed from pure nylon to a 50/50 copolymer. There was also a gradual increase in the width of the melting exotherm as the polyurea content in the block copolymer was increased, which decreased the precision of the melting point determination. The difficulties experienced in the preparation of the 50/50 copolymer were evidenced in the appearance of a definite exotherm for unreacted caprolactam at 68°C.

The crystallinities of the nylon–polyurea copolymers were calculated from the heats of fusion. This was not a precise calculation since the heat of fusion of crystalline nylon itself is the subject of controversy. For these calculations a compromise heat of fusion of 230 J/g proposed by Wunderlich[9] was used. As seen in Table III, the crystallinity of the block copolymer decreased from 48 to 20% with increased polyurea content. However, there was little if any change in the crystallinity of the nylon portion of the block copolymer. If the crystallinity were normalized by subtracting the amorphous polyurea content from the overall block copolymer composition, it was seen that, within experimental error, the crystallinity remained constant at 44 ± 4%.

The mechanical and morphological properties of the nylon–polyurea block copolymers will be described in subsequent papers.

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