Synthesis and characterization of novel nylon 6-<u>b</u>-polyimide-<u>b</u>-nylon 6 copolymers

Hong Ding and Frank W. Harris

The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

<u>Abstract</u>:   Novel nylon 6-<u>b</u>-polyimide-<u>b</u>-nylon 6 copolymers were synthesized by polycondensation and subsequent anionic ring-opening polymerization methods. Thus, an aromatic amine containing an N-acylated caprolactam moiety, i.e., 4-aminobenzoyl caprolactam (4-ABC), was used as an end-capping agent in the preparation of imide oligomers of 3,3'-dimethyl-4,4'-diaminobiphenyl (<u>o</u>-tolidine, OTOL), 3,3'4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2,2'-bis(3,4-dicarboxylphenyl)hexafluoropropane dianhydride (6FDA). The effects of the rigidity and molecular weight of the oligomers on their solubility in molten caprolactam were determined. The oligomer prepared from a 100/50/50 molar ratio of OTOL, BPDA and 6FDA was found to be the most rigid composition that could be dissolved in molten caprolactam. End-capped oligomers with this composition and different molecular weights were used as difunctional activators for the anionic, ring-opening polymerization of molten 6-caprolactam. The nylon 6-<u>b</u>-polyimide-<u>b</u>-nylon 6 triblock copolymers obtained, which contained 3-7 wt % polyimide, were successfully melt spun into fibers. The incorporation of the nylon 6 segments into the copolymers was substantiated by FTIR spectroscopy, solubility tests and GPC analysis. The fibers of the copolymers displayed mechanical properties superior to those of commercial nylon 6 fibers. The materials also exhibited improved chemical resistance, thermal stability and good melt processibility.

Keywords: molecular composite, polyimide, nylon 6, block copolymer, fibers.

INTRODUCTION

The enhancement of polymer properties through the physical incorporation of reinforcing materials has received great attention from both the academic and industrial communities. As an extension of reinforcing principles of fiber reinforced composites, a new concept of two-component molecular composites was independently proposed by Helminiak and Hwang (1) of the Air Force Materials Laboratory and Takayanagi (2) of Kyushu University in Japan. The basic hypothesis of this concept was that intimate blends of rigid polymers and flexible coil polymers could be prepared where the rigid polymer molecularly reinforced the flexible coil host. Although model systems were prepared that displayed superior properties, phase separation was often encountered with increasing levels of the rigid-rod molecules or during film casting and melt processing of the blends (3). The chemical resistance and thermal and mechanical properties of the phase separated composites were not enhanced beyond those of the matrix materials. Many attempts have been made to minimize the incompatibility of the rigid-rod molecule and flexible polymer matrix, including rapid coagulation (4) and the use of lower molecular weight rigid-rod polymers (5). A relatively recent approach has been to form chemically bonds between the two components. This has been accomplished in the preparation of graft copolymers with rigid polymer backbones and flexible thermoplastic side-chains and block copolymers containing rigid and flexible blocks (6-9). Most of these syntheses, however, have employed harsh solvents and have resulted in the formation of homopolymer byproducts.

The objective of this research was to develop novel one-component molecular composites that could be synthesized in bulk by a fast copolymerization technique. Well-defined structures were sought where all the flexible polymer chains grew from small amounts of rigid rods or extended chain polymers. This was to be accomplished by first incorporating an N-acylated caprolactam moiety in an aromatic amine. This amine, i.e., 4-aminobenzoyl caprolactam (4-ABC), was then to be used as an end-capping agent in the preparation of imide oligomers of 3,3'-dimethyl-4,4'-diaminobiphenyl (OTOL), 3,3',4,4'-biphenyltetracarboxyic dianhydride (BPDA) and 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA). The end-capped oligomers were to be used as difunctional activators for the subsequent anionic copolymerization of 6-caprolactam. Thus, they were to be dissolved in molten caprolactam at 140°C and treated with phenylmagnesium bromide. Nylon 6 chains were expected to grow from the activated groups at the ends of the imide chains to form well-defined nylon 6-b-polyimide-b-nylon 6 triblock copolymers. It was speculated that only small amounts of the imide component would be needed to effectively reinforce and, thus, significantly enhance the thermal and mechanical properties of nylon 6 (10,11).

EXPERIMENTAL

4-Nitrobenzoyl Caprolactam (1)

A mixture of 4-nitrobenzoyl chloride (50.16 g, 0.2704 mol), freshly distilled 6-caprolactam (30.59 g, 0.2704 mol), and 500 ml of benzene was added to a 1 L, three-necked, round-bottom flask equipped with an overhead stirrer, a condenser and a nitrogen inlet tube. The solution was heated to 90-100°C. After all the solids dissolved, 160 ml of pyridine was added. White pyridine salts formed immediately. After the reaction solution was heated at 90-100°C for 1 h, the pyridine salts were removed by filtration. The filtrate was evaporated to dryness under reduced pressure, and the residue was washed with a 5% NaHCO$_3$ aqueous solution and distilled water several times before being dried. The product was then recrystallized from a mixture of ethyl acetate and hexane (60/40, v/v) to obtain 67 g (95%) of pale white crystals: mp 106-106.5°C (lit.(12) 105°C); ^{1}H-NMR (CDCl$_3$): d 8.20 ppm (d, 2H, aromatic), 7.55 ppm (d, 2H, aromatic), 3.96 ppm (d , 2H, aliphatic), 2.65 ppm (d, 2H, aliphatic), 1.80 ppm (m, 6H, aliphatic); ^{13}C NMR (CDCl$_3$); 178.2 ppm(C=O), 172.5 ppm (C=O), 149.5 ppm (ArC-C=O), 143.5 ppm (ArC-NO$_2$), 128.5 ppm (ArC-H), 124 ppm (ArC-H), 45 ppm (aliphatic C), 39 ppm (aliphaticC), 29.7 ppm (aliphatic C), 29.2 ppm (aliphatic C), 23.7 ppm (aliphatic C); TLC: Rf=0.78 (ethyl acetate:hexane = 40:60, v/v).

4-Aminobenzoyl Caprolactam (2)

A mixture of 4-nitrobenzoyl caprolactam (9.05 g, 0.0345 mol), 0.50 g of 5% palladium on carbon and 120 ml of absolute ethanol was agitated under 1 atmosphere of hydrogen at room temperature. When the theoretical quantity of hydrogen (0.1035 mol, 2568 ml) had been absorbed, the solution was filtered through Celite under nitrogen. White, needle-like crystals formed after the filtrate was stored at -10°C. The product was collected by filtration and washed with cold ethyl ether to yield 6.0 g (75%) of white crystals: mp 153-154°C (lit.(12) 152-153°C); ^{1}H-NMR (CDCl$_3$): d 7.47 ppm (d, 2H, aromatic), 6.68 ppm (d, 2H, aromatic), 3.92 ppm (broad, 2H, NH$_2$), 3.85 ppm (d, 2H, aliphatic), 2.65 ppm (d, 2H, aliphatic); 1.80 ppm (m, 6H, aliphatic); ^{13}C NMR (CDCl$_3$); 178.2 ppm (C=O), 174.5 ppm (C=O), 151.0 ppm (ArC-C=O), 125.7 ppm (ArC-NH$_2$), 131.7 ppm (ArC-H), 114.0 ppm (ArC-H), 46.4 ppm (aliphatic C), 39.5 ppm (aliphatic C), 29.7 ppm (aliphatic C), 29.2 ppm (aliphatic C), 23.7 ppm (aliphatic C); IR (KBr) 3456 and 3346 cm^{-1} (NH$_2$).

Typical Synthesis of an N-Acylated Caprolactam End-Capped Oligomer (OTOL/BPDA/-6FDA, 100/50/50; Calculated Mn = 6,000)

To a solution of OTOL (0.6000 g, 2.826 mmol) in 9.7 ml of NMP, BPDA (0.4554 g, 1.548 mmol) was added. After the mixture was stirred at ambient temperature under nitrogen for 5 h, 6FDA (0.6876 g, 1.548 mmol) was added and the resulting solution was stirred for an additional 10 h. 4-Aminobenzoyl caprolactam (0.1253 g, 0.5396 mmol) was added and the reaction mixture was stirred for another 10 h. Pyridine (0.563 g, 3.10 mmol) and acetic anhydride (0.727 g, 3.10 mmol) were added, and the reaction mixture was stirred for another 24 h. The polymer solution was diluted with 10 ml of NMP and poured into methanol. The end-capped polyimide (OTOL/BPDA/6FDA = 100:50:50 molar ratio, target Mn = 6000 g/mol) that precipitated was collected by filtration, washed with methanol and dried under reduced pressure.

Typical Synthesis of a Nylon 6-b-Polyimide-b-Nylon 6 Copolymer

A 250 ml resin kettle equipped with an overhead stirrer and a nitrogen inlet was purged with dry nitrogen and charged with 6-caprolactam (2.9 g, 25 mmol). After the solid was melted by heating to 120-140°C, a 3.0 M solution of PhMgBr in diethyl ether (0.23 ml, 0.72 mmol) (molar ratio of PhMgBr, N-acylated caprolactam moieties in polyimide = 1:1) was injected and stirred under nitrogen. The homogeneous solution that formed was used as the initiator for the anionic, ring-opening polymerization of 6-caprolactam.

A four-necked, 50 ml resin kettle equipped with an overhead stirrer and a nitrogen inlet was purged with dry nitrogen and charged with 6-caprolactam (25.0 g, 0.221 mol). After the solid was melted by heating to 120-140°C, the polyimide (2.1 g, 0.7 mmol of acylated caprolactam moieties) that was obtained from OTOL/BPDA/6FDA with a molar ratio of 100:50:50 and a calculated Mn of 6,000 was gradually added. The molten mixture was stirred under nitrogen at 140°C for 1 h to ensure homogeneity. The polyimide solution was poured into the anionic initiator solution under nitrogen and stirred at 140°C. The mixture, which solidified within 8 min, was maintained at 140°C for 1 h under nitrogen. A homogeneous, tough, yellow polymer disk was obtained. The copolymer, which contained 7 wt% of polyimide, was cut into small pieces, extracted with NMP and methanol, and dried at 150°C under reduced pressure.

Preparation of Block Copolymer Fibers

The nylon 6-b-polyimide-b-nylon 6 copolymers and a commercial nylon 6 were melt spun into fibers at 250-265°C under nitrogen using an Instron Capillary Rheometer, which was fitted with a capillary die with a diameter of 1.27 mm and a length/diameter ratio of 28.7. A plunger speed of 0.03 in/min was used. The fibers were taken up on an 8.1 cm diameter roll using a speed-controlled, take-up motor. the fibers were first drawn as much as possible at room temperature, and then at 140°C. The total draw ratio was 4X. The drawn fibers were evaluated on an Instron Model 1130 using an elongation speed of 5 mm/min at room temperature.

Instrumentation

Infrared (IR) spectra were recorded on a Beckman FT-2100 infrared spectrometer using KBr pellets or film samples. Melting points were measured on a Meltemp capillary melting point apparatus and were uncorrected. Intrinsic viscosities were determined using a Cannon-Ubbelohde No. 150 or No. 200 viscometer in m-cresol at 30±0.1°C. Gel permeation chromatography (GPC) was performed on m-cresol solutions (0.25 ml, 2.5 mg/ml) of the block copolymer samples with a flow rate of 1.0 ml/min at 100°C.

RESULTS AND DISCUSSION

End-Capping Agent 4-Aminobenzoyl caprolactam (2)

The end-capping agent 4-aminobenzoyl caprolactam (2) was synthesized via the route shown in Scheme 1. 4-Nitrobenzoyl chloride was treated with 6-caprolactam to form 4-nitrobenzoyl caprolactam (1). Compound 1 was then hydrogenated under 1 atmosphere of hydrogen at room temperature to yield 2.
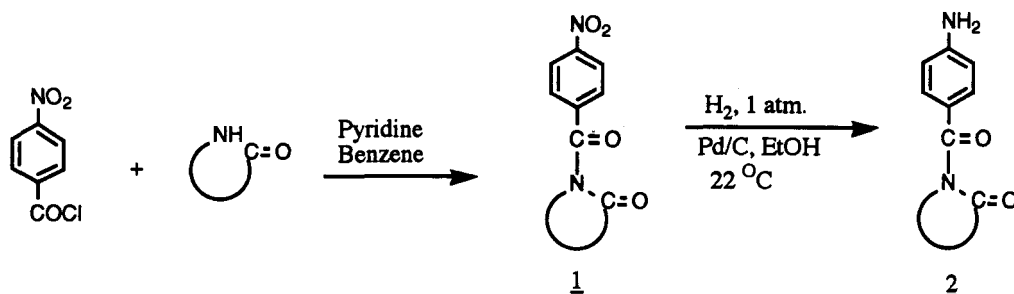
Scheme 1

N-Acylated Caprolactam End-Capped Imide Oligomers

N-Acylated caprolactam end-capped polyimides were prepared by a two-step method (Scheme 2). In the first step, a diamine, such as OTOL, was treated with an excess amount of dianhydride, such as BPDA and/or 6FDA, at ambient temperature in NMP, producing an anhydride-terminated polyamic acid (3). The molecular weight of the oligomer was controlled by varying the molar ratio of the diamine to the dianhydride. The end-capping agent 4-aminobenzoyl caprolactam (2) was then allowed to react with the anhydride chain-ends of 3. The intermediate oligomer 4 was converted to the acylated caprolactam-terminated imide oligomer 5 by chemical imidization with pyridine and acetic anhydride. The oligomer 5 was then precipitated in ethanol to produce a pale yellow powder.

The solubility of the difunctional imide oligomers in molten 6-caprolactam was very important in forming homogeneous activator solutions. In order to synthesize acylated caprolactam end-capped oligomers that were not only soluble in molten caprolactam but also rigid for the efficient reinforcement of the final products, the rigid diamine OTOL and the dianhydride BPDA were used. The less rigid dianhydride 6FDA was also used as a comonomer to adjust the balance of rigidity and solubility of the end-capped oligomers. Thus, a series of N-acylated caprolactam end-capped oligomers were prepared from OTOL, BPDA and 6FDA with calculated molecular weights of 6,000 and 12,000, respectively, as shown in Table I. The

TABLE 1. N-Acylated Caprolactam End-Capped Polyimides

End-Capped Polyimide	OTOL/BPDA/6FDA (Molar Ratio)	Mn^a (g/mol)	$[\eta]$ (dl/g)	Solubility[b] NMP	Caprolactam
PI-1	100/100/0	6000		I	I
PI-2	100/85/15	6000		I	I
PI-3	100/70/30	6000		S	PS
PI-4	100/50/50	6000	1.02	S	S
PI-5		12000	1.35	S	S
PI-6[c]		6000		S	S
PI-7	100/30/70	6000		S	S
PI-8		12000		S	S
PI-9	100/0/100	12000		S	S

a. Average $Mn = M_0 (1+r)/(1-r)$, where $r = Mole^{amine}/Mole^{anh}$
b. I = Insoluble, PS = Partially Soluble, S = Soluble
c. PI-6 was end-capped with phthalic anhydride

solubility of the end-capped oligomers in molten caprolactam depended more on the polymer composition than on the molecular weight. The more 6FDA that was incorporated, the less rigid the imide chain and the higher the solubility in molten caprolactam. The copolymers prepared from a 100/50/50 molar ratio of OTOL, BPDA, and 6FDA were the most rigid polymers that could be dissolved in molten caprolactam. Therefore, the polyimides with this composition and calculated molecular weights of 6,000 (PI-4) and 12,000 (PI-5) were chosen as the difunctional polymeric activators for the subsequent anionic, ring-opening polymerization of 6-caprolactam. In order to determine whether the caprolactam anion would attack the five-member imide ring under the copolymerization conditions, a non-reactive, phthalic anhydride end-capped polyimide (PI-6) was also prepared as a model polymer. The intrinsic viscosities of the rigid end-capped oligomers were in the range of 1.0 ~ 1.5 dl/g. The incorporation of N-acylated caprolactam moieties into the polyimide chain ends was confirmed by FTIR spectra at 2934 and 2864 cm⁻¹ (asymmetrical and symmetrical stretching of CH_2 in caprolactam ring, respectively).

Nylon 6-b-Polyimide-b-Nylon 6 Triblock Copolymers

The activator solutions were prepared by dissolving 3~7 wt% of the N-acylated caprolactam end-capped oligomers in molten 6-caprolactam at 140°C under nitrogen. After the initiator solution was prepared by treating PhMgBr with 6-caprolactam at 140°C under nitrogen, it was mixed with the activator solution (Scheme 2). The block copolymerization started

immediately, and the reaction mixture solidified within 10 min. The nylon 6 chains grew in two directions from the activator sites located at the oligomer chain ends to form nylon 6-b-polyimide-b-nylon 6 triblock copolymers (PIBN). The upper limit of oligomer loading depended on the solubility of the imide in molten caprolactam. Six different triblock copolymers (PIBN) were prepared in which the molecular weight and loading of the oligomer were varied (Table 2).
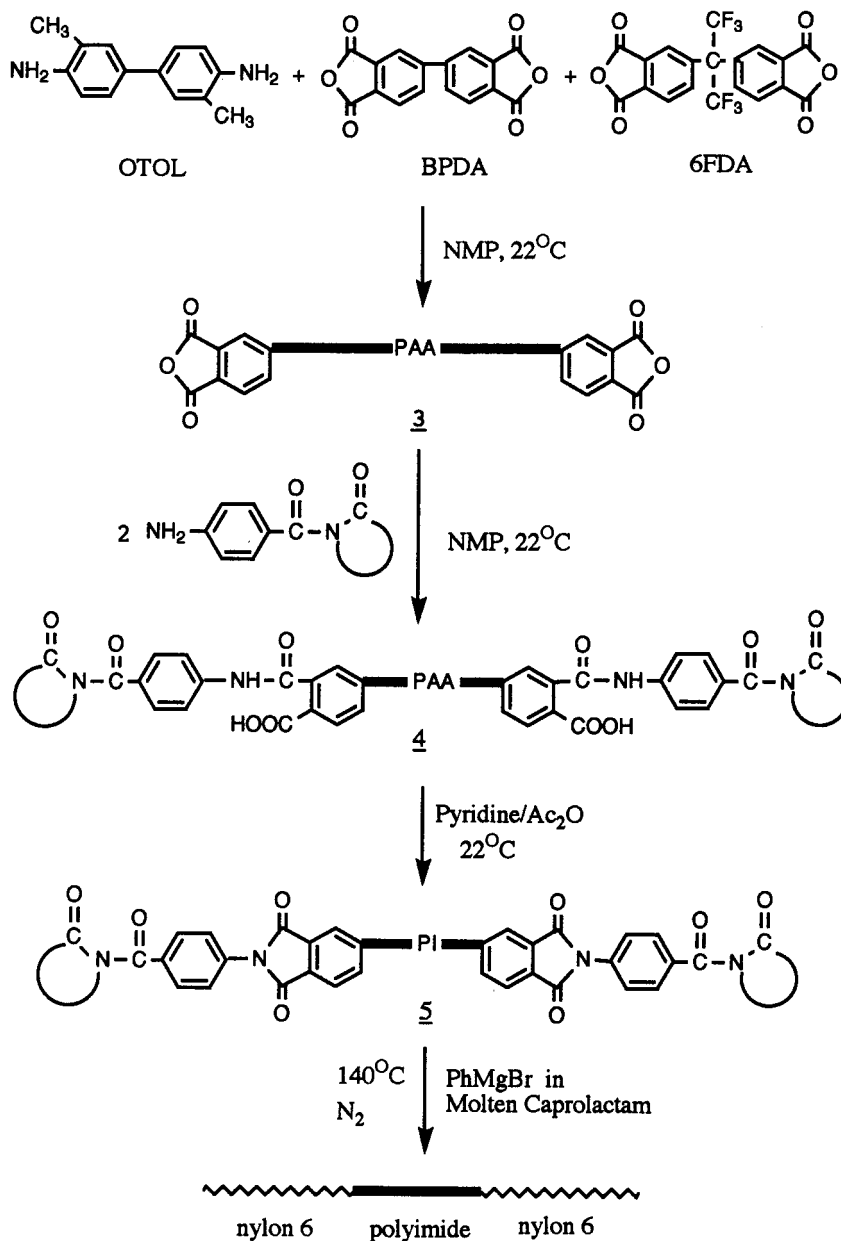
Scheme 2

In order to determine whether imides oligomers containing no activator groups at the chain ends or along the backbone could initiate the anionic polymerization of 6-caprolactam at 140°C, the model polyimide PI-6 was dissolved in molten caprolactam and treated with the 6-caprolactam anion solution at 140°C under nitrogen. Even at the highest initiator concentrations used for preparing the graft copolymers, solidification of the reaction mixtures did

not occur. As mentioned previously, solidification occurred in the block copolymerizations within 10 min. This control experiment demonstrated that: (1) the non-activated homopolymerization of 6-caprolactam did not proceed at the reaction temperature of 140°C; and (2) the five-member imide rings in the polyimide backbones were not attacked by the caprolactam anions under the reaction conditions.

The intrinsic viscosities of the block copolymers were in the range of 2.2 to 4.6 dl/g (Table 2). Solubility tests showed that the block copolymers were no longer soluble in formic acid and NMP, which were good solvents for nylon 6 and polyimide homopolymers, respectively. The block copolymers were only soluble in m-cresol, indicating that chemical resistance was dramatically improved over that of nylon 6. The fact that the copolymers were still soluble in at least one solvent, however, indicated that no crosslinking reactions occurred in these fast, bulk copolymerizations. The successful incorporation of nylon 6 segments into the copolymers was also substantiated by FTIR spectroscopy, as shown in Fig. 1. The GPC results and typical chromatograms of the end-capped polyimides and their corresponding block copolymers are shown in Table 2 and Fig. 2, respectively. The triblock copolymers exhibited narrow

TABLE 2. Nylon 6-b-Polyimide-b-Nylon 6 Copolymers

Block Copolymers	PI(OTOL/BPDA/6FDA)[a] Feed(wt%)	Mn(g/mol)	$[\eta]$[b] (dl/g)	Mn (x10-3)	Mw (x10-3)	Mw/Mn[c]
PIBN-1	3	6000	3.33	50	76	1.5
PIBN-2	5	6000	2.71	55	66	1.2
PIBN-3	7	6000	2.24	58	69	1.6
PIBN-4	4	12000	2.77	32	50	1.5
PIBN-5	5	12000	2.92	40	55	1.4
PIBN-6	6	12000	4.55	60	96	1.6

a. PI(OTOL/BPDA/6FDA) (100/50/50)
b. Intrinsic viscosity measured in m-cresol at 30°C.
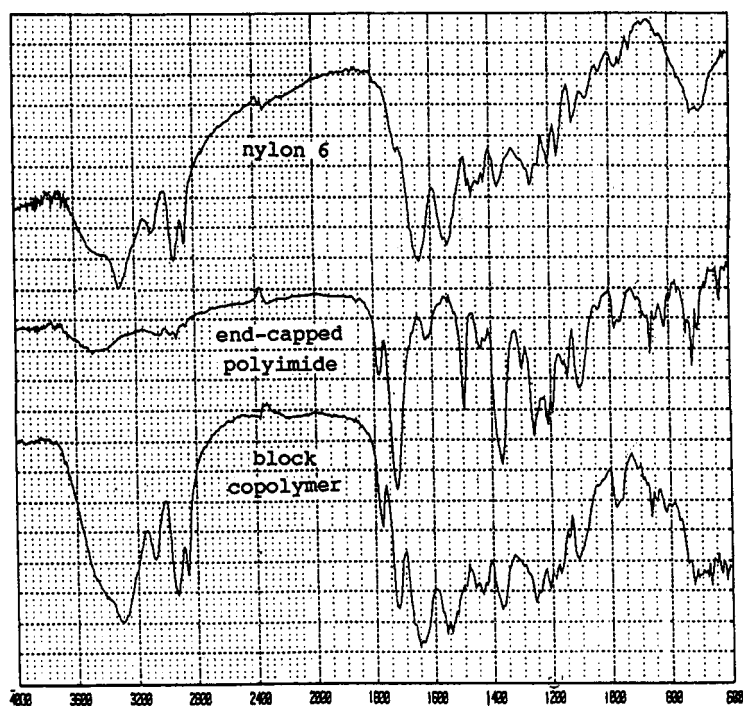c. GPC was performed in m-cresol at 100°C.

Fig. 1. FTIR spectra of nylon 6, the difunctionalized polyimide PI-4 and the block copolymer PIBN-3.
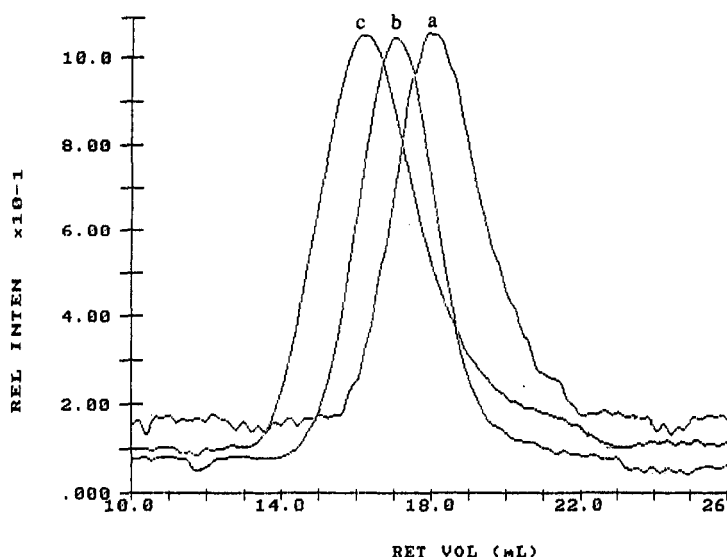
Fig. 2. Typical GPC chromatograms: (a) difunctional polyimide PI-5;
(b) block copolymer PIBN-4; (c) block copolymer PIBN-6.

polydispersities, ranging from 1.4 to 1.6. With increasing amounts of imide incorporation in the triblock copolymers, the GPC peak shifted to lower retention volumes, suggesting the formation of a triblock copolymer with a larger molecular size or a more extended conformation. The single, narrow peaks of the block copolymers in the GPC chromatograms as well as the selective extraction results confirmed that no homopolymerization of 6-caprolactam proceeded under the reaction conditions.

The block copolymers containing 3~7 wt% imide oligomers exhibited very good melt processibility. They could readily be compression-molded into dumbbell shapes and films. Macroscopic phase separation of the copolymer blocks did not occur during melt processing. However, macroscopic phase separation did occur when physical blends of nylon 6 and imide oligomers were melt processed. The triblock copolymers and unmodified nylon 6 were also melt spun into fibers. The mechanical properties of these fibers are summarized in Table 3. Upon increasing the imide content from 3 to 7 wt%, the elongations at break of the fibers reached a maxima at 5 wt% polyimide with Mn = 6,000 and at 4 wt% polyimide with Mn = 12,000. The highest tensile strengths were obtained with these two samples, i.e., 7.0 and 7.5 g/d, respectively, compared to 5.3 g/d for the nylon 6 fiber. Thus, by introducing only 5 wt% imide into the nylon 6 the tensile strengths of the fibers were increased by up to 40%. The morphology and thermal and mechanical properties of molded samples will be discussed in a future paper.

TABLE 3. Mechanical Properties of Nylon 6 and Nylon 6-b-Polyimide-
b-Nylon 6 Fibers[a]

Copolymer	Tensile Strength (g/d)	Elongation at Break (%)
Nylon 6	5.3	130
PIBN-1	6.2	160
PIBN-2	7.0	183
PIBN-3	6.0	160
PIBN-4	7.5	217
PIBN-5	7.5	160
PIBN-6	6.0	160

a. Fibers were melt spun at 245~260°C, drawn at 22°C and then at 140°C to 4 times of their original length.

CONCLUSIONS

N-Acylated caprolactam end-capped imides oligomers can be prepared by two-step condensation polymerizations and used as difunctional polymeric activators for the subsequent anionic, ring-opening copolymerizations of molten 6-caprolactam. The block copolymerizations can be carried out in bulk at a relatively low temperature of 140°C, where the homopolymerization of 6-caprolactam does not occur. Nylon 6 chains grow from the activated chain-ends of the oligomer to form linear triblock copolymers. The blocks of the copolymers do not undergo macroscopic phase separation during melt processing. The copolymers can be melt spun into fibers that display mechanical properties superior to those of commercial nylon 6 fibers.

ACKNOWLEDGEMENT

REFERENCES AND NOTES

1. T.E. Helminiak *ACS Div. of Org. Coat. Plast. Chem., Preprints* **40**, 475 (1979).
2. M. Takayanagi, T. Ogata, M. Morikawa and T. Kai, *J. Macromol. Sci. Phys.* **B17(4)**, 591 (1980).
3. W.F. Hwang and T.E.Helminiak *Mat. Res. Soc. Symp. Proc.* **134**, 507 (1989).
4. H.H. Chuah, T. Kyu and T.E. Helminiak *Polymer* **28**, 2130 (1987).
5. T. Nishihara, H. Mera and K. Matsuda *ACS Div. of Polymer. Mater. Sci. and Eng.* **55**, 821 (1986).
6. M. Takayanagi *Polym.. Composites* 3 (1986).
7. M. Dotrong, M.H. Dotrong and R.C. Evers *ACS Div. of Polym. Chem., Polym. Prepr.* **33(1)**, 477 (1992).
8. U.M. Vakil, C.S. Wang, C.Y.-C. Lee, M.H. Dotrong, M. Dotrong and R.C. Evers *ACS Div. of Polym.Chem., Polym. Prepr.* **33(1)**, 479 (1992).
9. D.R. Moore, Ph.D. Dissertation *"Molecular Composites Based on Aromatic Polyamides- Synthesis and Characterization; Poly(oxyvinylene)lactam: Novel Polymers from N-(chloroacetal)lactams,"* The University of Southern Mississippi, 1987.
10. F.W. Harris and H. Ding U.S. Patent, Application, U.S. Serial No. 08/171,523, 1993.
11. H. Ding, Ph.D. Dissertation *"Synthesis and Characterization of Novel Polyimide-g-Nylon 6 and Nylon 6-b-Polyimide-b-Nylon 6 Copolymers,"* The University of Akron, 1994.
12. L.G. Donaruma, R.P. Scelia and S.E. Schonfeld *J. Heterocyclic Chem.* **1**, 448 (1964).