

Preparation and Characterization of Polyimide-g-Nylon 6 Copolymers from Nonfunctionalized Polyimides

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ABSTRACT: In this research, the anionic polymerization of ϵ -caprolactam was carried out in the presence of small amounts of several different polyimides to generate polyimide-g-nylon 6 copolymers. The polyimides, which were prepared from 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride and commercially available diamines with a one-step method, were first dissolved in molten ϵ -caprolactam. Phenylmagnesium bromide was then added at 120°C. Under these conditions, caprolactam anions were formed that attacked the five-membered imide rings to form *N*-acyllactam moieties, which activated the anionic polymer-

ization of caprolactam. In essence, nylon 6 chains grew from the polyimide backbones. Probably because of a high activation energy, the process was relatively slow, requiring 1 h at 120°C. The introduction of 5 wt % polyimide into the graft copolymers produced significant increases in the tensile modulus and tensile strength in comparison with those of low- and high-molecular-weight nylon 6. The elongation to break, however, was reduced. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 292–299, 2006

Key words: copolymerization; nylon; polyimides

INTRODUCTION

An acyllactam or a reactive precursor to an acyllactam is required to carry out the anionic polymerization of lactams at a low temperature and high efficiency.^{1–5} In fact, numerous publications describing activating systems for the anionic polymerization of lactams have been published.^{6–11} Although no one has reported that five-membered imide rings can function as activator groups, it is postulated in this work that such activation might be possible. Specifically, it is postulated that lactam anions will attack the imide ring to generate acylated lactam moieties from which nylon chains can grow. Thus, if one carried out the anionic polymerization of ϵ -caprolactam in the presence of a small amount of a polyimide, one could generate a graft copolymer (Fig. 1).

The objective of this research was to investigate synthetic routes to polyimide/nylon 6 graft copolymers. In this research, the ability of imide-functional groups to activate the anionic polymerization of ϵ -caprolactam was investigated. It was postulated that caprolactam anions could attack imide groups under certain conditions to generate *N*-acyllactam structures that would then activate the polymerization. Thus, several polyimides were prepared from 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BisA-DA) and com-

mercially available diamines with a one-step method. The polyimides were dissolved in molten ϵ -caprolactam and then treated with ϵ -caprolactam anions. The reaction conditions were determined under which the anions would attack the imide linkages to generate acylated caprolactam moieties that would then initiate the polymerization of ϵ -caprolactam. Thus, the polyimides functioned as multifunctional activators in the ring-opening polymerization of ϵ -caprolactam and, therefore, generated graft copolymers. In essence, nylon 6 chains grew from the polyimide backbones. The mechanical and thermal properties of the graft copolymers were determined.

EXPERIMENTAL

Materials

Aniline (Aldrich Chemical Co., St. Louis, MO) was distilled under reduced pressure. 2,2'-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP; Chriskev Co., Leawood, KS) was recrystallized from *N,N*-dimethylformamide and methanol. BisA-DA (General Electric Co., Cincinnati, OH) was recrystallized from acetic anhydride (Ac₂O) and dried at 100°C under reduced pressure overnight. ϵ -Caprolactam (Aldrich Chemical) was distilled under reduced pressure. 3,3'-Dimethyl-4,4'-diaminobiphenyl [*o*-tolidine (OTOL); Aldrich Chemical] was recrystallized from ethanol. Isoquinoline (Aldrich Chemical) was used as received. Nylon 6 (Polyscience Co., Warrington, PA) was dried under reduced pressure at 100°C overnight. Phenylmagnesium bromide (PhMgBr; 3.0M solution in di-

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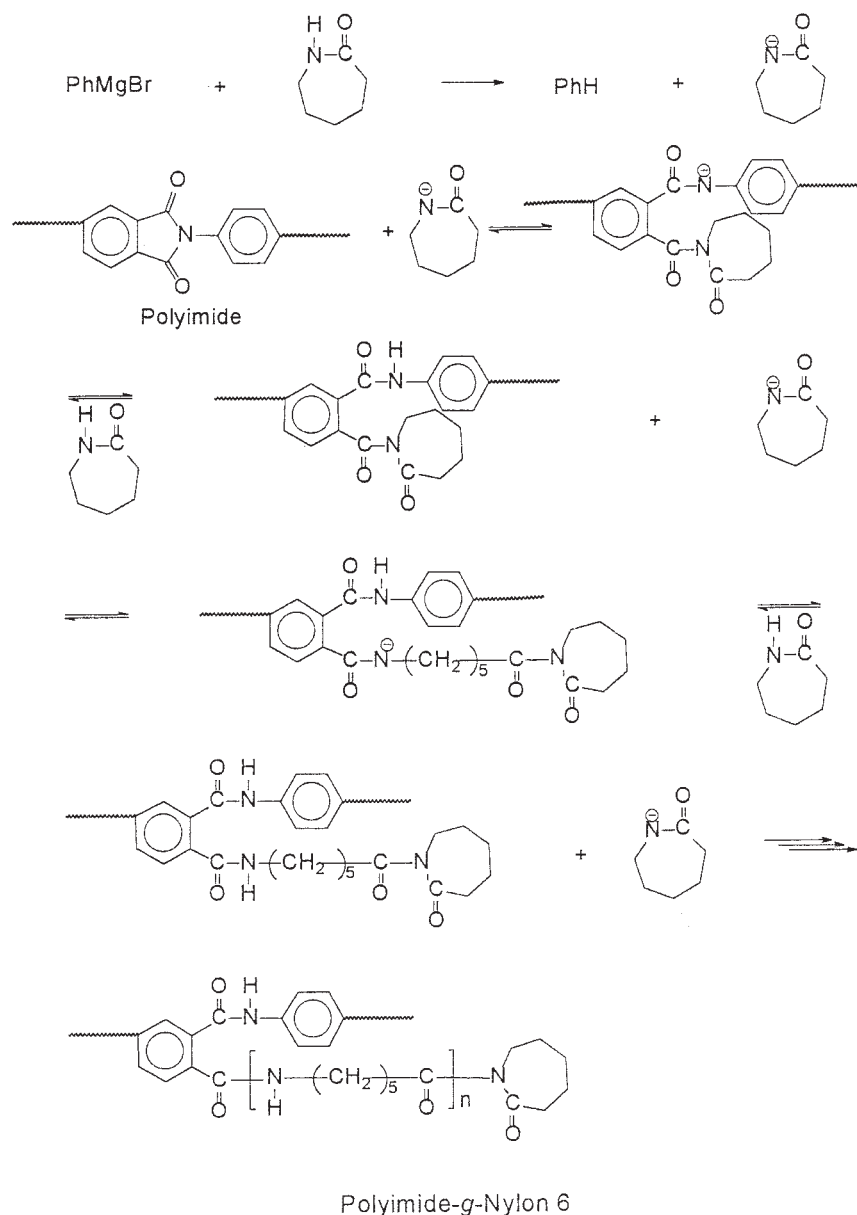


Figure 1 Proposed mechanism for the preparation of graft copolymers.

ethyl ether; Aldrich Chemical) and phosphorus pentoxide (P_2O_5 ; Fisher Scientific Co., Pittsburgh, PA) were used as received. Phthalic anhydride (Aldrich Chemical) was dried at 190°C under reduced pressure overnight. Ultem polyimide granule (General Electric), Ac_2O (Fisher Scientific), and chloroform ($CHCl_3$; Fisher Scientific) were used as received. *m*-cresol (Fisher Scientific) was distilled over P_2O_5 under reduced pressure. *N,N*-Dimethylformamide (Fisher Scientific), ethanol (Quantum Chemical Co., Cincinnati, OH), formic acid (Fisher Scientific), and methanol (Fisher Scientific) were used as received. *N*-Methyl-2-pyrrolidinone (NMP; Aldrich Chemical) was distilled over P_2O_5 under reduced pressure.

Synthesis of *N*-phenylphthalimide (1)

To a 100-mL, three-necked, round-bottom flask equipped with a condenser and a nitrogen inlet tube were added aniline (4.09 g, 0.0439 mol), phthalic anhydride (5.00 g, 0.0336 mol), and 35 mL of NMP. The reaction mixture was heated gradually to 200°C . A few drops of isoquinoline were added at 170°C . The mixture was stirred at 200°C for 12 h. The mixture was then allowed to cool to room temperature. The precipitate that formed was collected by filtration, washed with water, and then dried under reduced pressure. The solid was recrystallized from NMP and ethanol to afford 6.94 g (93%) of light brown crystals.

mp: 205–207°C (lit¹² ca. 205°C). IR (KBr): 1797, 718 (imide C=O), 1383 cm⁻¹ (imide C—N).

General procedure for the preparation of the nonfunctionalized polyimides

To a 500-mL, three-necked, round-bottom flask equipped with a mechanical stirrer and a nitrogen inlet were added the diamine (0.1 mol) and 300 mL of NMP. After the diamine dissolved completely, the dianhydride (0.1 mol) was added (solid content = 20% w/w). The reaction mixture was heated gradually to 200°C. Isoquinoline (10 drops) was added at 170°C. The mixture was stirred at 200°C for 12 h. The water liberated by the polycondensation was removed by distillation. The polymer was isolated by precipitation in methanol with vigorous stirring. The precipitate was collected by filtration and agitated in methanol in a blender. The polymer was collected by filtration and dried under reduced pressure at 260°C for 1 h.

General procedure for the preparation of graft copolymers from nonfunctionalized polyimides

To a 250-mL, three-necked, round-bottom flask equipped with a mechanical stirrer and an argon inlet were added the polyimide (2.37 g) and ϵ -caprolactam (45.0 g, 0.398 mol; solid content = 5% w/w). The mixture was heated at 140–150°C and stirred for 4–5 h to ensure homogeneity. After the homogeneous molten mixture was allowed to cool to 120°C, a 3.0M solution of PhMgBr in diethyl ether was added. Different amounts of the solution were used to provide three different concentrations of PhMgBr (0.08, 0.16, and 0.20 mol % based on caprolactam). The solution viscosity gradually increased, and solidification occurred in approximately 1 h. The solid mixture was maintained at 120°C for 5 h to ensure a complete reaction. A homogeneous, tough, yellow polymer was obtained. The polymer was cut into small pieces, extracted with hot methanol for 16 h, and dried at 160°C for 12 h under reduced pressure.

Differential scanning calorimetry (DSC)

A polymer film sample was placed in a tared DSC pan and sealed with pan crimpers. The sample pan was heated at 280°C for 3 min and then quenched in a dry-ice/acetone bath before the run on a DuPont model 2000 differential scanning calorimeter (Wilmington, DE). The scanning range was –50 to 300°C, and the heating rate was 10°C/min. The polymer glass-transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and degree of crystallinity (w^c) were obtained from the DSC thermogram. w^c was taken as the ratio of the heat of fusion of

the sample to the heat of fusion of nylon 6 crystals (26.0 kJ/g).¹³

Thermogravimetric analysis (TGA)

The thermal stability measurements were performed on a TA Hi-Res TGA 2950 thermogravimetric analyzer with a powdered sample at a heating rate of 10°C/min under nitrogen. The degradation temperature was taken as the temperature at which the sample lost 5% of its original weight.

Fourier transform infrared (FTIR) spectroscopy

Solution-cast films or KBr disks were used for the FTIR measurements, which were carried out on a Mattson Galaxy series FTIR 5000 IR spectrometer (Waltham, MA) at the ambient temperature in air.

Solution viscosity measurements

The inherent viscosities of the polyimides were determined with 0.5 wt % NMP solutions with a Cannon-Ubbelohde no. 100 viscometer at 30.0 ± 0.1°C.

Mechanical properties

The tensile tests were conducted at the ambient temperature according to ASTM D 882. Thin films for tensile testing were prepared by the casting of *m*-cresol solutions (5–10%) of the polymers onto glass plates with dimensions of 80 mm × 5 mm × 0.05–0.08 mm (length × width × thickness). The films were heated at 160°C for 24 h under reduced pressure before testing to remove any trace of *m*-cresol and then slowly cooled to room temperature. The tensile tests were carried out on an Instron model 1130 tensile testing machine (Norwood, MA) with an initial strain rate of 0.1 mm/mm min. At least 14 replicates of each sample were tested to determine the Young's modulus, tensile strength, and elongation at break.

RESULTS AND DISCUSSION

Model compound study

A model compound study was carried out with **1**. The objective of this study was to determine if this compound could activate the melt polymerization of ϵ -caprolactam (Fig. 2). Thus, the model compound was dissolved in molten ϵ -caprolactam at 120°C, and this was followed by the addition of PhMgBr. Nylon 6 was obtained in 1 h. This was confirmed by a comparison of the FTIR spectrum of the product with that of commercial nylon 6 (Fig. 3). No polymerization occurred under these conditions when the imide was not added.

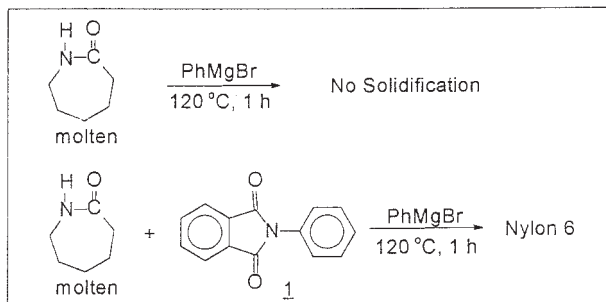
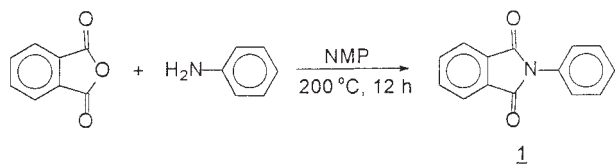


Figure 2 Model reaction ($1/\epsilon$ -caprolactam = 0.013 mol/mol; a 20% molar excess of the designated amount of PhMgBr was used).

Polyimide synthesis

Two polyimides were synthesized for use in this work. Thus, OTOL and BAPP were polymerized with BisA-DA in refluxing NMP containing isoquinoline to afford the polyimides poly(OTOL/BisA-DA) (**2a**) and poly(BAPP/BisA-DA) (**2b**), respectively (Fig. 4). The solvent was heated at reflux so that the intermediate poly(amic acid)s spontaneously cyclized to the imides. The polymers were subsequently heated at 260°C un-

der reduced pressure to complete the imidization process. The polyimide structure and physical properties are summarized in Table I. The properties of a sample of a commercial polymer (Ultem) that was also used in this work are included in Table I.

Graft polymerizations

The polyimides were dissolved in molten ϵ -caprolactam at 120°C under argon to form homogeneous solutions. The amount of polyimide that could be incorporated into the molten caprolactam varied because of the different polyimide solubilities. For comparison, the amount of polyimide was kept constant at 5 wt %. The copolymerizations, leading to polyimide-g-nylon 6, were carried out by the addition of the initiator (PhMgBr) to the polyimide/ ϵ -caprolactam solutions at 120°C. The reaction mixtures solidified in 1 h. The temperature was maintained at 120°C for another 5 h to ensure high conversion to the product. The homogeneous samples were cut into small pieces and extracted with hot water or methanol to remove the unreacted monomer.

At reaction temperatures below 150°C, the nonactivated homopolymerization of ϵ -caprolactam does not proceed because of the high activation energy of the initial slow step of the nucleophilic attack by the anion of the lactam on the carbonyl carbon atom of the monomer.¹⁻⁵ Thus, there was no ϵ -caprolactam homopolymer formed at 120°C. When *N*-acylated caprolactams, which are the most common activators for

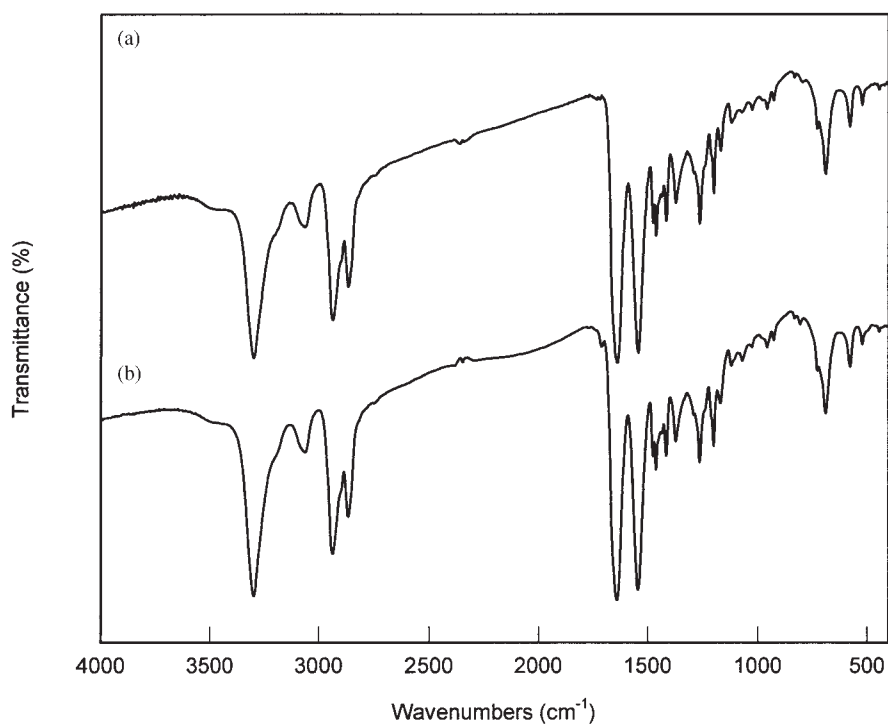


Figure 3 FTIR spectra of (a) commercial nylon 6 and (b) nylon 6 obtained with **1** as an activator.

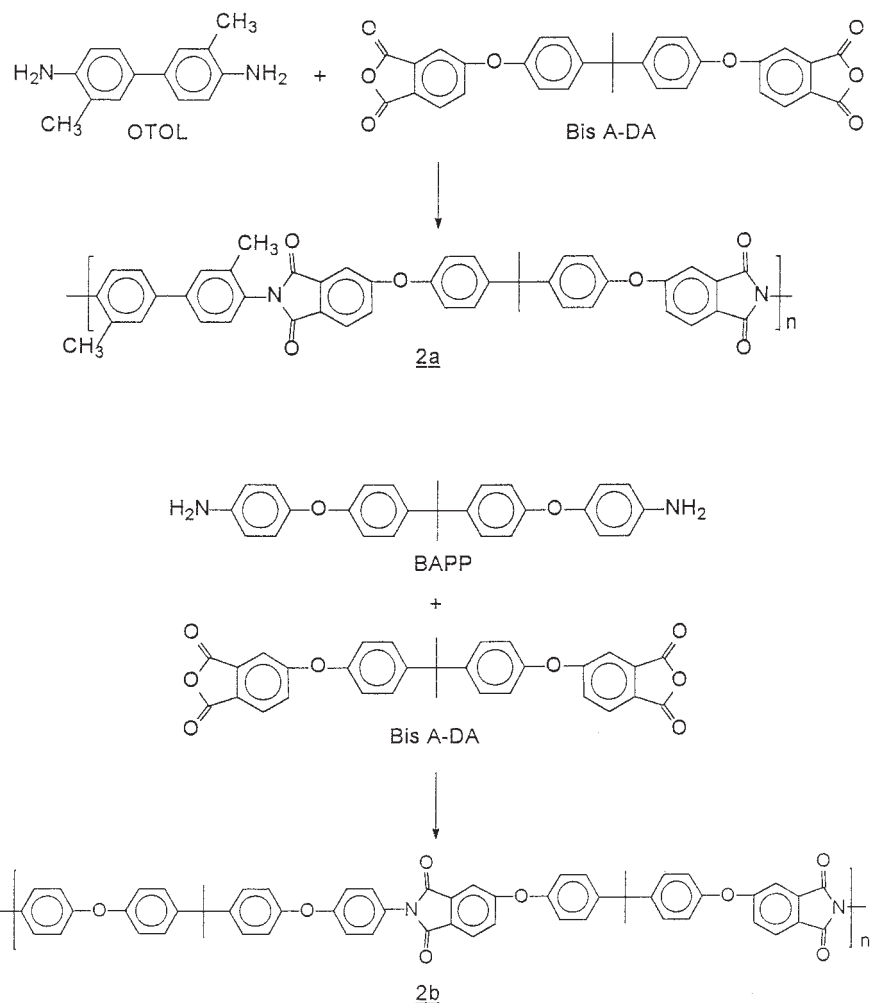


Figure 4 Synthesis of polyimides.

TABLE I
Physical Properties of Polyimides 2a–2c

No.	Structure	T_g (°C)	η_{inh}^a
2a	Poly(OTOL/BisA-DA)	262	0.94
2b	Poly(BAPP/BisA-DA)	201	0.72
2c	Ultem	218	0.49

^a Inherent viscosity measured at 0.5 wt % in NMP at $30.0 \pm 0.1^\circ\text{C}$.

TABLE II
Characteristic FTIR Absorptions of Commercial Nylon 6,
Polyimide 2b, and Its Graft Copolymer

Band (cm ⁻¹)	Nylon 6	Polyimide 2b	Graft copolymer
ν N—H	3298		3298
ν as,CH ₂	2936		2937
ν s,CH ₂	2867		2867
ν s,imide C=O		1777	1777
ν as,imide C=O		1723	1723
ν C=O	1637		1640
δ N—H	1543		1545

ν = stretching; δ = bending; s = symmetrical; as = asymmetrical.

ϵ -caprolactam polymerization, are used as activators, the anionic polymerization of ϵ -caprolactam takes place in a few minutes because of the much lower activation energy for the initial nucleophilic attack of caprolactam anion on the *N*-acylated caprolactam.^{14,15} The use of benzoylcaprolactam in this study resulted in the polymerization of ϵ -caprolactam in less than 5 min at 120°C. The fact that the use of five-membered imide rings as activators resulted in a long induction period indicates that the activation energy for the initial nucleophilic attack of caprolactam anion on the stable ring is high.

Characterization of the graft copolymers

To prove that the polyimide and nylon 6 components were bonded to each other, the graft copolymers were

characterized by selective extractions. Thus, the graft copolymers were first extracted with methanol to remove unreacted ϵ -caprolactam. Less than 4 wt % of the monomer was recovered. The polyimide-g-nylon 6 copolymers were then successively extracted with CHCl₃ (a solvent for the polyimides) and with formic acid (a solvent for nylon 6). During these extractions, the graft copolymers remained insoluble; that is, they did not undergo any weight loss. Thus, over 96% of the ϵ -caprolactam was polymerized during the anionic ring-opening polymerizations, and no detectable amount of nylon 6 homopolymer was formed.

The FTIR absorptions of commercial nylon 6, polyimide (2b), and its graft copolymer are summarized in Table II and Figure 5. The majority of the nylon absorption bands¹⁶ are those corresponding to the C—C, C—H, N—H, and C=O moieties. The C—C stretching vibrations produce weak absorptions in the 1250–800-cm⁻¹ region. Strong absorptions related to the C—H bands appear at 2936 and 2867 cm⁻¹, and a weaker one appears at 1462 cm⁻¹. The N—H and C=O absorptions are strong ones, characteristic of the amide function, and appear at 3298 and 1637 cm⁻¹; another strong N—H absorption can be seen at 1543 cm⁻¹, and a well-defined but weaker absorption occurs at 3063 cm⁻¹. The bands that have been most widely reported for polyimides¹⁷ are the imide absorptions near 1780 and 1720 (C=O stretch), 1380 (C—N stretch), and 720 cm⁻¹ (bending of C=O). As shown in Table II, the graft copolymer displayed absorptions characteristic of both nylon 6 and its polyimide.

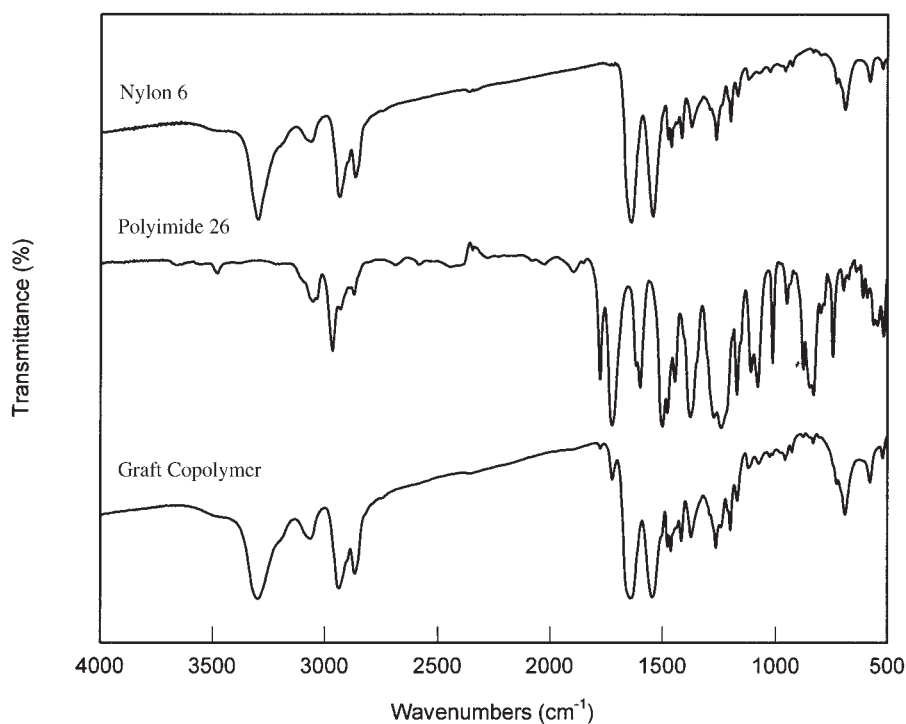


Figure 5 FTIR spectra of commercial nylon 6, polyimide 2b, and its graft copolymer.

TABLE III
Tensile Properties of the Graft Copolymers

Polyimide backbone	Polyimide content (wt %)	Concentration of the initiator (mol %) ^a	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
Nylon 6 (24K) ^b			542.0 ± 61.0	41.5 ± 2.0	240 ± 18
Nylon 6 (80K)			1100 ± 18.0	58.4 ± 2.5	84.3 ± 3.5
BAPP/BisA-DA	5	0.08	1775 ± 16.0	55.2 ± 1.1	66.1 ± 12
Ultem ^c	5	0.08	1704 ± 141	51.0 ± 1.2	102 ± 10
OTOL/BisA-DA	5	0.08	1783 ± 173	55.6 ± 2.5	58.3 ± 9.5
OTOL/BisA-DA	5	0.16	1817 ± 153	58.1 ± 2.9	52.4 ± 11
OTOL/BisA-DA	5	0.20	1928 ± 171	8.5 ± 0.70	49.2 ± 14

^a Initiator molar percentage = (mol of initiator/mol of caprolactam) × 100.

^b Obtained from Polyscience, Inc.

^c Obtained from General Electric Co.

Films of nylon 6 and the graft copolymers, which were cast from *m*-cresol solutions and then annealed at 160°C for 24 h, were used for tensile property tests. Table III summarizes the tensile properties of the graft copolymers. The introduction of 5 wt % polyimide in the nylon 6 matrices produced significant increases in the tensile modulus and tensile strength in comparison with those of low- and high-molecular-weight nylon 6. The tensile modulus was increased by 3.3–3.6 times over that of low-molecular-weight nylon 6. The elongations of the graft copolymers, however, were reduced to 20.5–42.5% in comparison with low-molecular-weight nylon 6. Increasing the concentration of the initiator from 0.08 to 0.20 mol % (based on caprolactam) in the **2a**/nylon 6 graft copolymer also resulted in increased modulus and decreased elongation.

Table IV summarizes the thermal properties of nylon 6 and the graft copolymers. T_g 's of the graft copolymers were about 5–7°C higher than T_g of pure nylon 6 samples. T_c 's of the graft copolymers were slightly higher than T_c of the pure nylon 6 samples. This implies that the polyimide segments hinder the crys-

tallization of the nylon 6 segments, presumably by restricting chain mobility. The decomposition temperatures increased by about 50°C upon the incorporation of 5 wt % polyimide in the graft copolymers (Table V).

CONCLUSIONS

Graft copolymers of nylon 6 and several polyimides were successfully prepared with nonfunctionalized polyimide. In this research, polyimides were used as latent macroactivators in the anionic polymerization of ϵ -caprolactam. In these polymerizations, a small amount of polyimide was dissolved in molten ϵ -caprolactam before the addition of PhMgBr. A model compound study with **1** indicated that under these conditions the caprolactam anion attacked the imide groups to generate *N*-acyllactam moieties, which activated the anionic polymerization of ϵ -caprolactam. However, at 120°C, there was a long induction period (1 h) before the polymerization of caprolactam. It is postulated that this was due to a high activation energy for the initial nucleophilic attack of caprolactam anion on the stable five-membered imide ring.

TABLE IV
DSC Analysis of the Graft Copolymers

Polyimide backbone	Polyimide content (wt %)	Concentration of the initiator (mol %) ^a	T_g (°C)	T_c (°C)	T_m (°C)	w^c (%) ^b
Nylon 6 (24K) ^c			41	66	219	27
Nylon 6 (80K)			43	68	218	23
BAPP/BisA-DA	5	0.08	48	70	217	23
Ultem ^d	5	0.08	48	70	217	23
OTOL/BisA-DA	5	0.08	46	69	214	21

Data were obtained on the second run after heating to 280°C in the first run and then quenching to –50°C with dry-ice/acetone.

^a Initiator molar percentage = (mol of initiator/mol of caprolactam) × 100.

^b Based on area under melting endotherm and heat of fusion (ΔH_m) of 26.0 kJ/mol for pure nylon 6.

^c Obtained from Polyscience, Inc.

^d Obtained from General Electric Co.

TABLE V
TGA of the Graft Copolymers

Polyimide backbone	Polyimide content (wt %)	Concentration of the initiator (mol %) ^a	T_{dec} (°C) ^b	T_{dec} Copolymer (°C)
Nylon 6 (24K) ^c				351
Nylon 6 (80K)				360
BAPP/BisA-DA	5	0.08	506	403
Ultem ^d	5	0.08	510	400
OTOL/BisA-DA	5	0.08	484	402

^a Initiator molar percentage = (mol of initiator/mol of caprolactam) × 100.

^b Temperature at which a 5% weight loss occurred when the sample was subjected to TGA in nitrogen at a heating rate of 10°C/min.

^c Obtained from Polyscience, Inc.

^d Obtained from General Electric Co.

More specifically, a series of polyimides, which had different structures, were prepared from BisA-DA and commercially available diamines with the one-step method in refluxing *m*-cresol. Graft copolymers with nylon 6 side chains and polyimide backbones were prepared by the anionic ring-opening polymerization of ϵ -caprolactam in the presence of the polyimides. In essence, the nylon 6 side chains were grown from the imide rings in the polyimide backbones, as the polyimides functioned as multifunctional activators in the ring-opening polymerization of ϵ -caprolactam. The introduction of 5 wt % polyimide into the nylon 6 matrices produced significant increases in the tensile modulus and tensile strength in comparison with those of low- and high-molecular-weight nylon 6. T_g 's of the graft copolymers were higher than T_g of pure nylon 6. The temperatures at which the graft copolymers lost 5% of their weight when subjected to TGA in N₂ were about 50°C higher than that of nylon 6. This is another indication that the polyimide hindered the chain mobility of nylon 6.

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