Preparation of Polyimide/Nylon 6 Graft Copolymers from Polyimides Containing Ester Moieties: Synthesis and Characterization

Youlee Pae

Cheil Industries Inc., 332-2, Gocheon-Dong, Uiwang-Si, Gyeonggi-Do, 437-711, South Korea

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ABSTRACT: Polyimide-*g*-nylon 6 copolymers were prepared by the polymerization of phenyl 3,5-diaminobenzoate with several diamines and dianhydrides with a one-step method. The polyimides containing pendant ester moieties were then used as activators for the anionic polymerization of molten ε-caprolactam. In the graft copolymer syntheses, the phenyl ester groups reacted quickly with caprolactam anions at 120°C to generate *N*-acyllactam moieties, which activated the anionic polymerization. The thermal stability and chemical resistance were dramatically increased by the incorporation of only 5 wt % polyimide in the graft copolymers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 309–318, 2006

Key words: copolymerization; nylon; polyimides

INTRODUCTION

During the last 20 years, many attempts have been made to achieve high modulus and high strength in flexible chain polymers via molecular reinforcement with rigid-rod polymers to form so-called molecular composites.[1–3] Such molecularly reinforced systems display enhanced tensile strengths, moduli, elongations, and heat resistance over conventional fiber-reinforced systems. Although the preparation of molecular composites via physical blending has now been extensively studied, phase separation due to the formation of rigid-rod-molecule aggregates in solution or during subsequent heating has seldom been avoided. One approach that has been proposed to solve this problem is to chemically bond the rigid-rod molecules to the random coil polymers in a block or graft copolymer. However, only a few examples of this approach have been reported.[4–6]

A project aimed at the preparation of chemically bonded polyimide/nylon 6 molecular composites was initiated in this laboratory several years ago.[7,8] However, the synthesis of the polyimide-*g*-nylon 6 copolymers required acylated caprolactam moieties that were difficult to prepare. The objective of this research was to investigate alternative synthetic routes to these materials. Polyimide/nylon 6 graft copolymers were to be prepared with latent activating groups, that is, phenyl ester groups. These groups were expected to react with ε-caprolactam anions to generate acylated caprolactam moieties. Thus, graft copolymers were to be prepared by the incorporation of a phenyl ester group in a diamine monomer, such as phenyl 3,5-diaminobenzoate (PDB or **IV**). PDB was to be copolymerized with several diamines and dianhydrides with a one-step method to afford polyimides containing pendant phenyl ester moieties. The polyimides were to be dissolved in molten ε-caprolactam and then treated with ε-caprolactam anions. The anions were expected to attack the ester groups to generate acylated caprolactam moieties, from which nylon 6 chains would grow. In essence, the polyimides were to function as polymeric activators for the anionic ring-opening polymerization of ε-caprolactam.

The expected advantages of using phenyl ester groups included their ease of preparation. The molecules containing these groups were also expected to be useable in a one-pot procedure, in which the graft copolymer precursors would be prepared in molten ε-caprolactam. The chemistry was also expected to be amenable to reaction-injection-molding technology. All the polyimide-*g*-nylon 6 copolymers prepared were to be characterized with respect to their thermal properties and chemical resistance.

EXPERIMENTAL

Materials

Aniline (Aldrich Chemical Co., St. Louis, MO) was distilled under reduced pressure. Benzoyl chloride

Correspondence to: Y. Pae (youleepae@empal.com).

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(Aldrich Chemical) was used as received. 1,3-Bis(4-aminophenoxy)-2,2-dimethylpropane (BADP) was obtained from this laboratory. 2,2′-Bis[4-(4-aminophenoxyl)phenyl]propane (BAPP; Chriskev Co., Leawood, KS) was recrystallized from *N,N*-dimethylformamide and methanol. 2,2′-Bis[4-(3,4-dicarboxyphenoxy)]propane dianhydride (BisA-DA; General Electric Co., Cincinnati, OH) was recrystallized from acetic anhydride (Ac_2O) and dried at 100°C under reduced pressure overnight. ε-Caprolactam (Aldrich Chemical) was distilled under reduced pressure. Celite (Aldrich Chemical) was used as received. 3,3′-Dimethyl-4,4′-diaminobiphenyl [*o*-tolidine (OTOL); Aldrich Chemical] was recrystallized from ethanol. 3,5-Dinitrobenzoyl chloride (98%; Aldrich Chemical) and isoquinoline (Aldrich Chemical) were used as received. Nylon 6 (Polyscience Co., Warrington, PA) was dried under reduced pressure at 100°C overnight. Palladium on activated carbon (Pd/C; Aldrich Chemical) was used as received. Phenol (Fisher Scientific Co., Pittsburgh, PA) was distilled under reduced pressure. *m*-Phenylenediamine (MPD; Aldrich Chemical) was recrystallized from ethanol and water. Phenylmagnesium bromide (PhMgBr; 3.0*M* solution in diethyl ether; Aldrich Chemical), phosphorus pentoxide (P_2O_5; Fisher Scientific), sodium bicarbonate ($NaHCO_3$; Aldrich Chemical), Ac_2O (Fisher Scientific), benzene (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. Ethanol (Quantum Chemical Co., Cincinnati, OH), *N,N*-dimethylacetamide (DMAc; Fisher Scientific), *N,N*-dimethylformamide (Fisher Scientific), dimethyl sulfoxide (DMSO; Fisher Scientific), formic acid (HCOOH; Fisher Scientific), methanol (Fisher Scientific), and methylene chloride (CH_2Cl_2; Fisher Scientific) were used as received. *N*-Methyl-2-pyrrolidinone (NMP; Aldrich Chemical) was distilled over P_2O_5 under reduced pressure. Pyridine (Fisher Scientific) and tetrahydrofuran (THF; Fisher Scientific) were used as received.

N-Benzoylcaprolactam (I)

To a 1-L, three-necked, round-bottom flask equipped with a condenser and a nitrogen inlet tube were added ε-caprolactam (113 g, 1.00 mol), pyridine (119 g, 1.50 mol), and 300 mL of benzene. After the ε-caprolactam was dissolved completely, benzoyl chloride (70.3 g, 0.50 mol) was added at the ambient temperature. A white pyridine salt formed immediately. The mixture was heated at reflux for 2 h and then allowed to cool to room temperature. After the pyridine salt was removed by filtration, the solution was reduced in volume with a rotary evaporator. The solution was then stored in a refrigerator. The white crystals that formed were collected by filtration and washed first with a 5% $NaHCO_3$ aqueous solution and then several times with distilled water to afford 65.2 g (60%) of a white powder.

mp: 69–70°C (lit.[9] 69°C). IR (KBr): 3066 (Ar), 2938, 2856 (CH_2), 1690, 1671 (C═O), 1390 cm^{-1} (C—N). ^{1}H-NMR ($CDCl_3$, δ): 7.5–7.2 (5H, Ar), 3.9 (2H, CH_2), 2.6 (2H, CH_2), 1.7 (4H, CH_2), 1.5 ppm (2H, CH_2).

Phenyl benzoate (II)

Phenol was treated with benzoyl chloride in the same manner described for **I** to afford an 80% yield of a white powder.

mp: 68–70°C (lit.[10] 69°C). IR (KBr): 1729 (ester C═O), 1262 cm^{-1} (C—O).

Phenyl 3,5-dinitrobenzoate (III)

Phenol was treated with 3,5-dinitrobenzoyl chloride in the same manner described for **I** to afford an 85% yield of a white powder.

mp: 148–149°C (lit.[11] 145.5–146°C). ^{1}H-NMR (DMSO-d_6, δ): 9.2–9.0 (3H, Ar), 7.6 (2H, Ar), 7.4 ppm (3H, Ar). ANAL. Calcd for $C_{13}H_8N_2O_6$: C, 54.18%; H, 2.80%. Found: C, 54.15%; H, 2.93%.

Phenyl 3,5-diaminobenzoate (PDB or IV)

A mixture of **III** (21.2 g, 7.36 mmol), 5% Pd/C (0.84 g), and 300 mL of absolute ethanol was shaken with hydrogen at 40 psi at room temperature for 12 h. The solution was filtered through Celite to remove the catalyst. The solution was then reduced in volume on a rotary evaporator. Several drops of water were added, and the solution was stored overnight at room temperature. The product that crystallized was collected by filtration to afford 12.4 g (74%) of brown needles.

mp: 95–96°C (lit.[12] 74–77°C). IR (KBr): 3474–3300 (N—H), 3058–3013 (Ar), 1720 (C═O), 1225, 1198 cm^{-1} (C—O). ^{1}H-NMR ($CDCL_3$, δ): 7.4 (2H, Ar), 7.2 (3H, Ar), 6.9 (2H, Ar), 6.2 (1H, Ar), 3.7 ppm (4H, NH_2). ANAL. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41%; H, 5.30%. Found: C, 68.31%; H, 5.20%.

General procedure for the preparation of substituted polyimides

To a 500-mL, three-necked, round-bottom flask equipped with a mechanical stirrer and a nitrogen inlet were added the diamine, PDB, a small amount of aniline (according to the target molecular weight and graft density), and 300 mL of NMP. After the diamine dissolved completely, the dianhydride was added (solid content = 20% w/w). The 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 that formed 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 polyimides containing ester moieties

To a 250-mL, three-necked, round-bottom flask equipped with a mechanical stirrer and an argon inlet were added the functionalized polyimide oligomers (2.37–7.94 g) and ε-caprolactam (45.0 g, 0.398 mol; solid content = 5–15% 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 3.0*M* solution of PhMgBr in diethyl ether was injected with vigorous stirring. A 20% molar excess of the desired amount of PhMgBr based on the amount of ester moieties was used (molar ratio of PhMgBr to ester moieties in polyimide = 2.4 : 1). The solution viscosity gradually increased, and solidification occurred within 5–10 min. 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.

Measurements

IR spectra were obtained with a Mattson Galaxy series Fourier transform infrared (FTIR) 5000 spectrophotometer with neat or film samples. ^{1}H-NMR spectra were measured at 200 MHz on a Varian Gemini-200 spectrometer. The melting temperatures (T_m's) were determined on a Mel-Temp melting-point apparatus. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN). Gel permeation chromatography (GPC) was carried out on a Waters 150-CV (Milford, MA) equipped with a refractive-index detector. THF was used as the elution solvent. The inherent viscosities of the polyimides were determined on 0.5 wt % NMP solutions with a Cannon-Ubbelohde no. 100 viscometer at 30.0 ± 0.1°C. The graft copolymer inherent viscosities were measured on 0.5 wt % *m*-cresol solutions with a Cannon-Ubbelohde no. 200 viscometer at 30.0 ± 0.1°C. Differential scanning calorimetry (DSC) analysis were performed with a DuPont model 2000 in nitrogen at a heating rate of 10°C/min. The sample was heated at 280°C for 3 min and then quenched in a dry-ice/acetone bath before the run on DSC. The degree of crystallinity (w^c) of the graft copolymer 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) data were obtained in nitrogen with a TA Hi-Res TGA 2950 thermogravimetric analyzer at a heating rate of 10°C/min. The degradation temperature was taken as the temperature at which the sample lost 5% of its original weight. 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 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.

RESULTS AND DISCUSSION

A study was carried out to find an activating group whose use would result in the fast polymerization of ε-caprolactam at 120°C and whose structure would be stable under the high-temperature conditions used in the one-step synthesis of aromatic polyimides. Earlier work in this laboratory showed that *N*-acyllactam activating groups undergo side reactions when present in the one-step polymerization of diamine and dianhydrides.[7,8] Thus, a less reactive, less expensive group was sought. This led to an investigation of phenyl ester groups.[14–16] These groups have been reported to function as latent activators; that is, they react with caprolactam anions to form *N*-acylcaprolactams, which activate lactam polymerization. It was postulated that if phenyl ester groups were attached to polyimide backbones, it would be possible to grow nylon 6 chains from these sites. The proposed mechanism for the preparation of graft copolymers is shown in Figure 1.

Model compound study

A model compound study with **II** was carried out to evaluate the ability of the phenyl ester group to activate the polymerization of ε-caprolactam (Fig. 2). The reaction of benzoyl chloride with phenol in benzene afforded model compound **II** in an 80% yield. The model compound was then dissolved in molten ε-caprolactam at 120°C. The anionic polymerization of ε-caprolactam occurred within 10 min after the addition of PhMgBr. The FTIR spectrum of the product was identical to that of a commercial nylon 6 sample (Fig. 3). No polymerization of ε-caprolactam occurred when the model compound was not added to the polymerization mixture.

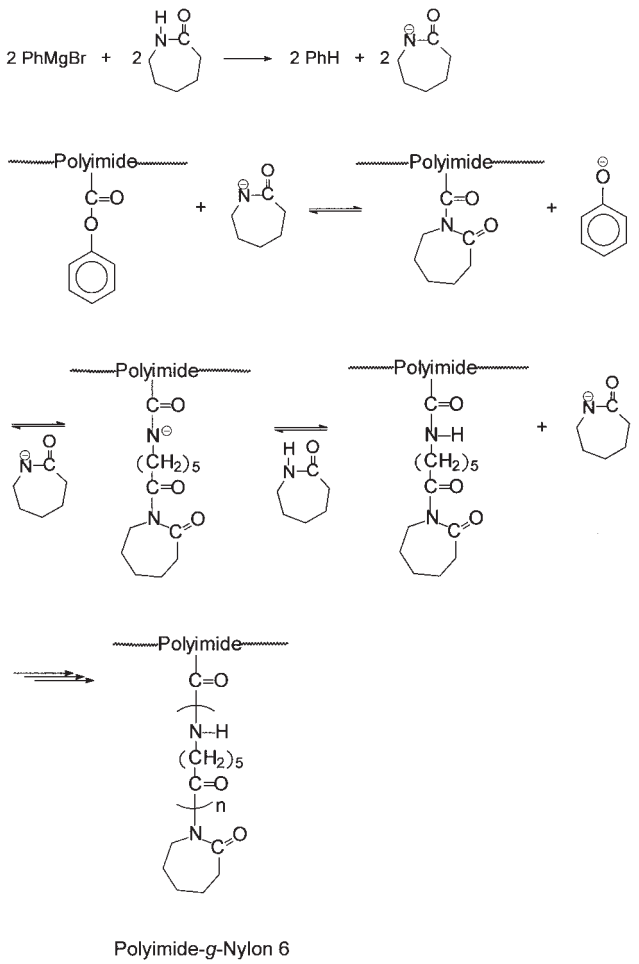


Figure 1 Mechanism for the preparation of graft copolymers.

Synthesis of functionalized amine

PDB was prepared via the route shown in Figure 4. This route began with the reaction of 3,5-dinitrobenzoyl chloride with phenol in an 85% yield. The hydrogenation of **III** was carried out in a Parr hydrogenator under 40 psi at room temperature to obtain PDB in a high yield.

Synthesis of functionalized polyimides

Polyimide oligomers containing pendant phenyl ester groups were prepared with the one-step method (Fig. 5) in NMP containing a catalytic amount of isoquinoline. Thus, diamine mixtures of BAPP, BADP, MPD, or OTOL with PDB were mixed with aniline and then polymerized with BisA-DA.

The ratios of the nonsubstituted to PDB were varied to vary the amount of pendant phenyl ester groups in the oligomer. Aniline was used to cap the anhydride end groups of the polyimide, which were present because excess dianhydride was used with respect to the amount of the diamines. The molecular weight of the oligomer was controlled by the variation of the molar ratio of the diamine to the dianhydride. A high-molecular-weight polyimide was also synthesized from a 1 : 1 ratio of a mixture of BAPP and PDB to BisA-DA. The solvent was heated at reflux so that the intermediate poly(amic acid)s spontaneously cyclized to imide oligomer. The imide oligomers and polymer were also subsequently heated at 260°C under reduced pressure to complete the imidization process. The GPC results and the physical properties of the functionalized polyimides are summarized in Table I.

Graft copolymerizations

The polyimides containing pendant phenyl ester groups were dissolved in molten ε-caprolactam at 140–150°C and stirred for 4–5 h to ensure homogeneity. The amount of imide added was varied from 5 to 15 wt %. After the mixtures were allowed to cool to 120°C, a solution of phenyl magnesium bromide (PhMgBr) in diethyl ether was injected to initiate the anionic ring-opening polymerization of ε-caprolactam (Fig. 6). After a few minutes at 120°C, the mixtures solidified, and this indicated that polymerization had taken place. The solid mixtures were maintained at 120°C for 5 h to ensure a complete reaction. They were then extracted with hot water or methanol to remove unreacted ε-caprolactam. Less than 4 wt % of the monomer was recovered (Table II). The polyimide-*g*-nylon 6 copolymers obtained were then successively extracted with $CHCl_3$ (a solvent for the polyimides) and with HCOOH (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

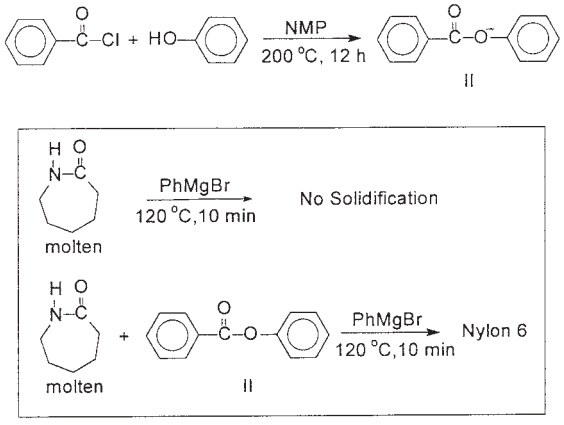


Figure 2 Model reaction (**II**/ε-caprolactam = 0.013 mol/mol; a 20% molar excess of the designated amount of PhMgBr was used).

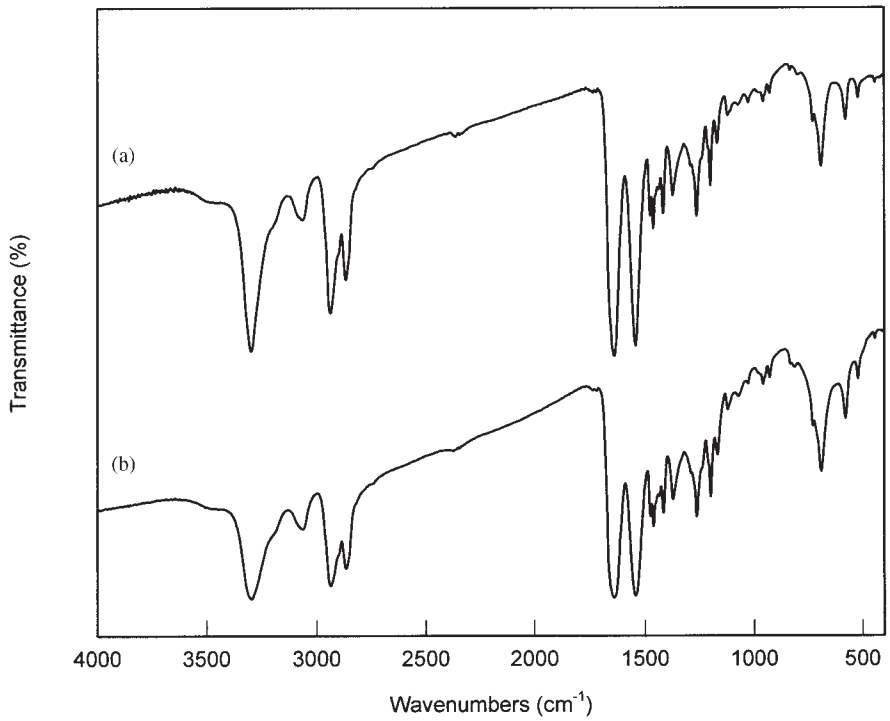


Figure 3 FTIR spectra of (a) commercial nylon 6 and (b) nylon 6 obtained with **II** as an activator.

no detectable amount of nylon 6 homopolymer was formed.

The copolymers that were prepared are summarized in Table II. The following is an explanation of the copolymer designations. A typical designation for a graft copolymer is G-BA-12K-20g-05. In this case, the letter G designates a graft copolymer. The next two letters, BA, refer to the diamine from which the prepolymer was made. The diamines BADP, MPD, and OTOL are designated by the letters BP, MP, and OT, respectively. All the prepolymers were prepared from PDB and BisA-DA in addition to the designated diamine. The next three digits, 12K, refer to the prepoly-

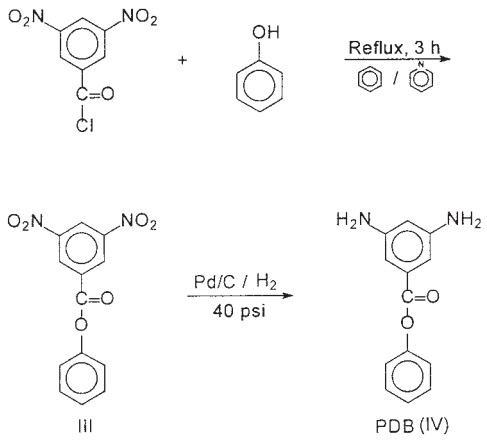


Figure 4 Preparation of PDB.

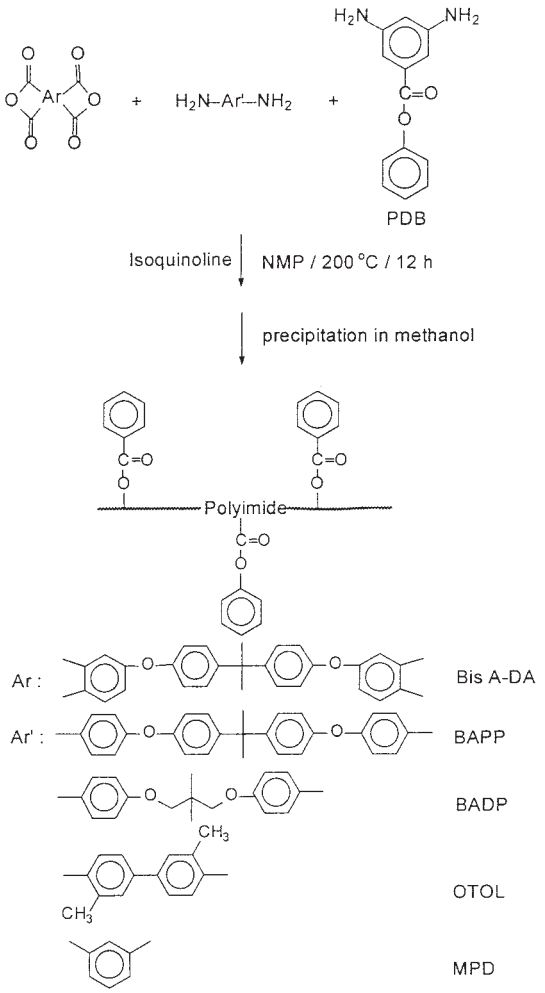


Figure 5 Preparation of functionalized polyimides.

TABLE I
GPC Analysis and Physical Properties of the Polyimides Containing Pendant Phenyl Ester Groups

Polyimide component: diamine/activator/ dianhydride	Molar ratio	Calculated M_n (g/mol)[a]	M_n (g/mol)[b]	M_w (g/mol)[b]	M_w/M_n[b]	T_g (°C)	η_{inh} (dL/g)[c]
BAPP/PDB/BisA-DA	83.7/9.3/100	12,000	7,910	20,900	2.64	190	0.36
BAPP/PDB/BisA-DA	74.5/18.6/100	12,000	7,910	21,900	2.77	191	0.35
BAPP/PDB/BisA-DA	65.3/28.0/100	12,000	8,620	22,800	2.65	194	0.36
BAPP/PDB/BisA-DA	46.8/46.8/100	12,000	8,810	23,100	2.62	198	0.35
BAPP/PDB/BisA-DA	77.2/19.3/100	24,000	12,200	29,400	2.88	196	0.42
BAPP/PDB/BisA-DA	80.0/20.0/100	Infinite	—	—	—	206	1.20
BADP/PDB/BisA-DA	75.1/18.8/100	12,000	9,070	17,800	1.96	186	0.36
MPD/PDB/BisA-DA	76.0/19.0/100	12,000	8,390	18,700	2.23	208	0.31
OTOL/PDB/BisA-DA	75.2/18.8/100	12,000	9,480	21,300	2.26	232	0.54

M_n = number-average molecular weight; M_w = weight-average molecular weight.
[a] Calculated M_n = molecular weights of the amine and anhydride units $(M_o)(1 + r)/(1 - r)$, where $r = \text{mol}^{\text{amine}}/\text{mol}^{\text{anhydride}}$.
[b] GPC was performed in THF at 25°C.
[c] Inherent viscosity for polyimides measured at 0.5 wt % in NMP at 30.0 ± 0.1°C.

mer calculated number-average molecular weight. The next three digits, 20g, refer to the molar percentage of PDB, that is, 20 mol %, in the diamine mixture used to prepare the prepolymer. In essence, they also designate the graft density as this is the molar percentage of the graft sites in the prepolymer backbone. The final two numbers, that is, 05, refer to the weight percentage of the prepolymer added to the ε-caprolactam during the graft copolymer preparation.

As can be seen in Table II, as the amount of the prepolymer added to ε-caprolactam was increased, the inherent viscosities of the resulting copolymer decreased. This is because the length of the nylon 6 segments decreased on account of the availability of more activator sites. The graft copolymers with graft densities from 10 to 30% had side chains with approximately the same molecular weights; thus, the inherent viscosity was relatively independent of the graft density. The inherent viscosity of G-BA-24K-20g-05 was slightly higher than that of G-BA-12K-20g-05, probably because of the increased molecular weight of nylon 6 segments.

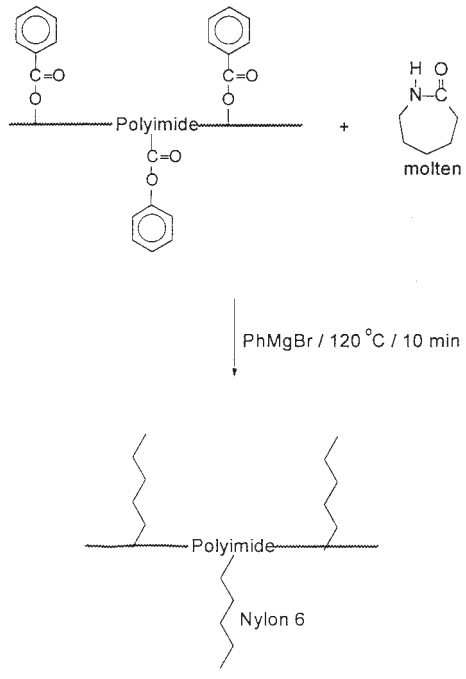


Figure 6 Preparation of graft copolymers.

Characterization of graft copolymers

The characteristic FTIR absorptions of commercial nylon 6, the graft copolymer G-BA-12K-20g-05, and its imide precursors are summarized in Table III. The graft copolymer G-BA-12K-20g-05 displayed characteristic absorptions of nylon 6 and its polyimide precursor. This is evidence that the polyimide segments are linked to nylon 6. Thus, the imide precursors displayed characteristic imide absorptions[17] near 1780 and 1720 (stretching, C═O), 1380 (C—N stretch), and 720 cm^{-1} (bending of C═O). Nylon 6 displayed absorptions near 3330 (N—H stretch vibration), 1650 (C═O), 2900 and 2770 (—CH_2— stretch vibration), and 1550 cm^{-1} (N—H deformation).[18] The FTIR spectra of nylon 6, the graft copolymer, and the graft copolymer imide precursor are shown in Figure 7. The carbonyl stretching bands near 1780 and 1720 cm^{-1}, characteristic of polyimides, are evident in the IR spectra of the graft copolymer G-BA-12K-20g-05.

Comparison of the polymerization times with different activators

Table IV shows the times required for different polymerization mixtures to solidify after the addition of

TABLE II
Polyimide-*g*-Nylon 6 Copolymers

Sample	Polyimide component	Calculated M_n[a]	Polyimide content (wt %)	Graft density (%)[b]	Yield (%)[c]	η_{inh} (dL/g)[d]
Nylon 6 (24K)[e]						1.35
Nylon 6 (80K)					97.5	2.64
Graft copolymer	Diamine/activator/dianhydride					
G-BA-12K-20g-05	BAPP/PDB/BisA-DA	12,000	5	20	97.3	3.73
G-BA-12K-20g-10	BAPP/PDB/BisA-DA	12,000	10	20	97.4	2.49
G-BA-12K-20g-15	BAPP/PDB/BisA-DA	12,000	15	20	98.6	2.36
G-BA-12K-10g-05	BAPP/PDB/BisA-DA	12,000	5	10	97.5	3.79
G-BA-12K-30g-05	BAPP/PDB/BisA-DA	12,000	5	30	96.9	4.29
G-BA-24K-20g-05	BAPP/PDB/BisA-DA	24,000	5	20	98.0	4.11
G-BA-1:1K-20g-05[f]	BAPP/PDB/BisA-DA	Infinite	5	20	97.9	—
G-BP-12K-20g-05	BADP/PDB/BisA-DA	12,000	5	20	98.9	3.94
G-MP-12K-20g-05	MPD/PDB/BisA-DA	12,000	5	20	96.6	2.68
G-OT-12K-20g-05	OTOL/PDB/BisA-DA	12,000	5	20	96.6	3.48

M_n = number-average molecular weight.
[a] Calculated $M_n = M_o(1 + r)/(1 - r)$, where r = $mol^{amine}/mol^{anhydride}$.
[b] Graft density-molar percentage of activating monomer (PDB) used to form the copolymer.
[c] Yield (%) = (Copolymer weight after caprolactam extraction/Copolymer weight before extraction) × 100.
[d] Inherent viscosity for copolymers measured at 0.5 wt % in *m*-cresol at 30.0 ± 0.1°C.
[e] Obtained from Polyscience, Inc.
[f] Graft copolymer was synthesized from polyimide with a 1 : 1 ratio of a mixture of BAPP and PDB to BisA-DA.

the initiator. The use of different activators, that is, **I**, **II**, and a polyimide prepared from an 80 : 20 molar mixture of BAPP and PDB and BisA-DA with a calculated number-average molecular weight of 12,000 g/mol, resulted in different rates of polymerization. With the same concentration of the activator and temperature (120°C), the time to solidification increased in the following order: **I** < **II** < substituted polyimide. However, the differences in the times were small. As the concentration of the activator increased in all three cases, the time to solidification decreased. As the polymerization temperatures were increased from 110 to 130°C, the time to solidification decreased.

Solubility of graft copolymers

Nylon 6 is only soluble in HCOOH, phenol, and *m*-cresol at room temperature or in aliphatic diols at an elevated temperature. The polyimides based on BisA-DA were soluble in $CHCl_3$, THF, CH_2Cl_2, and aprotic polar solvents such as NMP, DMAc, and DMSO. The graft copolymers were insoluble in most of the polyimide and nylon 6 solvents. The only common solvents for nylon 6, the polyimides, and the graft copolymers at room temperature were phenol and *m*-cresol (Table V). Aliphatic diols, such as 1,5-pentanediol and 1,6-hexanediol, were effective solvents for the copolymers above 160°C. Thus, the solvent resistance of the copolymers was higher than that of nylon 6 and the polyimides.

Thermal properties

Table VI shows the thermal properties of the graft copolymers determined with DSC. All the glass-transition temperatures (T_g's) of the graft copolymers were higher than that of the nylon 6 homopolymer. As the polyimide content increased in each series of copolymers, the magnitude of the increase became larger. It is speculated that the increase in T_g was due to con-

TABLE III
Characteristic FTIR Absorptions of Commercial Nylon 6, the Graft Copolymer G-BA-12K-20g-05, and the Graft Copolymer Precursors

Sample	Band (cm^{-1})						
	$\upsilon_{N—H}$	$\upsilon_{as,CH2}$	$\upsilon_{s,CH2}$	$\upsilon_{s,imide\ C=O}$	$\upsilon_{as,imide\ C=O}$	$\upsilon_{C=O}$	$\delta_{N—H}$
Nylon 6	3298	2936	2867			1637	1543
Substituted polyimide precursor				1777	1723		
Graft copolymer	3299	2937	2867	1775	1722	1642	1543

υ = stretching, δ = bending, s = symmetrical, as = asymmetrical.

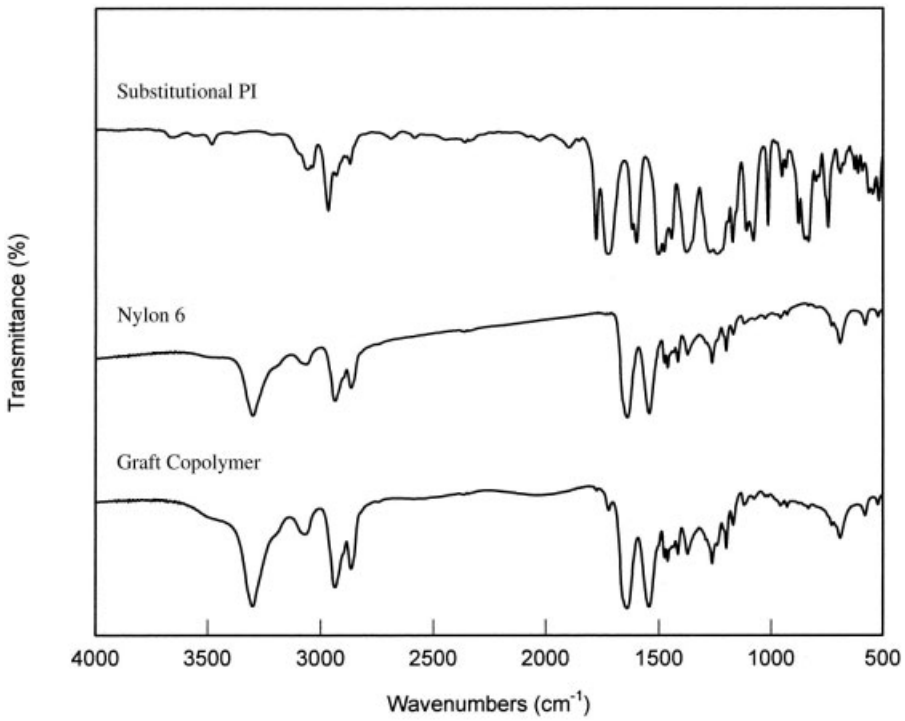
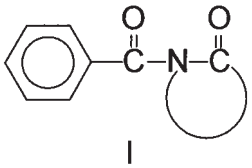
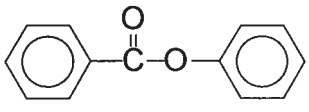
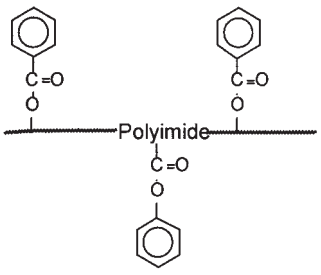


Figure 7 FTIR spectra of commercial nylon 6, graft copolymer G-BA-12K-20g-05, and graft copolymer imide precursors.

TABLE IV
Comparison of Polymerization Times with Different Activators

Activator	Polyamide Content (wt %)	Concentration of the activator (mol/mol of E-Caprolactam)	Reaction time (min)		
 I		0.0013		120°C	
		0.0025		8	
		0.0045		5	
				3	
 II		0.0013		120°C	
		0.0025		10	
		0.0045		7	
				4	
 Macroactivator[a]	5	0.0013	110°C	120°C	130°C
	10	0.0025	15	13	7
	15	0.0045	12	10	3
			10	5	<3

A 20% molar excess of the designated amount of PhMgBr was used in all cases.
[a] Poly(BAPP/PDB/BisA-DA) with a graft density of 20%; calculated M_n = 12,000 g/mol.

TABLE V
Solubility of the Graft Copolymers

Solvent	ε-Caprolactam	Substituted polyimides	Nylon 6	Graft copolymers
H_2O	+	−	−	−
Methanol	+	−	−	−
HCOOH	+	−	+	−
THF	+	+	−	−
$CHCl_3$	+	+	−	−
CH_2Cl_2	+	+	−	−
NMP	+	+	−	−
DMAc	+	+	−	−
DMSO	+	+	−	−
m-Cresol	+	+	+	+
Phenol	+	+	+	+

5 wt % solid was tested in each solvent at room temperature. The solubility test was performed at 40°C. + = soluble; − = insoluble.

strained chain mobility in the nylon 6 segment resulting from its chemical attachment to the rigid polyimide backbone. One T_g was observed for each sample. (T_c's) crystallization temperature of the graft copolymers were about 7–16°C higher than T_c of the pure nylon 6 sample (66°C). This implies that the polyimide segments hinder the crystallization of the nylon 6 segments, presumably by the restriction of chain mobility. T_m's of the graft copolymers were slightly lower than that of nylon 6.

The thermal decomposition behavior of the graft copolymers was evaluated with TGA in a nitrogen atmosphere. (Table VI). The decomposition temperatures were about 37–52°C higher than that of pure nylon 6 (24K) upon the incorporation of 5–15 wt % polyimide into the graft copolymers. Thus, the thermal stabilities of the graft copolymers were significantly better than that of commercial nylon 6, even with only 5 wt % polyimide incorporation. The decomposition temperatures rose gradually with increasing polyimide content in the graft copolymers.

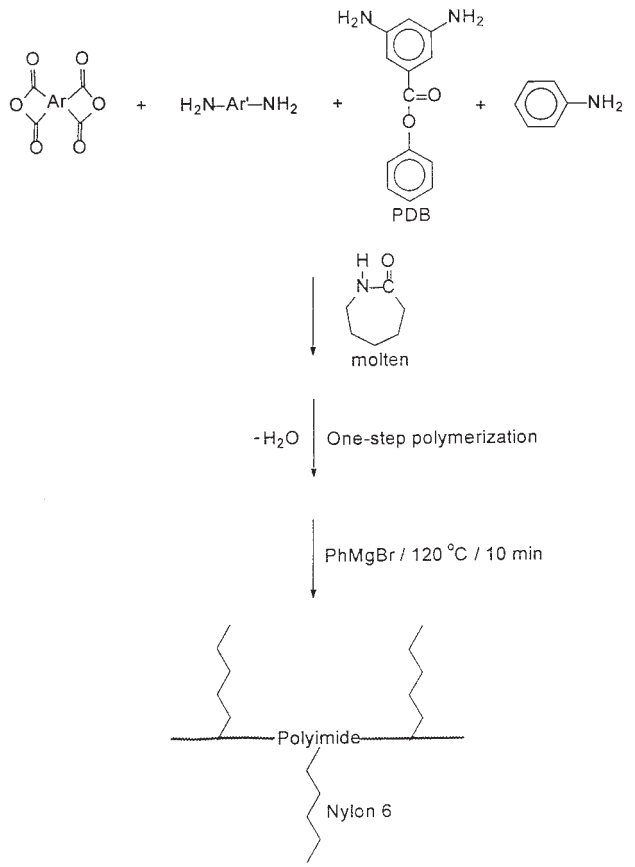


Figure 8 One-pot process for the preparation of graft copolymers.

TABLE VI
Thermal Properties of the Graft Copolymers

Polymer	T_g (°C)	T_c (°C)	T_m (°C)	w^{ca} (%)	Polyimide backbone T_{dec} (°C)[b]	Graft copolymer T_{dec} (°C)
Nylon 6 (24K)[c]	41	66	219	27		329
Nylon 6 (80K)	43	68	218	23		360
G-BA-12K-20g-05	46	75	216	24	493	367
G-BP-12K-20g-05	48	74	216	25	463	369
G-OT-12K-20g-05	48	74	215	22	468	366
G-BA-12K-20g-10	49	77	215	25	493	371
G-BA-12K-20g-15	50	82	214	25	493	381
G-BA-12K-10g-05	45	73	216	25		
G-BA-12K-30g-05	46	74	213	28		
G-BA-24K-20g-05	45	74	215	26		
G-BA-1:1K-20g-05	46	74	215	26		

Data were obtained from the second run after heating to 280°C in the first run and then quenching to −50 °C with dryice/acetone.

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

[b] Temperature at which a 5% weight loss occurred in N_2 with a heating rate of 10°C/min.

[c] Obtained from Polyscience, Inc.

TABLE VII
Comparison of the Tensile Properties of the Graft Copolymers Obtained by Different Processes

Polyimide backbone	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
Nylon 6 (24K)[a]	542.0 ± 61	41.5 ± 2.0	240 ± 18
Nylon 6 (80K)	1100 ± 18	58.4 ± 2.5	84.3 ± 3.5
G-BA-12K-20g-10	1393 ± 92	59.3 ± 1.2	224 ± 58
G-BA-12K-20g-10 made by the one-pot method	1408 ± 98	54.0 ± 6.5	212 ± 35

[a] Obtained from Polyscience, Inc.

One-pot polymerization

The key potential advantage of using the polyimide activators containing ester groups in the preparation of the desired copolymers is the possibility of a one-pot process. Such a one-pot process to make graft copolymers is outlined in Figure 8. In this process, ε-caprolactam is used in place of NMP in the preparation of the polyimide activator. Thus, polyimide oligomers containing pendant ester groups were prepared by the one-step method in ε-caprolactam containing a catalytic amount of isoquinoline. The solvent was heated at 290°C for 1 h so that the intermediate poly(amic acid)s spontaneously cyclized to imide oligomers. After the solution was allowed to cool to 120°C, PhMgBr was added to initiate the anionic polymerization of ε-caprolactam.

No appreciable differences in the tensile properties were observed between those of the copolymers obtained by the conventional two-step method and those obtained by the one-pot method (Table VII). Thus, the method of preparation of the graft copolymers had little or no effect on the tensile properties.

CONCLUSIONS

A series of new polyimide-*g*-nylon 6 copolymers was prepared with phenyl ester groups in the polyimides as activator sites. A model compound study with **II** indicated that the caprolactam anion attacked the phenyl ester to generate an *N*-acyllactam moiety, which activated the anionic polymerization of ε-caprolactam. At 120°C, solidification of the molten ε-caprolactam mixture occurred within 10 min, and this indicated that the attack on the phenyl ester groups and the subsequent polymerization proceeded very quickly. Graft copolymers were also prepared in a one-pot process, in which the polyimide containing pendant ester groups was prepared in molten ε-caprolactam. The ε-caprolactam, which had served as the polymerization solvent, was then polymerized by the addition of PhMgBr. Extraction studies of the graft copolymers showed that more than 96% of the ε-caprolactam reacted during the polymerization and that no detectable amount of nylon 6 homopolymer was formed. FTIR studies substantiated the successful incorporation of the nylon 6 segments into the graft copolymers. The graft copolymers exhibited improved chemical resistance over that of nylon 6. The decomposition temperatures of the graft copolymers were about 37–52°C higher than that of pure nylon 6.

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