

Structure and Properties of Polyimide-g-Nylon 6 and Nylon 6-*b*-Polyimide-*b*-Nylon 6 Copolymers

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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. Nylon 6-*b*-polyimide-*b*-nylon 6 copolymers were prepared by the use of phenyl 4-aminobenzoate as an end-capping agent in the preparation of a series of imide oligomers. The oligomers were then used to activate the anionic polymerization of ϵ -caprolactam. In both the graft and copolymer syntheses, the phenyl ester groups reacted quickly with caprolactam anions at 120°C to generate *N*-acyllactam moieties, which activated the anionic polymerization. All the block copolymers had higher moduli and tensile strengths than those of nylon 6. However, their

elongations at break were much lower. The graft copolymers based on 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride and 2,2'-bis[4-(4-aminophenoxy)phenyl]propane displayed elongations comparable to that of nylon 6 and the highest moduli and tensile strengths of all the copolymers. The thermal stability, moisture resistance, and impact strength were dramatically increased by the incorporation of only 5 wt % polyimide into both the graft and block copolymers. The graft and block copolymers also exhibited improved melt processability. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 300–308, 2006

Key words: graft copolymers; mechanical properties; nylon; polyimides

INTRODUCTION

The concept of a molecular composite was proposed in the early 1980s to improve the mechanical and physical properties of flexible chain polymers via molecular reinforcement.^{1–5} A molecular composite is now defined as being dispersions of a small amount of a reinforcing rigid-rod or extended-chain polymer in a random-coil polymer matrix. Such molecularly reinforced systems display enhanced tensile strengths, moduli, elongations, and heat resistance over conventional fiber-reinforced systems. Although molecular composites can be prepared via physical blending of the components, phase separation is often encountered during melt processing. This results from the limited compatibility between rigid-rod and random-coil polymers. A possible solution to 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.^{6–12}

Thus, the objective of this research was to develop a series of novel polyimide-*g*-nylon 6 and nylon 6-*b*-polyimide-*b*-nylon 6 copolymers and investigate

structural effects on the macroscopic properties for these systems. Polyimide/nylon 6 block and graft copolymers were 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. The effects of four structural parameters, that is, the polyimide content, graft density, polyimide backbone length, and polyimide backbone rigidity, on the mechanical properties of the graft copolymers were determined. All the polyimide-*g*-nylon 6 copolymers and the nylon 6-*b*-polyimide-*b*-nylon 6 copolymers prepared were characterized with respect to their thermal properties, moisture resistance, mechanical properties, toughness, and rheology.

EXPERIMENTAL

Preparation of graft and block copolymers

The method used to prepare polyimide/nylon 6 copolymers involved the use of phenyl ester groups as latent activators in the anionic polymerization of ϵ -caprolactam. In these polymerizations, a small amount of polyimide containing either pendant or terminal phenyl ester groups was dissolved in molten ϵ -caprolactam before the addition of phenylmagnesium bromide (PhMgBr). The detailed synthetic route has been reported elsewhere.^{13,14} In brief, graft copolymers

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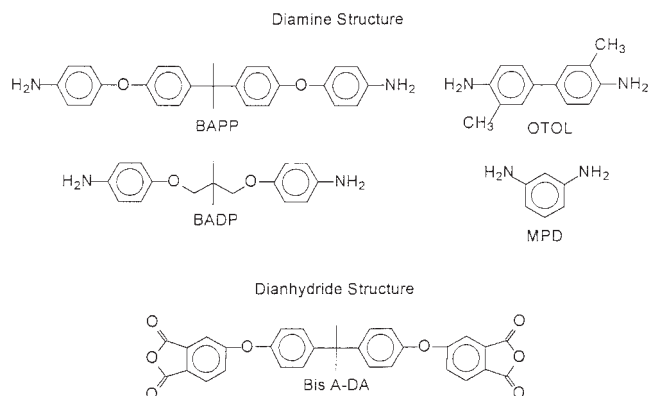


Figure 1 Diamine and dianhydride structure (MPD = *m*-phenylenediamine).

were prepared by the incorporation of a phenyl ester group into the diamine monomer phenyl 3,5-diaminobenzoate (PDB). PDB was polymerized with several diamines and dianhydrides with a one-step method in refluxing *N*-methyl-2-pyrrolidinone (NMP) to afford polyimides containing pendant ester moieties. Aniline was used to control the polyimide molecular weight. The number of incorporated pendant groups and the rigidity of the backbones were controlled by copolymerization with different diamines. The chemical structures of the diamines and dianhydrides used are shown in Figure 1. The polyimides were then used as multifunctional latent activators for the anionic ring-opening polymerization of molten ϵ -caprolactam (Fig. 2).

In the preparation of block copolymers, a phenyl ester moiety was incorporated into an aromatic monoamine, that is, phenyl 4-aminobenzoate (PAB). This compound was then used as an end-capping agent in the preparation of a series of imide oligomers. The end-capped oligomers were then used to activate the anionic polymerization of ϵ -caprolactam (Fig. 3). Extraction studies of the graft and block 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. The copolymers that were prepared are summarized in Table I.

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).¹⁵

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.

Mechanical properties

The tensile tests were conducted at the ambient temperature according to ASTM D 882. Thin films for

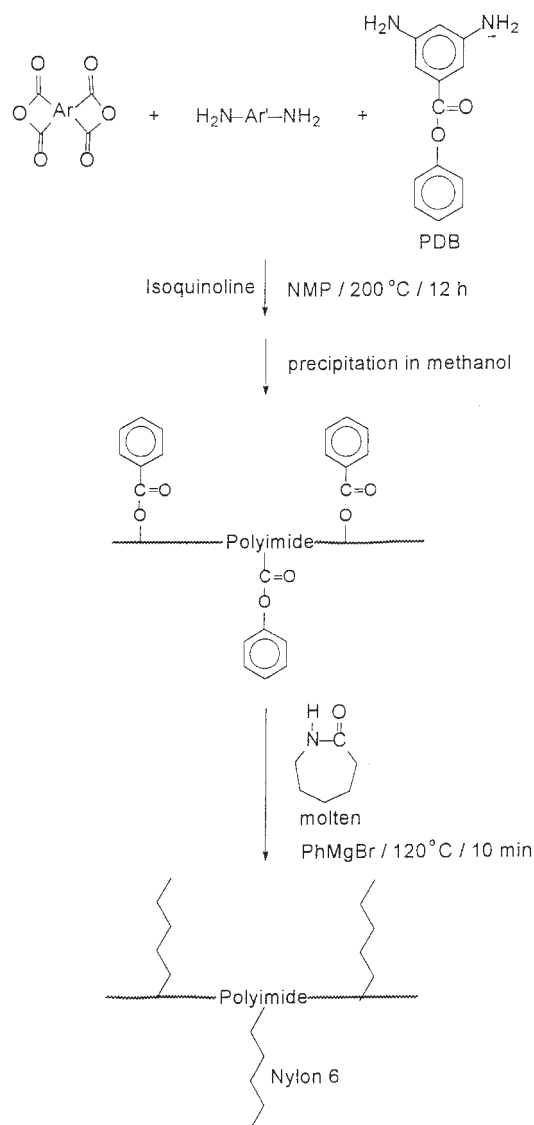


Figure 2 Preparation of graft copolymers.

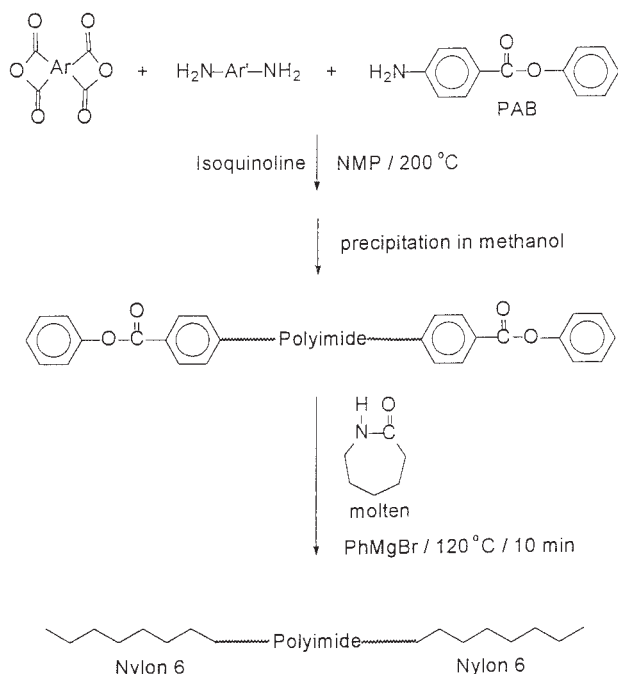


Figure 3 Preparation of block copolymers.

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 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.

Water absorption measurements

Water absorption measurements were conducted at the ambient temperature according to ASTM D 570. The sample dimensions were 76.2 mm × 25.4 mm × 3.2 mm (length × width × thickness). The samples were immersed in water, and their water absorption was determined by the measurement of their weight gain with time.

Rheological measurements

A Rheometrics model RMS-900 mechanical spectrometer was used for the rheological measurements. Circular samples were prepared with a radius of 12.5 mm and a thickness of 1.0 mm. Dynamic measurements were carried out with a parallel-plate mode. The gap between the parallel plates was 1 mm. All measurements were conducted with a strain of 4% (within the linear viscoelastic range) over a frequency range of 10⁻¹ to 10² rad/s under nitrogen. The storage modulus, loss modulus, and complex viscosity [$\eta^*(\omega)$] were calculated with the RMS-900 computer program.

TABLE I
Sample Information for the Graft and Block Copolymers

Sample	Polyimide Component	Calculated M_n^a	Polyimide content (wt %)	Graft density ^b (%)
Block copolymer	Diamine/Dianhydride			
B-Copoly-1	BAPP/BisA-DA	9,000	5	
B-Copoly-2	BAPP/BisA-DA	9,000	10	
B-Copoly-3	BAPP/BisA-DA	12,000	5	
B-Copoly-4	BAPP/BisA-DA	12,000	10	
B-Copoly-5	BAPP/BisA-DA	12,000	15	
B-Copoly-6	BAPP/BisA-DA	15,000	5	
B-Copoly-7	BAPP/BisA-DA	15,000	10	
B-Copoly-8	BADP/BisA-DA	12,000	5	
B-Copoly-9	OTOL/BisA-DA	12,000	5	
Graft copolymer	Diamine/Activator/Dianhydride			
G-Copoly-1	BAPP/PDB/BisA-DA	12,000	5	20
G-Copoly-2	BAPP/PDB/BisA-DA	12,000	10	20
G-Copoly-3	BAPP/PDB/BisA-DA	12,000	15	20
G-Copoly-4	BAPP/PDB/BisA-DA	12,000	25	20
G-Copoly-5	BAPP/PDB/BisA-DA	12,000	5	10
G-Copoly-6	BAPP/PDB/BisA-DA	12,000	5	30
G-Copoly-7	BAPP/PDB/BisA-DA	12,000	5	50
G-Copoly-8	BAPP/PDB/BisA-DA	24,000	5	20
G-Copoly-9	BAPP/PDB/BisA-DA	Infinite	5	20
G-Copoly-10	BADP/PDB/BisA-DA	12,000	5	20
G-Copoly-11	MPD/PDB/BisA-DA	12,000	5	20
G-Copoly-12	OTOL/PDB/BisA-DA	12,000	5	20

^a Calculated M_n = the molecular weights of the amine and anhydride units (M_0)(1 + r)/(1 - r), where r = mol^{amine}/mol^{anhydride}.

^b Graft density-molar percentage of activating monomer (PDB) used to form the copolymer.

TABLE II
Tensile Properties of the Block Copolymers

Polymer	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
Effect of polyimide content			
B-Copoly-3	1453 ± 15	74.1 ± 1.0	41.4 ± 9.5
B-Copoly-4	1471 ± 13	76.0 ± 1.4	33.6 ± 2.9
B-Copoly-5	1463 ± 20	74.3 ± 2.1	31.3 ± 7.2
Effect of polyimide chain length			
B-Copoly-2	1585 ± 19	66.3 ± 2.7	50.3 ± 7.4
B-Copoly-4	1471 ± 13	76.0 ± 1.4	33.6 ± 2.9
B-Copoly-7	1648 ± 20	65.5 ± 5.5	20.2 ± 4.2
Effect of polyimide structure			
B-Copoly-3	1453 ± 15.0	74.1 ± 1.0	41.4 ± 9.5
B-Copoly-8	1548 ± 117	56.5 ± 0.70	35.5 ± 15
B-Copoly-9	1296 ± 90.0	72.8 ± 2.1	30.5 ± 2.1

^a Obtained from Polyscience, Inc.

Izod impact tests

Izod impact tests were conducted on a mini-max impact tester (model CS-183TI, Custom Scientific, Inc.) at the ambient temperature according to ASTM D 256. At least five replicates of each sample were tested. The average impact strength was calculated by the division of the absorbed energy by the width of each specimen.

RESULTS AND DISCUSSION

Mechanical properties of block and graft copolymers

The mechanical properties of the block copolymers are shown in Table II. Very low elongations at break were observed for the block copolymers. In general, as the polyimide content, the polyimide chain length, and the rigidity of the imide segment increased, the elongation decreased. All the block copolymers tested had higher moduli and tensile strengths than nylon 6. However, because the elongation of the block copolymers was much lower than that of pure nylon 6, their toughness was less. The block copolymers with high polyimide contents were strong and hard in comparison with those containing only 5 wt % imide. As the calculated number-average molecular weight (M_n) was increased from 9000 to 15,000, the tensile strength and the modulus did not change very much, whereas the elongation decreased. The major effect of increasing the backbone rigidity was to decrease the elongation.

The effects of the polyimide content, graft density, polyimide chain length, and polyimide structure on the tensile properties of the graft copolymers are shown in Table III. The tensile strength and modulus increased and the elongation decreased slightly as the imide content was increased from 5 to 15 wt %. However, when

the imide content was increased from 15 to 25 wt %, there was a dramatic increase in the modulus and tensile strength and a large decrease in the elongation. The tensile strength was relatively independent of the graft density. The tensile modulus increased slightly as the graft density increased. The maximum elongation was displayed by the graft copolymer with a 20% graft density. As the graft density increased above this value, the elongation decreased. The tensile strength was relatively independent of the chain length. Although the modulus increased slightly as the imide molecular weight increased, the elongation dramatically decreased. It is speculated that this was due to an increase in phase separation. As the rigidity of the imide backbone increased, the tensile modulus and strength increased, whereas the elongation decreased.

Typical stress-strain curves for nylon 6, a block copolymer, and a graft copolymer are shown in Figure 4. The extensibility of nylon 6 was entirely lost in the block copolymers. On the other hand, the improvement in the ultimate elongation displayed by the graft copolymers was remarkable. The values of the elongation to break enable us to draw conclusions regarding the miscibility and degree of phase separation that exist in these two-component systems. It is well known that weak interfaces between phase-separated domains in polymer blends or copolymers allow for easy crack propagation and much lower ultimate elongations.^{6,7,16} The excellent retention of extensibility in the graft copolymers suggests that the imide and nylon phases are well mixed. The reduced elongations in the block copolymers, however, suggest that some phase separation has occurred. The difference between the two systems may be due to the difference in the number of chemical linkages between the two phases. There are many more such linkages in the graft copolymers.

TABLE III
Tensile Properties of the Graft Copolymers

Polymer	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
Nylon 6 (24K) ^a	542.0 ± 61.2	41.5 ± 2.0	240 ± 18
Nylon 6 (80K)	1100 ± 18.1	58.4 ± 2.5	84.3 ± 3.5
Effect of polyimide content			
G-Copoly-1	1355 ± 23.3	57.0 ± 2.6	234 ± 9.1
G-Copoly-2	1394 ± 92.4	59.3 ± 1.2	229 ± 8.0
G-Copoly-3	1409 ± 123	60.5 ± 2.1	224 ± 30
G-Copoly-4	1759 ± 70.0	80.7 ± 3.5	134 ± 7.6
Effect of graft density			
G-Copoly-5	1459 ± 31	65.0 ± 5.6	74.5 ± 14
G-Copoly-1	1355 ± 23	57.0 ± 2.6	234 ± 9.1
G-Copoly-6	1556 ± 40	63.0 ± 3.8	136 ± 11
G-Copoly-7	1580 ± 16	64.0 ± 4.5	40.3 ± 1.5
Effect of polyimide chain length			
G-Copoly-1	1355 ± 23	57.0 ± 2.6	234 ± 9.1
G-Copoly-8	1386 ± 32	59.6 ± 3.4	58.5 ± 3.5
G-Copoly-9	1456 ± 19	56.3 ± 1.7	20.0 ± 8.4
Effect of polyimide structure			
G-Copoly-10	1255 ± 30	54.0 ± 4.4	230 ± 52
G-Copoly-1	1355 ± 23	57.2 ± 2.6	234 ± 9.1
G-Copoly-12	1418 ± 62	61.0 ± 6.2	201 ± 8.4

^a Obtained from Polyscience, Inc.

Thermal properties

Table IV shows the thermal properties of the block and graft copolymers determined with DSC. All T_g 's of the graft and block copolymers were higher than

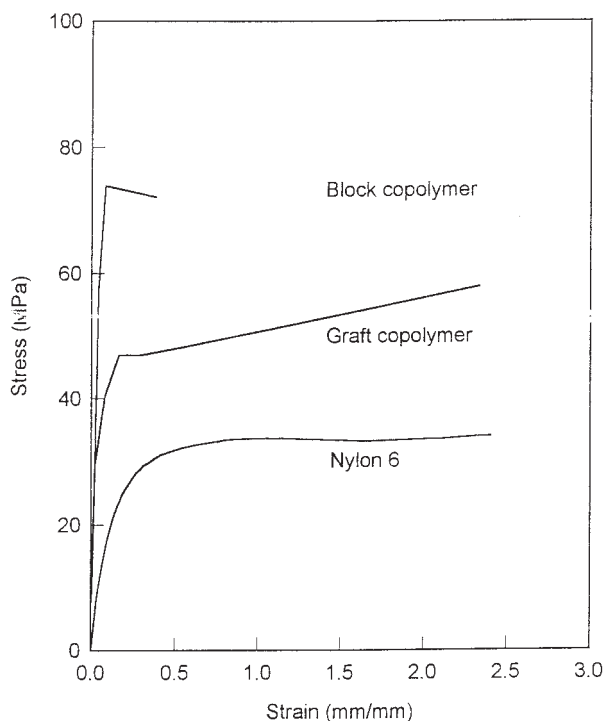


Figure 4 Typical stress-strain curves for nylon 6 (24K), a block copolymer (B-Copoly-3), and a graft copolymer (G-Copoly-1).

that of 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 constrained chain mobility in the nylon 6 segment resulting from its chemical attachment to the rigid polyimide backbone. The magnitude of the T_g increase also became larger as the rigidity of the polyimide backbone increased in both the graft and block copolymers. One T_g was observed for each sample. T_c 's of the graft and block copolymers were about 4–16°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 restriction of chain mobility. T_m 's of the block and graft copolymers were slightly lower than that of nylon 6. Typical DSC thermograms of pure nylon 6, graft copolymer G-Copoly-3, and block copolymer B-Copoly-5 are shown in Figure 5. The copolymers had similar polyimide segments with the same calculated M_n and the same polyimide loading levels. The graft polymer had a slightly higher T_g than the block copolymer.

The thermal decomposition behavior of the block and graft copolymers was evaluated with TGA in a nitrogen atmosphere. The decomposition temperature was taken as the temperature at which the polymers lost 5% of their weight when heated at 10°C/min (Table IV). The decomposition temperatures were about 36–56°C higher than that of pure nylon 6 (24K) upon the incorporation of 5–15 wt % polyimide into both the graft and block copolymers. Thus, the thermal stabilities of the copolymers were significantly

TABLE IV
Thermal Properties of the Block and Graft Copolymers

Polymer	T_g (°C)	T_c (°C)	T_m (°C)	w^c a (%)	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
B-Copoly-3	44	71	215	23	500	367
B-Copoly-4	44	72	214	24	500	384
B-Copoly-5	45	73	214	25	500	385
B-Copoly-8	43	70	215	26	467	365
B-Copoly-9	47	71	215	23	488	382
G-Copoly-1	46	75	216	24	493	367
G-Copoly-10	48	74	216	25	463	369
G-Copoly-12	48	74	215	22	468	366
G-Copoly-2	49	77	215	25	493	371
G-Copoly-3	50	82	214	25	493	381
G-Copoly-5	45	73	216	25		
G-Copoly-6	46	74	213	28		
G-Copoly-8	45	74	215	26		
G-Copoly-9	46	74	215	26		

^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 N₂ with a heating rate of 10°C/min.

^c Obtained from Polyscience, Inc.

better than that of commercial nylon 6, even with only 5 wt % polyimide incorporation. The decomposition temperatures rose gradually with increasing polyimide content in both the block and graft copolymers. No appreciable differences in the decomposition temperatures were observed between the block copolymers and the graft copolymers.

Izod impact strength

Izod impact strengths of the block and graft copolymers are shown in Table V. All the block and graft copolymers had higher impact strengths than the

corresponding nylon 6 homopolymers. The impact strength tended to be independent of the polyimide chain length in the block copolymers. As the polyimide content increased from 5 to 15 wt % in the graft copolymers, the Izod impact strength increased significantly. This can be attributed to an increase in the concentration of tie molecules between the crystalline blocks. The block and graft copolymers based on 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (BAPP)/2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BisA-DA; G-Copoly-1) and 1,3-bis(4-aminophenoxy)-2,2-dimethylpropane (BADP)/BisA-DA (G-Copoly-10), which were quite soluble in molten ϵ -caprolactam, displayed higher impact strengths than copolymers based on *o*-tolidine (OTOL)/BisA-DA (G-Copoly-12), which had a much lower solubility in the monomer. Unnotched specimens and notched specimens after water saturation could not be broken on the machine used.

Rheological properties

The melt viscosity behavior of a graft copolymer (G-Copoly-3) and linear nylon 6 with the same molecular weight at 280°C is shown in Figure 6. Because of the graft structure, the graft copolymer had a lower melt viscosity.

Curves of the melt viscosity versus the frequency (shear rate) for graft samples with different polyimide contents are shown in Figure 7. In addition to the graft copolymers, two nylon 6 samples have been included for comparison. Because the weight percentage of polyimide in the copolymer changed, the length of the

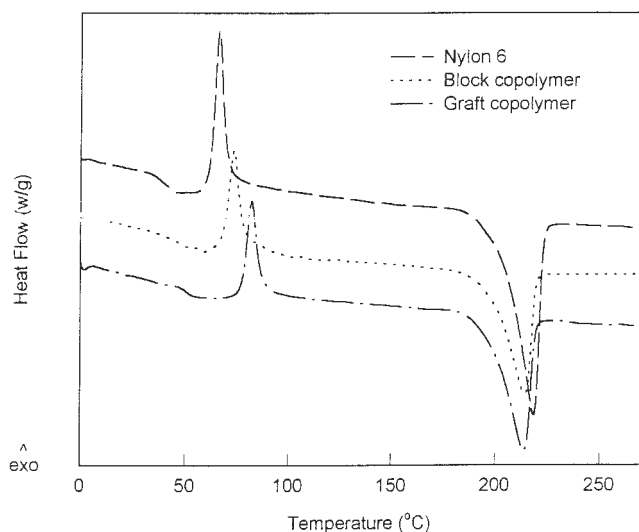


Figure 5 DSC thermograms of commercial nylon 6, block copolymer B-Copoly-5, and graft copolymer G-Copoly-3.

TABLE V
Izod Impact Strengths of the Block and Graft Copolymers

Polymer	Unnotched (J/m)	Notched (J/m)	Notched after water saturation (J/m)
Nylon 6 (24K) ^a	Not broken	41.4 ± 3.8	Not broken
Nylon 6 (80K)	Not broken	52.7 ± 12	Not broken
B-Copoly-1	Not broken	140 ± 22	Not broken
B-Copoly-3	Not broken	158 ± 10	Not broken
B-Copoly-6	Not broken	105 ± 13	Not broken
B-Copoly-8	Not broken	163 ± 33	Not broken
B-Copoly-9	Not broken	124 ± 9.2	Not broken
G-Copoly-1	Not broken	153 ± 12	Not broken
G-Copoly-2	Not broken	191 ± 13	Not broken
G-Copoly-3	Not broken	204 ± 28	Not broken
G-Copoly-10	Not broken	165 ± 2.6	Not broken
G-Copoly-11	Not broken	120 ± 16	Not broken
G-Copoly-12	Not broken	90.6 ± 0.50	Not broken

^a Obtained from Polyscience, Inc.

nylon 6 chains must also have changed; that is, as the polyimide content increased, the length of the nylon 6 chains decreased. As can be seen from the graphs, the molecular weight of the copolymers had a large effect on the melt viscosity at low frequencies. With decreasing molecular weight, the zero-shear viscosity decreased, but at a shear rate of 10^2 rad/s, the viscosity appeared to be relatively independent of the molecular weight because all the copolymers had similar

viscosities. Thus, it appears that at high frequencies the entanglements were broken to such an extent that the molecular weight dependence of the shear viscosity was lost.

The effect of the polyimide backbone rigidity on the melt viscosities of the graft copolymers at 280°C is shown in Figure 8. As the rigidity of the polyimide backbone increased, the melt viscosity also increased. The graft copolymers G-Copoly-11 and G-Copoly-12, which had more rigid backbones than G-Copoly-1 and

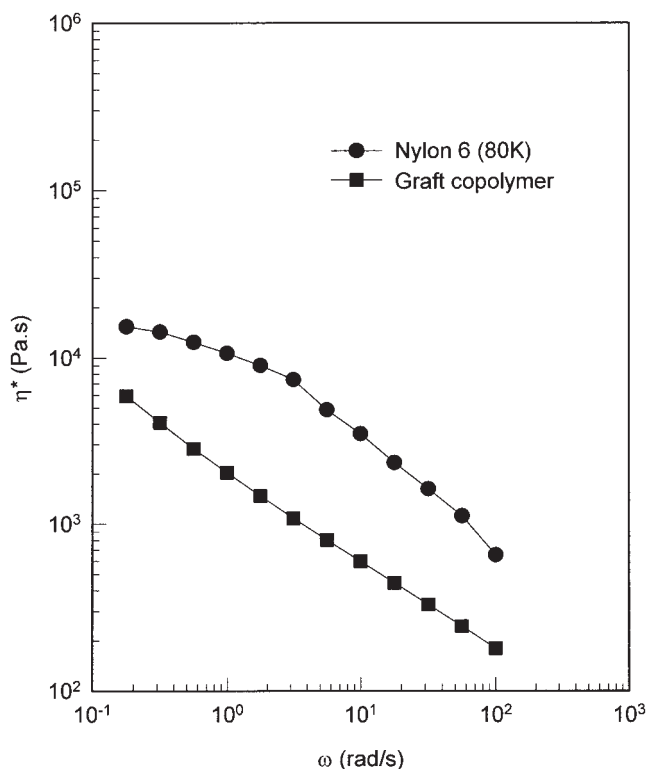


Figure 6 Comparison of the melt viscosities of a graft copolymer (G-Copoly-3) and linear nylon 6 (80K) with the same molecular weight at 280°C (ω = frequency).

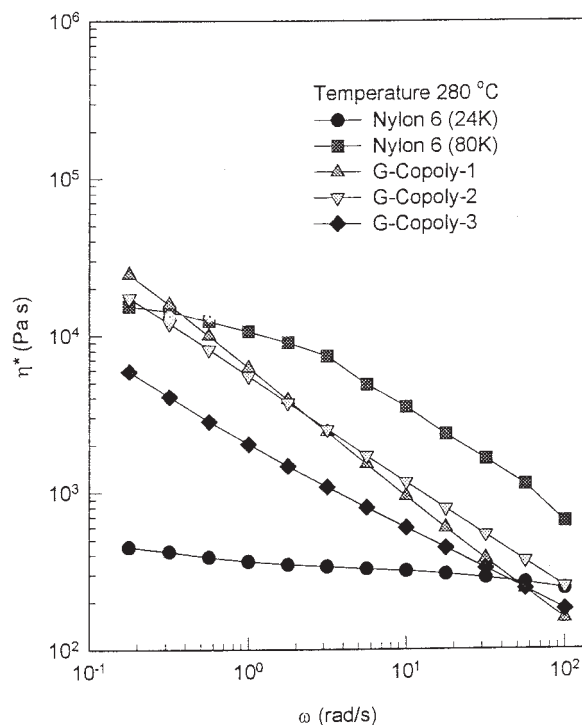


Figure 7 Comparison of the melt viscosities of graft copolymers with different polyimide contents at 280°C (ω = frequency).

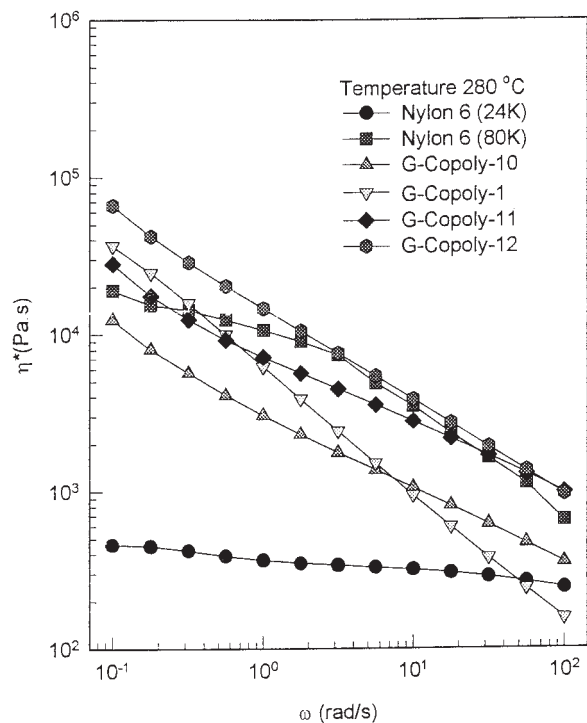


Figure 8 Effect of the polyimide backbone on the melt viscosities of graft copolymers at 280°C (ω = frequency).

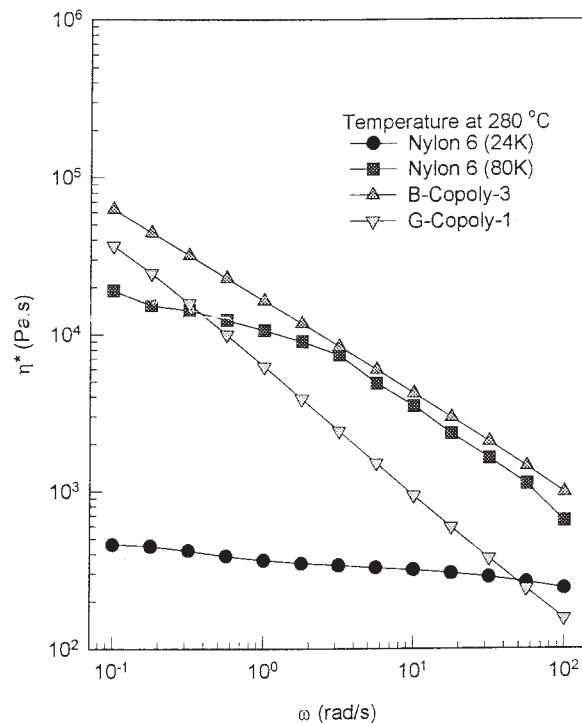


Figure 9 Effect of the molecular architecture on the melt viscosities of copolymers at 280°C (ω = frequency).

G-Copoly-10 on the basis of the T_g values of the polyimides, displayed higher melt viscosities over the entire shear rate range. Shear-thinning behavior was clearly observed for all the graft copolymers. As the polyimide backbone flexibility increased, the onset of the shear rate dependence shifted progressively to lower rates of shear, and the shear-thinning behavior became more marked.

The effect of the molecular architecture on the melt viscosities of the copolymers is shown in Figure 9. The block copolymer B-Copoly-3 and the graft copolymer G-Copoly-1 contained the same polyimide backbone with the same calculated molecular weight. The graft copolymer displayed a lower melt viscosity over the entire range of frequencies. The graft copolymer also showed a much greater degree of shear thinning.

Water absorption

Because of the hydrophobic nature of polyimides, the moisture resistance of the copolymers was expected to be better than that of pure nylon 6. To test this hypothesis, the water absorptions of three graft copolymers with different polyimide contents and a block copolymer were determined as a function of time (Figs. 10 and 11). All the graft copolymers, that is, G-Copoly-1, G-Copoly-2, and G-Copoly-3, had lower moisture absorptions than that of nylon 6 after 1000 h of immersion in water at room temperature (Fig. 10).

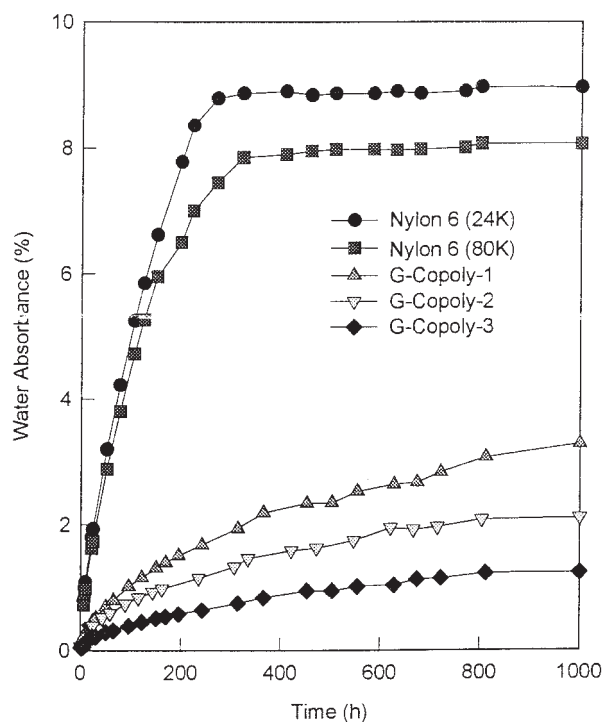


Figure 10 Water absorbance of graft copolymers G-Copoly-1, G-Copoly-2, and G-Copoly-3 at room temperature.

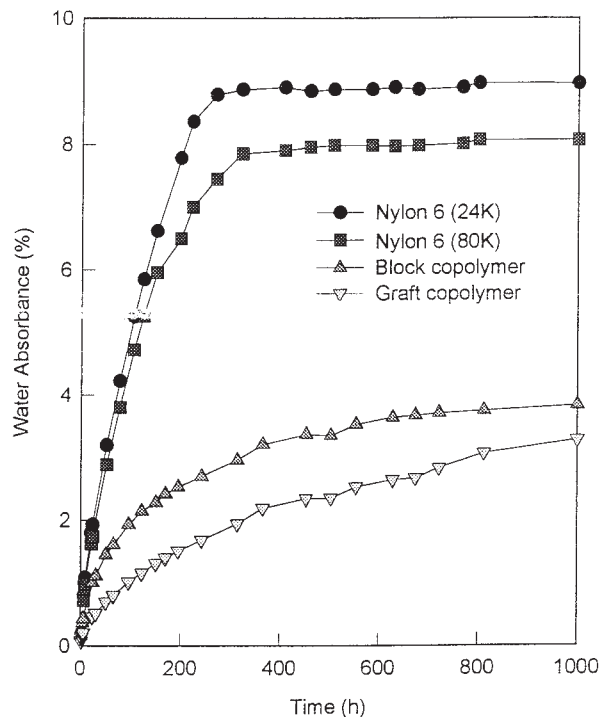


Figure 11 Water absorbance of block copolymer B-Copoly-3 and graft copolymer G-Copoly-1 at room temperature.

The copolymer water absorption rate decreased with increasing polyimide content.

The water absorption of the graft copolymer, G-Copoly-1, was lower than that of the analogous block copolymer, B-Copoly-3 (Fig. 11). Thus, it is postulated that the graft copolymers would display greater dimensional stability.

CONCLUSIONS

All the block copolymers displayed higher moduli and tensile strengths than those of nylon 6; however, the elongations at break were much lower than that of pure nylon 6, and this resulted in less toughness. The graft copolymers also had higher moduli and tensile strengths. The graft copolymers based on BAPP and BisA-DA displayed the highest moduli, tensile strengths, and elongations. The graft copolymers had

slightly higher T_g 's than the block copolymers. The higher T_g 's of the graft copolymer may indicate that the polyimide and nylon 6 were more miscible than in the block copolymers. The decomposition temperatures of the graft and block copolymers were about 36–59°C higher than that of pure nylon 6. The decomposition temperatures rose gradually with increasing polyimide content in both the block and graft copolymers. Both the block and graft copolymers had much higher impact strengths than nylon 6. This was probably due to polyimide tie molecules located between nylon 6 crystalline blocks. The graft copolymers had lower melt viscosities than nylon 6 samples with the same molecular weight. The graft copolymers also displayed a lower melt viscosity than the block copolymer. The graft copolymers had lower moisture absorption than nylon 6. Because of the hydrophobic nature of the polyimides, the initial water absorption rate decreased with increasing polyimide content. The graft copolymers had lower water absorption than the block copolymers.

References

1. Helminiak, T. E. *Am Chem Soc Div Org Coat Plast Chem Prepr* 1979, 40, 475.
2. Hwang, W. F.; Wiff, D. R.; Benner, C. L.; Helminiak, T. E. *J Macromol Sci Phys* 1983, 22, 231.
3. Kumamaru, F.; Oono, T.; Kajiuama, T.; Suehiro, K.; Takayanagi, M. *Polym Compos* 1983, 4, 135.
4. Kumamaru, F.; Oono, T.; Kajiuama, T.; Suehiro, K.; Takayanagi, M. *Polym Compos* 1983, 4, 141.
5. Oishi, Y.; Itoya, K.; Kakimoto, M.; Imai, Y. *Polym J* 1989, 21, 771.
6. Takayanagi, M.; Ogata, T.; Morikawa, M.; Kai, T. *J Macromol Sci Phys* 1980, 17, 591.
7. Krause, S. J.; Haddock, T. B.; Price, G. E.; Adams, W. W. *Polymer* 1988, 29, 195.
8. Moore, D. R.; Mathias, L. J. *J Appl Polym* 1986, 32, 6299.
9. Dotrong, M.; Dotrong, M. H.; Evers, R. C. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1992, 33, 477.
10. Ding, H. Ph.D. Dissertation, University of Akron, 1994.
11. Lin, F. Ph.D. Dissertation, University of Akron, 1995.
12. Lee, Y. Ph.D. Dissertation, University of Akron, 1996.
13. Pae, Y.; Harris, F. W. *J Polym Sci Part A: Polym Chem* 2000, 38, 4247.
14. Pae, Y. *J Appl Polym Sci*, submitted.
15. Wundrich, B. *Macromolecular Physics*; Academic: New York, 1973; Vol. 2.
16. Tsai, T. T.; Arnold, F. E.; Hwang, W. F. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1985, 26, 144.