

Liquid Crystal Polymers. III. Preparation and Properties of Poly(ester Amides) from *p*-Aminobenzoic Acid and Poly(ethylene Terephthalate)

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Synopsis

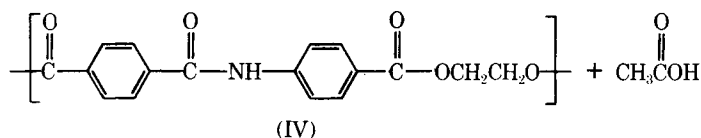
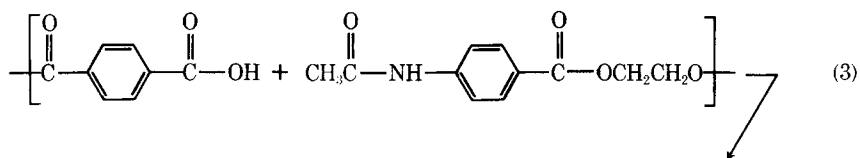
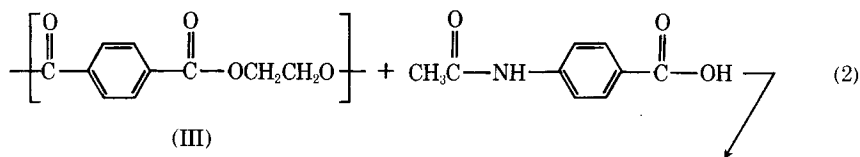
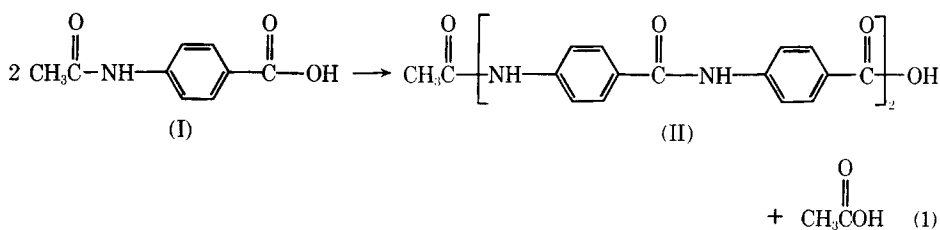
Poly(ester amides) with physical properties similar to those of liquid crystalline polyesters were prepared by acidolysis of poly(ethylene terephthalate) with *p*-acetamidobenzoic acid and then polycondensation through the acetamido and carboxyl groups. The ester amide polymers had a random sequence distribution, contained some branching, and at low frequencies had relaxation times appreciably longer than those of poly(ethylene terephthalate). Because of the extended chain orientation of the polymer segments that contained *p*-aminobenzoic acid (PAB) units, the mechanical properties of injection-molded polymers containing 20–30 mole % PAB were anisotropic. The liquid crystalline characteristics and mechanical properties were further increased by incorporating *p*-hydroxybenzoic acid units into the polymers.

INTRODUCTION

The first article¹ in this series described the preparation and properties of *p*-hydroxybenzoic acid (PHB) copolyesters obtained by the reaction of *p*-acetoxybenzoic acid with poly(ethylene terephthalate) (PET). The mechanical properties of the injection-molded copolyesters with 40–90 mole % PHB were highly anisotropic and dependent upon a number of variables. In general, these compositions were characterized by very high tensile strength, stiffness, and Izod impact strength, as measured in the direction of flow of the polymer melt, and the coefficient of thermal expansion was either very low or, usually, zero. The second article² in this series presented data showing that these unusual properties are due to the liquid crystalline nature of the polymer melts.

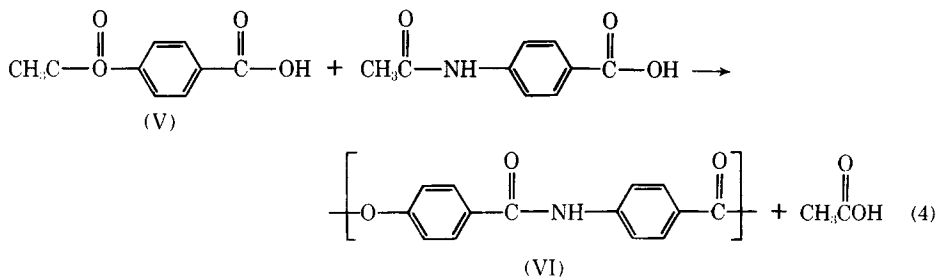
Since it was thought that poly(ester amides) with properties of interest might be obtained by a reaction similar to that used in preparing the liquid crystalline copolyesters, the reaction of *p*-acetamidobenzoic acid with PET was studied. *p*-Acetamidobenzoic acid (I) reacts with itself to form polyamide blocks [eq. (1)] and also with PET (III) to give short acetamido-terminated and carboxy-terminated segments [eq. (2)] that can be condensed by being heated under reduced

pressure to give a high-molecular-weight poly(ester amide) [eq. (3)]:



The final poly(ester amides), disclosed in our recent patent,³ then contain segments II and IV in addition to PET segments (III).

During this investigation, poly(ester amides) were also prepared by the reaction of *p*-acetoxybenzoic acid, *p*-acetamidobenzoic acid, and PET. The *p*-acetoxybenzoic acid (V) can react with itself and with PET, as described in our earlier article,¹ and also with *p*-acetamidobenzoic acid to give segment VI [eq. (4)]:



Because of the presence of PET segments, these poly(ester amides) melted at sufficiently low temperatures to be melt processable. Poly(ester amides) prepared in a Schotten-Baumann reaction from various ratios of the acid chlorides of PHB and *p*-aminobenzoic acid (PAB) (to give segment VI) have been reported,⁴ but because of their very high melting points, these polymers cannot be melt processed. These polymers are reported to be soluble in hot, concen-

trated sulfuric acid, however. Poly(ester amides) also have been prepared from the acid chlorides of PAB and substituted PHBs in 2,4-dimethyltetramethylene sulfone.⁵ These polymers can be dissolved in appropriate solvents and spun into fibers.

The homopolyamide of PAB has been spun into high-tenacity, high-modulus fibers from liquid crystalline solutions in solvents such as hydrofluoric acid, *N,N*-dimethylacetamide-lithium chloride, and tetramethylurealithium chloride.^{6,7}

EXPERIMENTAL

Materials

PET with an inherent viscosity (IV) of 0.56 was prepared conventionally from dimethyl terephthalate and ethylene glycol with zinc acetate (65 ppm zinc) and antimony triacetate (230 ppm antimony) catalysts.

p-Acetamidobenzoic acid and *p*-acetoxybenzoic acid were prepared by conventional acetylations of PAB and PHB with acetic anhydride (sulfuric acid catalyst). The *p*-acetamidobenzoic acid melted at 255–256°C after recrystallization from dimethyl formamide, and the *p*-acetoxybenzoic acid melted at 189–191°C after recrystallization from *n*-butyl acetate.

Methods

Inherent viscosities were measured at 25°C in 60/40 (by volume) phenol/tetrachloroethane at a polymer concentration of 0.50 g/100 ml.

A differential scanning calorimeter (Perkin-Elmer DSC-2) was used for determining melting points (first cycle) and glass transition temperatures (second cycle).

Carbon-13 NMR spectra were determined on trifluoroacetic acid solutions of the polyesters with a Bruker HX90-E spectrometer. Proton spectra were determined with a Perkin-Elmer R-32 90-MHz spectrometer, and proton wide-line NMR spectra of the solid and molten polymer were collected on a Bruker model SXP spectrometer at 90 MHz by a pulsed, fast-Fourier-transform technique. Polystyrene equivalent molecular weights were determined in *m*-cresol at 100°C with a Waters Associates model 200 gel permeation chromatograph. Relaxation times were determined with a Rheometrics mechanical spectrometer model RMS-7200 by use of the eccentric rotating disk mode. Melt viscosities were determined with a Sieglaff-McKelvey rheometer.

The polymers were injection molded into unheated molds in a 1-oz Watson-Stillman injection-molding machine to produce $2\frac{1}{2} \times \frac{3}{8} \times \frac{1}{16}$ -in. bars for tensile measurements and $5 \times \frac{1}{2} \times \frac{1}{8}$ -in. bars for determination of hardness, flexural properties, Izod impact strength, and heat-deflection temperature. ASTM procedures were used for measuring tensile strength and elongation at break (ASTM D1708), flexural modulus and flexural strength (ASTM D790), Izod impact strength (ASTM D256 Method A), Rockwell hardness (ASTM D785 Method A), heat-deflection temperature (determined at 264 psi, ASTM D648), mold shrinkage (ASTM D955), and coefficient of linear thermal expansion (ASTM D696). The oxygen index of $\frac{1}{8}$ -in. bars was determined with a GE flammability index tester, model FL 101.

Polymer Preparation

Poly(ester Amides) from p-Acetamidobenzoic Acid and Poly(ethylene Terephthalate)

These polymers were prepared by the procedure described in our earlier article for copolyesters¹ but by using *p*-acetamidobenzoic acid instead of *p*-acetoxybenzoic acid. At the 275 °C reaction temperature, poly(ester amides) prepared with 10–30 mole % *p*-acetamidobenzoic acid had fairly high melt viscosities, and IVs were about 0.4. Solid-state polymerization of particles ground to pass a 20-mesh screen and then heated under reduced pressure (0.1 mm) at 180°C for 1 hr, 220°C for 3 hr, and 230°C for 10 hr gave IVs of 0.56–0.67. The polymers were yellow–brown.

Poly(ester amides) prepared with 35 mole % or more of *p*-acetamidobenzoic acid solidified in the reaction flask because of their high melting points. Solid-state polymerization gave polymers that were insoluble in the phenol-tetrachloroethane IV solvent.

Poly(ester Amides) from p-Acetamidobenzoic Acid, p-Acetoxybenzoic Acid, and Poly(Ethylene Terephthalate)

These copolymers were prepared in the same manner as the preceding poly(ester amides) but with the addition also of *p*-acetoxybenzoic acid. Useful IVs were obtained on melt polymerization at 280–290°C with 10 mole % *p*-acetamidobenzoic acid and 50–60 mole % *p*-acetoxybenzoic acid. Other polymers had low IVs after melt polymerization. (Solidification owing to high melting points was a problem with many compositions.) When the PAB content was 10–30 mole %, the polymer molecular weights were increased by solid-state polymerization at temperatures up to 280°C, depending upon the polymer melting points. The polymers were yellow.

RESULTS AND DISCUSSION

Polymer Preparation

Preparation of the poly(ester amides) involved a two-step process: (1) cleavage of poly(ethylene terephthalate) by acidolysis with *p*-acetamidobenzoic acid [eq. (2)] and with *p*-acetoxybenzoic acid, if also present, and (2) condensation under vacuum of the carboxy-terminated and acetyl-terminated segments (including the self-condensation of *p*-acetamidobenzoic acid and, if present, *p*-acetoxybenzoic acid). Precautions were taken to eliminate all air and moisture from the reactants just before polymerization by evacuating and purging the flask containing the ingredients several times with nitrogen and then heating at 100°C and 0.5 mm for 30 min.

Poly(ester amides) containing no PHB component all had low IVs after melt polymerization. These low IVs were due to (1) solidification of the polymers because they had high melting points when the higher amounts (35 mole % or more) of the PAB component were present, or (2) the presence of unreactive ethylene acetate end groups, $-\text{CH}_2\text{CH}_2\text{OAc}$, when the lower amounts (10–30 mole %) of the PAB component were present. The ethylene acetate groups,

observed on NMR spectra (peak at 2.25 ppm), presumably resulted from acidolysis of PET by the acetic acid. Ethylene acetate end groups are generally not a problem when the PET component is limited to 50 mole % or less by the presence of PAB and PHB components. Thus high IVs can be attained on melt polymerization at 275–300°C if a high polymer melting point does not cause solidification of the poly(ester amide). If solidification occurred or if ethylene acetate groups limited melt polymerization, high-molecular-weight polymers (indicated by tough, creasable pressed films) were obtained by solid-state polymerization when the PAB content was 10–35 mole % and the PET content was at least 20 mole %. When the PAB content was 40 mole % or greater or when the PET content was less than 20 mole %, the polymer melting points were very high and tough films were not obtained by pressing.

Polymer Structure

The presence of segments II, III, and IV in the poly(ester amides) [eqs. (1)–(3)] was confirmed by ^{13}C NMR spectra of compositions prepared from PET and *p*-acetamidobenzoic acid. These spectra also suggest that the polymers have a random sequence distribution. The PAB–PAB and PAB–terephthaloyl dyad concentrations were determined by measuring the intensity of two chemically shifted peaks of the aromatic carbon attached to the amide nitrogen of the PAB. The ^{13}C NMR peak at 142.5 ppm was assigned to the PAB–PAB dyad (II), and the peak at 143.3 ppm was assigned to the PAB–terephthaloyl dyad in IV. In PET/25PAB, 14% of the PAB-containing dyads were PAB–PAB, which agrees exactly with the calculated, statistically random dyad distribution. In PET/35PAB, 21% PAB–PAB dyads were found (23% calculated for random distribution), and in PET/40PAB, 25% PAB–PAB dyads were found (27% calculated).

As will be discussed later, the maximum tensile strength and stiffness of PET/PAB copolymers were obtained with PET/25PAB. The proton wide-line NMR spectra of PET/25PAB exhibit a single broad line that narrows as the temperature is increased; above its melting point (254°C), the polymer gives a single line, which is characteristic of an isotropic melt. The melt, however, is turbid, a characteristic of liquid crystallinity. Since a broad component of the NMR spectra would be expected of molecules in a nematic mesophase² and no broad component was observed here, very little of the anisotropic molecular motion characteristic of nematic liquid crystallinity appears to be present in the molten polymer.

Optically anisotropic materials depolarize plane polarized light when observed between crossed polarizers,⁸ and this test has been applied to polyester melts to confirm the presence of optical anisotropy.⁹ Except for a small number of bright birefringent particles in a melt of PET/25PAB, however, the field remained dark under crossed polarizers. The birefringent particles were probably high melting moieties owing to high concentrations of PAB/PAB and PAB/terephthaloyl structures. This lack of an optically anisotropic melt, then, is in agreement with the proton wide-line NMR spectra.

Gel permeation chromatographic (GPC) analysis indicated that some branching occurred; the GPC curves had a high-molecular-weight tail; and the ratios of the polystyrene equivalent-weight-average (\bar{M}_w) to number-average

TABLE I
Polystyrene Equivalent Molecular Weights of PET Modified with PAB

PAB (mole %)	IV	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
20	0.68	149,000	30,000	5.0
25	0.67	160,000	24,000	6.7
30	0.62	120,000	20,000	6.0

molecular weights (\bar{M}_n) were 5.0 to 6.7 for PET modified with 20–30 mole % PAB (Table I). The absolute values of these molecular weights have no specific significance; however, the \bar{M}_w/\bar{M}_n ratios are strongly indicative of polymer branching. Table I also suggests that at a constant value of \bar{M}_w the branching increases with PAB content. The branching occurred presumably because of the reaction of the hydrogen atoms on the amide groups.

The melt viscosities of the poly(ester amides) increased as the PAB content was increased to 30 mole %, and at the higher PAB level the shear sensitivity also increased significantly (Fig. 1). IVs of these polymers were 0.56–0.58 initially and 0.53–0.56 after the melt viscosity measurements.

Because of the rigid chain components of liquid crystalline polymers, the relaxation times of the melts of these materials are appreciably longer than the relaxation times of normal polymer melts, and this effect is much greater in low-rate processes, such as the relaxation that occurs during cooling of a polymer after injection molding or after melt spinning. Figure 2 compares the relaxation times of PET/25PAB with those of PET and PET modified with 30 and 60 mole % PHB at temperatures at which the polymers can be processed. The relaxation times of the poly(ester amide) and PET/60PHB are greatly affected by frequency, whereas the PET relaxation times are affected only slightly. Values for PET at frequencies of 10 rad/sec and less could not be determined because the mechanical spectrometer was not sensitive enough to measure the modulus. At frequencies comparable to low-rate processes, that is, at less than 1 rad/sec, the relaxation times of the poly(ester amide) are between those of the two copolyesters. As will be shown, the strength and stiffness of the injection-molded poly(ester amide) also are in between those of the copolyesters.

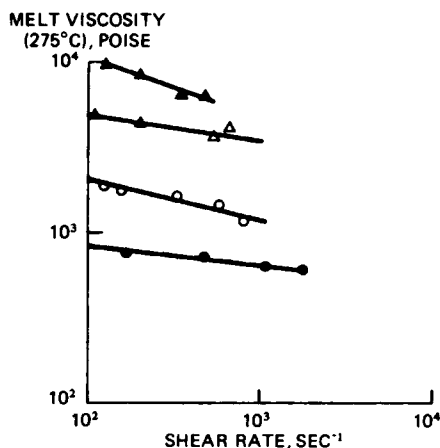


Fig. 1. Melt viscosity of PET modified with PAB. (●) PET; (○) PET/10PAB; (△) PET/20PAB; (▲) PET/30PAB.

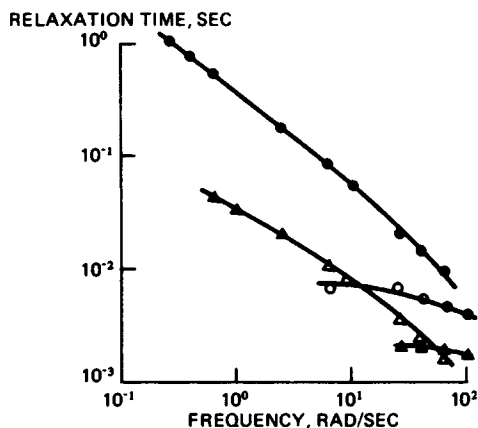


Fig. 2. Relaxation times of PET copolymers. (▲) PET, IV 0.64 at 285°C; (△) PET/25PAB, IV 0.69 at 290°C; (○) PET/30PHB, IV 0.69 at 275°C; (●) PET/60PHB, IV 0.65 at 260°C.

Polymer Properties

Because of the PAB acid component, the polymers were yellow or yellow-brown. Table II lists a number of the properties of the PET/PAB poly(ester amides). Pressed films of unmodified PET and of PET modified with up to 35 mole % PAB were tough and creasable, whereas a film of the higher-melting PET/40PAB cracked on creasing. When these poly(ester amides) are compared with the copolyesters of PET modified with PHB,¹ it is apparent that PAB is more effective than PHB in increasing the polymer T_g (77°C for PET/20 PHB).

Although the wide-line NMR spectra and the test for optical anisotropy of PET/25PAB did not show the presence of liquid crystallinity, the comparatively long relaxation times did increase the probability of retaining extended chain orientation after injection molding, extruding, or spinning polymers containing PAB segments. In the final analysis, the practical consequence of anisotropic melts and liquid crystallinity, if present, is that they permit attainment of improved, useful polymer properties. Table III lists a number of the properties of injection-molded PET/PAB compositions.

Whereas 10 mole % PAB had very little effect on tensile and flexural properties, a very large increase in strength and stiffness occurred when the PAB content

TABLE II
Properties of PET Modified with PAB

PAB (mole %)	IV	T_g (°C)	M_p (°C)	Melt and film appearance ^a
0	0.60	78	252	Clear
10	0.56	92	248	Clear
20	0.57	101	248	Clear
25	0.67	102	254	Hazy
30	0.62	103	255	Hazy
35	Insol	105	354	Opaque
40	Insol	101	371	Opaque

^a Films were pressed at about 275–375°C, depending on melting point, and quenched in water.

TABLE III
 Properties of Injection-Molded PET Modified with PAB

PAB content (mole %)	0	10	20	25	30
Cylinder temperature (°C)	275	295	265	260	285
Inherent viscosity					
Before molding	0.76	0.58	0.63	0.67	0.83
After molding	0.62	0.55	0.62	0.64	0.62
Tensile strength (10 ³ psi)	8.0 ^a	8.4 ^a	17.5	24.4	19.8
Elongation to break (%)	240	116	17	10	8
Flexural modulus (10 ⁵ psi)	3.3	3.4	5.0	7.6	7.1
Flexural strength (10 ³ psi)	13.2	14.6	17.0	20.2	21.7
Izod impact strength					
Notched (ft lb/in.)	0.3	0.4	0.6	0.8	0.5
Unnotched (ft lb/in.)	9.5	27	17.1	3.5	—
Rockwell hardness, <i>L</i>	73	79	92	99	99
Heat-deflection temperature (°C)	66	72	85	88	97
Mold shrinkage (%)	0.6	0.6	0.6	—	0.4
Oxygen index	21 ^b	28	29	29	32

^a Yield strength; break strength was somewhat lower. The other polymers did not exhibit a yield point.

^b Determined on bar reinforced with 20 wt % glass fibers to avoid abnormally high value because of dripping.

was 20–30 mole %. These properties of PET/20PAB are similar to those of injection-molded PET/30PHB,¹ and the strength and stiffness of PET/25PAB are similar to those of PET/35PHB. The melting point of PET/40PAB was too high for this polymer to be injection molded without decomposition.

PET/25PAB was also molded into edge-gated plaques that were then cut along and across the flow direction of the polymer melt to determine the effect of polymer orientation on mechanical properties. Table IV shows the properties to be highly anisotropic, as was observed earlier with several liquid-crystalline PET/PHB copolyesters.¹ The Izod impact strength and heat-deflection temperature were not determined because $\frac{1}{8}$ -in. thick specimens are required and the plaque thickness was $\frac{1}{16}$ in.

PAB is more effective than PHB in increasing the oxygen index (OI) of PET copolymers. PET/10PAB bars $\frac{1}{8}$ in. thick formed a char on burning and had an OI of 28, whereas about 45 mole % PHB was required to impart a similar OI in PET/PHB copolyesters. Although PET/30PAB had an OI of 32, the test bars

 TABLE IV
 Anisotropic Properties of Injection-Molded PET/25PAB^a

Property	Along flow	Across flow
Tensile strength (10 ³ psi)	18.0	7.2
Elongation (%)	18	10
Flexural modulus (10 ⁵ psi)	8.4	3.6
Flexural strength (10 ³ psi)	20.3	10.3
Mold shrinkage (%)	0.17	0.53
Coefficient of linear thermal expansion (10 ⁻⁵ in./in./°C)	2.1	7.6

^a $3 \times 3 \times \frac{1}{16}$ -in. plaques, gated along one edge and injection molded in a 1-oz Newbury HV1-25T machine (cylinder temperature 260°C, mold temperature 23°C) were cut into 0.5-in. wide specimens and milled into the standard tensile bar shape for tensile measurements; polymer IV was 0.69 before molding and 0.65 after molding.

had a flammability rating of V-2 in the Underwriters Laboratories Vertical Flammability Test 94 (fire extinguished by a flaming drop).

Table V shows the effect on the molding-plastic properties of modifying PET with PAB and PHB. Copolymers containing a total PAB and PHB content of 30 mole % had the increased properties characteristic of liquid crystalline polymers, and injection-molded bars had higher strength and stiffness values than PET/30PHB.¹ No attempt was made to determine the injection-molding temperature that would give the maximum mechanical properties of the various compositions, but it may be significant that the maximum tensile strength, stiffness (flexural modulus), and Izod impact strength were obtained with a composition in which the PAB and PHB content totaled 60 mole %, which is similar to the observation made with the PET/PHB copolyesters.¹ Because of a very low or zero coefficient of thermal expansion, the mold shrinkage of these copoly(esteramides) is low or zero.

As shown in Table III, the PAB significantly increased the OI of the PET/PAB polymers, but none of the compositions had a UL 94V-1 flammability rating. This rating was achieved with test bars ($\frac{1}{16}$ in. thick) of PET modified with 20 mole % PAB and 60 mole % PHB (Table V). Because of the large amount of char formed, these bars were self-extinguishing without dripping.

CONCLUSIONS

Poly(ester amides) with physical properties similar to those of liquid crystalline polyesters can be prepared by the reaction of PET with *p*-acetamidobenzoic acid. The polymers have a random sequence distribution; they contain some branching; and, at low frequencies, they have relaxation times appreciably longer than those of PET. Because of the high melting points imparted by the PAB, the practical limit of PAB content for a melt-processable polymer is about 30 mole %. The mechanical properties of injection-molded polymers containing 20–30 mole % PAB are anisotropic: strength and stiffness can be obtained which

TABLE V
Properties of Injection-Molded PET Modified with PAB and PHB

PAB content (mole %)	0	10	10	20	20	20
PHB content (mole %)	0	20	50	10	30	60
Cylinder temperature (°C)	275	260	300	260	340	380
Inherent viscosity						
Before molding	0.76	0.52	0.66	0.80	0.70	Insol
After molding	0.62	0.49	0.55	0.78	0.61	Insol
Tensile strength (10 ³ psi)	8.0 ^a	23.7	36.4	24.8	23.5	29.7
Elongation to break (%)	240	13	10	11	9	9
Flexural modulus (10 ⁵ psi)	3.3	7.8	14.1	9.8	10.4	11.8
Flexural strength (10 ³ psi)	13.2	—	20.6	25.1	21.1	21.3
Izod impact strength						
Notched (ft lb/in.)	0.3	0.6	2.2	1.0	1.1	1.0
Unnotched (ft lb/in.)	9.5	2.3	10.9	10.6	6.0	3.0
Rockwell hardness (L)	73	89	67	96	80	82
Heat-deflection temperature (°C)	66	80	77	92	90	141
Mold shrinkage (%)	0.6	0.4	0.0	0.0	0.0	0.1

^a Yield strength; the poly(ester amides) did not exhibit a yield point.

are more than twice as high in the direction of flow of the polymer melt as in the perpendicular direction, and the coefficient of linear thermal expansion is very low in the direction of flow. These properties are due to the long relaxation times, which are due to the extended chain orientation of polymer segments containing PAB. The PAB also appreciably increases the OI of the polymers. The liquid crystalline characteristics and mechanical properties can be further enhanced by incorporating *p*-hydroxybenzoic acid units into the polymer chains.

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