

# Preparation, Morphology, and Deformation Behavior of Polyoxypropylene-co-Nylon 6 Thermoplastic Elastomers

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## SYNOPSIS

Segmented block copolymers consisting of nylon 6 and polyoxypropylene blocks were prepared and characterized. Pronounced phase separation in the solid phase was deduced from differential calorimetry and from small-angle X-ray scattering, as well as from dynamic mechanical measurements. The morphology (from X-ray diffraction) and anisotropy in mechanical properties strongly suggest phase separation in the melt (which is optically clear). Elastomerlike properties are described and discussed.

## INTRODUCTION

A polyamide analog of the well-known polyether ester thermoplastic elastomer (TPE) materials (Arnitel E; Hytrel)<sup>1</sup> was studied. Enhanced domain demixing<sup>2</sup> was envisioned by combining nylon 6 and polyoxypropylene, compared with poly-THF/polyester or poly-THF-nylon 12 (Pebax) combinations. The noncrystallizability of the polyoxypropylene component was expected to lead to superior low-temperature properties. The unusually pronounced domain separation led to unusual morphologies in molded specimens and to unusual anisotropy of mechanical properties—at least in high viscosity, harder grades of polyoxypropylene-co-polyamide 6 (POP6).

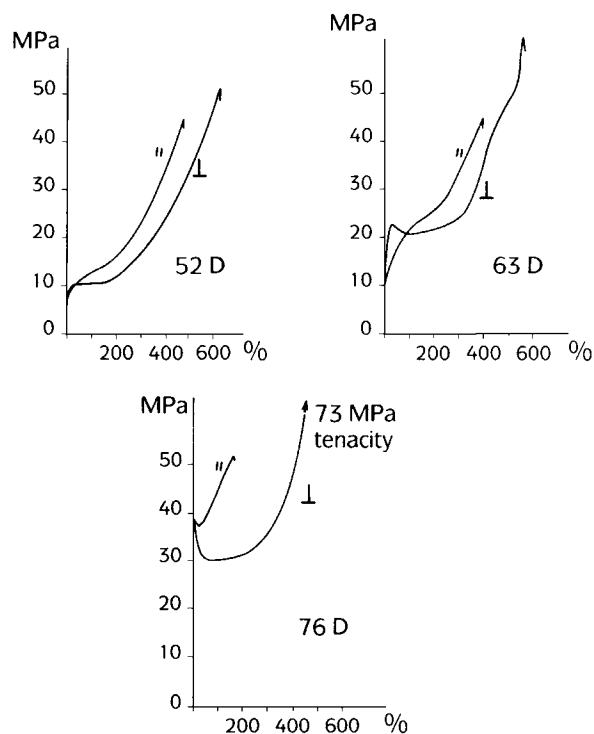
## EXPERIMENTAL

POP6 products were prepared from commercial fiber-grade caprolactam and adipic acid and from polyoxypropylene diamine available from Texaco (Jeffamine D 2000), by polymerizing for 8 h at 225°C (0.2% of phosphoric acid as a catalyst). The products were washed for 24 h with boiling distilled

water to remove remaining monomers and oligomers. Yields were 90%.

The prepolymers were characterized by proton and <sup>13</sup>C-NMR spectroscopy using a Bruker WH 270 FT instrument (enabling, *inter alia*,  $M_n$  determinations) and by IR spectroscopy (Perkin-Elmer 457 machine). End-group analyses were performed by acid-base potentiometry (polyoxypropylene diamines; POP6 TPEs) and by acetylation-mild hydrolysis-acetic acid titration (hydroxylic end groups in prepolymers). GPC of prepolymers was done using Waters Micro Styragel (500 Å pore size) columns. Relative viscosities were measured in solutions of 1 g of polymer in 100 mL of *m*-cresol at 25°C.

Injection molding was performed at barrel temperatures of 250–280°C with low-viscosity POP6 (RV 2.2–2.4) or 270–300°C with high-viscosity material (RV 2.5–3.0), mold temperature of 90°C, and cycle time of 30 s. POP6 was spun as a monofilament at 260°C from a 750 μm spinneret (275 bar spinning pressure) and cold drawn without a pin in a two-stage experiment. Spindrawing was studied at draw ratios of 2–2.8 and winding rate of 2500 m/min, without external heating in the drawing stage. Dynamic mechanical measurements on injection-molded specimens, and on the POP6 melt, were carried out on a Rheovibron DDV-II-C machine. Statton X-ray diffraction patterns were recorded in small samples cut out from injection-molded slabs at various locations in the slabs.



**Figure 1** Stress-strain curves of POPN6 test bars (ISO II) (Crosshead 50 mm/min).

## RESULTS

POPN6-type polymers of hardness  $> 60$  shore D show anisotropy in injection-molded specimens, the higher modulus being found perpendicular to the direction of polymer flow during filling of the mold (Fig. 1). Wide-angle X-ray diffraction supports a model featuring nylon crystals oriented with the hydrogen-bond plane perpendicular to the direction of flow during mold filling. The unusual direction of mechanical anisotropy is not found in low molecular weight POPN6 grades. Dynamic mechanical measurements on the material at temperatures above the melting point indicate anomalous behavior attributable to a two-phase texture that disappears at still higher temperatures (Fig. 2). An organization of the melt into discrete nylon and POP phases is not surprising in view of the pronounced immiscibility of these polymers. Both DSC and torsion pendulum measurements (Fig. 3) underline the perfect phase separation and the liquid behavior of the POP domains down to the  $T_g$  at  $-60^\circ\text{C}$ . The phase behavior of polyetheresteramides prepared by esterifying carboxyl-terminated polyamide 12 with poly-

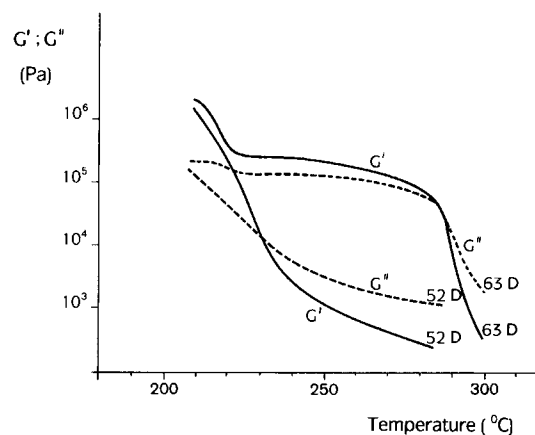
THF was reported recently.<sup>3</sup> As expected, relatively weak phase separation was observed in that system.

Elongational set measurements proved the material to be slightly inferior to the traditional types of poly-THF-*co*-PBT known as Arnitel E (Table I), in terms of plastic deformation. POPN6 outperforms other TPE types in low-temperature flexibility.

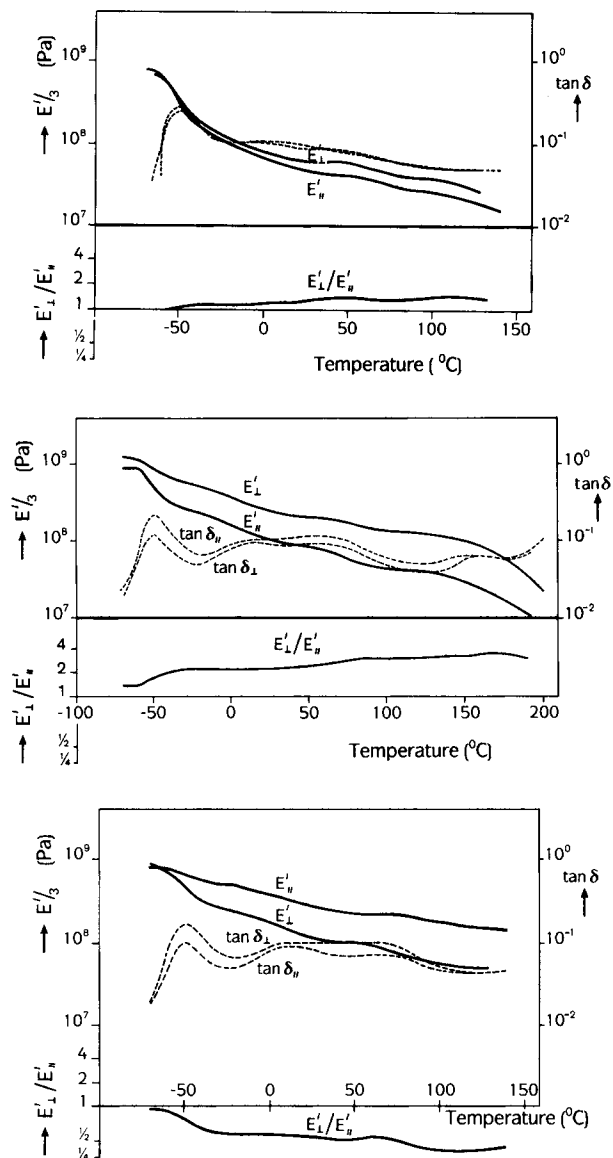
TPEs often show better elastic recovery after drawing. Spindrawing (Fig. 4A) experiments with POPN6 seemed to substantiate hopes for yarn applications; spindrawing (Table II) did not result in the virtually 100% elastic recovery (Fig. 4A) that a two-step process had shown. The yarn suffered a disastrous shrinkage upon washing. The washed yarns behaved more or less like undrawn or incompletely drawn materials (Fig. 4B).

## DISCUSSION

The anisotropy found in POPN6 injection moldings, with the higher modulus (and usually the higher tenacity) in the direction perpendicular to flow during mold filling, i.e., the “wrong” way about, in the higher viscosity  $> 60$  D polymers may be understood by visualizing the polymer molecules being oriented parallel to the flow, at the same time being grouped into phase-separated domains. In this situation, domains can overlap much easier in the perpendicular direction than in the parallel direction—due to the alternating chemical identity in the chain (flow) direction. This picture is supported by WAXD analysis, showing nylon crystallites with the hydrogen-bond structure oriented close to perpendicular to



**Figure 2** Visco-elastic behavior of POPN6 in the melt.

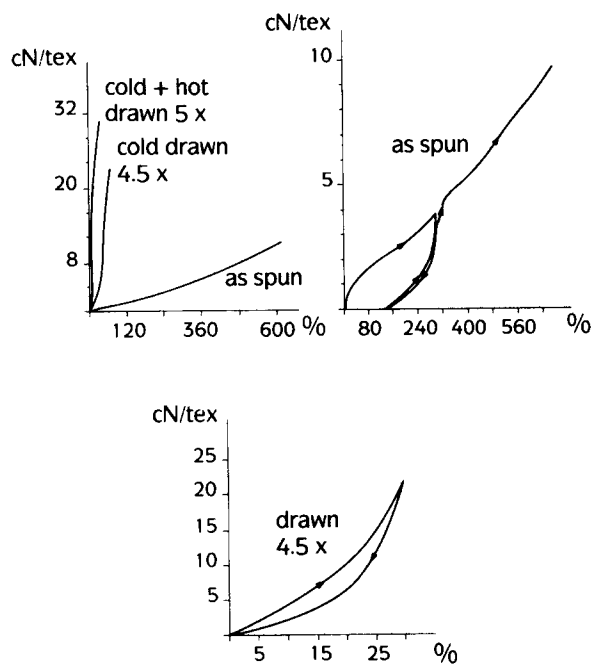


**Figure 3** Dynamic tensile behavior of POPN6. Top to bottom: 52, 63 (RV = 2.65) and 63 (RV = 2.17); Shore D hardness.

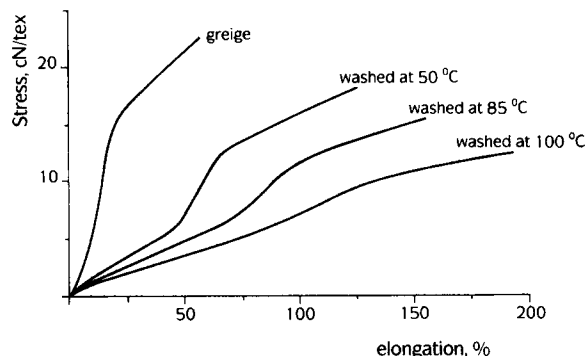
polymer flow. The lower viscosity polymer cannot build up the high-shear forces needed for this orientation effect in the injection-molding experiments. In addition to the overall WAXD picture sketched above, further detail in the nylon crystallite orientation and its variation with location in injection-molded slabs was observable, no doubt originating in complexities of the flow pattern during mold filling. A continuous hard-phase submatrix is clearly present: Compare the stress-strain curves of TPEs with those of normal rubber (Fig. 5).

**Table I** Residual Elongation After 24 h Loading at 25% Strain

Material	Hardness (Shore D)	Residual Elongation (%)
Arnitel E	55	6.5
Arnitel E	63	7.5
POP6	43	8
POP6	52	10
POP6	63	12



**Figure 4** Stress-strain curves of 52 Shore D POPN6 yarns. Top three figures: "two-stage" (spinning, then drawing) experiments. Bottom figure: spindrawn sample (Experiment B, Table II).

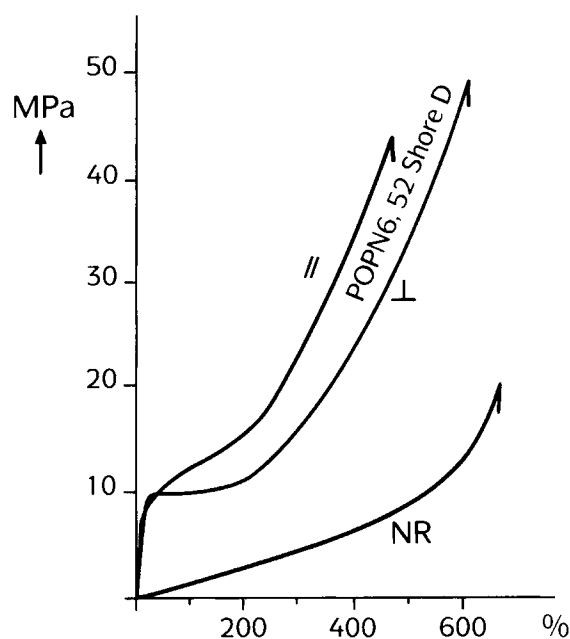


**Table II Spindrawn POPN6 (55 Shore D) Yarn**

	Sample		Sample B Washed at (°C)		
	A	B	50	85	100
Draw ratio	2.12	2.77			
Shrinkage (%)			26	40	47
Count (dtex fl)	69.2	58.8	74.3	82.0	96.3
Tenacity (cN/tex)	18	23	18	16	13
Elongation (%)	92	57	126	155	190
Max modulus (cN/tex)	89	143	42	21	11
At % elongation	7	15	56	87	109
Load at Strain (cN/tex)					
(1%)	0.8	0.7	0.6	0.6	0.6
(5%)	3.3	1.9	1.1	0.9	0.8
Quickset (%) of specimen length after loading at half-breaking strain					
1st cycle	7	3	15	19	23
2nd cycle	9	3	17	22	26
5th cycle	10	4	18	23	30
10th cycle	11	4	20	25	31

Initial deformation is NOT significantly counteracted by the liquid soft segment but by strain in the hard submatrix. Yield behavior in TPAs is no different from that in other plastics.

Interestingly, a recent paper<sup>4</sup> discussed polyure-



**Figure 5** Stress-strain responses of POPN6 and natural rubber (NR) compared. Note the high *initial* modulus of the thermoplastic material compared with NR.

thane deformation in terms of stress applied on the SOFT domains, although the presence of a hard domain submatrix was taken for granted. Spherulites of about 10  $\mu\text{m}$  and crystallite size of 5.5 nm $\dagger$  were reported in polyetherester TPEs<sup>5</sup>; load bearing by the hard submatrix was discussed as the force counteracting low strain by Buck et al., but, nevertheless, these authors, also attributed the high elastic recovery at 0.1–1% elongation in polyetheresters, to elastic strain energy storage in the soft domains.<sup>5</sup> Of course, at these small deformations, good recovery is also shown by PBT homopolymer.

It is not hard to see that once a large deformation such as yarn drawing has resulted in destroying hard material continuity the elastic behavior must be much improved (Fig. 4A). However, heating past the hard segment  $T_g$ , or lowering the hard segment  $T_g$  (for instance, during washing), or combining such treatments will result in

- (a) shrinkage due to retractive forces built into the soft domains during the irreversible part of the TPE deformation (breakup of the hard-phase continuum) and

$\dagger$  With individual blocks being of the order of 150 (POPN6) or 300 (Arnitel E) atoms long, the characteristic domain size cannot be larger than 10 nm. Electron microscopic work in the literature centers on styrene-butadiene-styrene triblock polymers with much higher block molecular weights and typically concludes domain sizes of 10–50 nm, cf., e.g., Ref. 2.

- (b) recrystallization of the hard domains, especially detrimental in contact areas between individual hard domains, thus reforming a hard submatrix.

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