

X-Ray Diffraction Studies of ABA Propylene-Ethylene Block Copolymers

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Synopsis

ABA triblock copolymers of propylene and ethylene, where the central block is a random copolymer of ethylene and propylene and the A blocks are either isotactic polypropylene or polyethylene, are described. Structural changes induced by stretching at room and elevated temperatures are reported. WAXS was used to monitor these changes. The results indicate that block copolymers were synthesized and that different combinations of mechanical properties may be obtained by varying the type and length of the A blocks and adjusting the monomer ratio in the random B block.

INTRODUCTION

Recently, evidence was obtained demonstrating that true $(AB)_n$ -type propylene-ethylene block copolymers may be synthesized using dry Ziegler-Natta catalysts and a gas-phase polymerization technique.¹ This procedure was used to obtain cleaner block sequencing than possible in solution polymerizations.

In this article, some properties of ABA block copolymers, where B is a random copolymer of propylene and ethylene and the A end blocks are either isotactic polypropylene or polyethylene are reported. In particular, the structural changes induced by stretching such block copolymers at room and elevated temperatures are discussed.

EXPERIMENTAL

The preparation of the active dry catalyst from Et_2AlCl and $\text{TiCl}_3(\text{AA})$, and the technique for sequential addition of propylene and ethylene have been described previously.^{1,2} The random blocks were synthesized by simultaneously admitting both monomers, in various ratios, to the reaction vessel. The end block lengths were kept the same for individual samples but were varied from sample to sample (see Table I) by controlling the propylene (or ethylene) additions. Polymerization times varied from 80 to 143 min.

The copolymers were dissolved in xylene (containing phenyl- β -naphthylamine) and reprecipitated with methanol-HCl to remove catalyst residues. Films were prepared by compression molding the copolymers between aluminum foil at 150°C and under 103 MPa (15,000 psig) pressure for 90 sec in a Carver Laboratory press. The resulting films were annealed at 100°C in a vacuum desiccator for one week.

Film strips, 4×1.2 cm, were elongated with an Instron tester using a C-cell (load range 0.454–22.7 kg) calibrated to a full-scale load of 4.54 kg, a crosshead speed of 2.54–10⁻³ m/min, a chart speed of 2.54×10⁻² m/min, and a constant gauge

TABLE I
Summary of Copolymerizations

Sample No.	Composition, wt % E/P	Length of end block	E/P feed ratio random block	Length of random block	Polymer time, min	
					Random block	Total
PRP-6	26/74	3	1:2	15	104	143
PRP-3	32/68	5	2:1	11	57	82
PRP-7	24/76	8	3:1	7	77	123
ERE-12	75/25	4	2:4	7	85	98
ERE-14	80/20	7	2:2	20	93	103

length of 2.54×10^{-2} m. Each sample was stretched at 21°C and 65% RH. The samples with polypropylene end blocks were also stretched at $\sim 75^\circ\text{C}$ by directing a stream of hot air from a heat gun onto the film strips.

After stretching, the samples were removed from the Instron tester and allowed to relax for 24–48 hr at 21°C in air. The majority of the elongation was almost instantaneously recovered following removal from the tester, with very little recovery occurring during subsequent storage. To obtain the x-ray diffraction patterns the samples were clamped and stretched just sufficiently to remove any unevenness in the films.

Copolymer compositions were determined by IR spectroscopy and evaluated by Wei's method.³ Films were prepared by melt casting using a Carver Laboratory press with heated plates. About 50–60 mg of copolymer between layers of Al foil were placed on the platens, preheated to 150°C, and a pressure of 28–36 MPa (4000–5000 psig) was applied for 30–45 sec. A Beckman IR-20A-X IR spectrophotometer was used. Samples were scanned between 2000 and 600 cm^{-1} . Absorbances at 1149 and 7.9 cm^{-1} were calculated using the method suggested by Zichy.⁴

¹³C-NMR spectra were obtained with a JEOL FX60 pulsed Fourier-transform NMR spectrometer equipped with a Texas Instrument 12K computer and a variable temperature probe. Spectra were recorded at 15.01 MHz under conditions of proton broad-band decoupling at 15.01 MHz. The copolymer (100 mg) was dissolved in 1,2,4-trichlorobenzene (2 ml) containing 0.05% (w/w polymer) phenyl- β -naphthylamine, at 150°C. Nitrobenzene-*d*₅, in a 5-mm tube inserted in the polymer solution, was used for the deuterium lock. The spectrum was recorded at 150°C. Chemical shifts are reported in ppm downfield from TMS.

A Siemens x-ray system was used to obtain wide angle x-ray diffraction (WAXS) patterns of the samples before and after stretching. The patterns were recorded on a polaroid cassette, type 57 film. All samples were exposed under the same conditions for 60 min. The sample-to-film distance was 5.07×10^{-2} m.

RESULTS AND DISCUSSION

Table I summarizes the polymerization data for the various PRP and ERE copolymers. The PRP copolymers are listed in order of increasing length of the end blocks. The end block lengths represent the number of times the g/mol of monomer, corresponding to a pressure drop from 0.11 to 0.10 MPa, were fed to the reactor system. Each addition of monomer corresponds to ~ 0.8 mmol.

TABLE II
Stress-Elongation Data

Sample No.	Tensile strength		Elongation at break, %
	MPa	psi	
PRP-6	9.1	(1317)	262
PRP-3	12.0	(1747)	267
PRP-7	14.4	(2092)	357
ERE-12	9.9	(1435)	588 ^a
ERE-14	7.3	(1054)	88 ^b

^a Slipped in Instron jaws at 588%.

^b Slipped in Instron jaws at 88%.

Stress-elongation data for the different copolymers are listed in Table II. These copolymers were selected from a number of others for further study on the basis of their high elongation-at-break values, except for ERE-14 which was used to obtain a ¹³C-NMR spectrum.

Figure 1 is the WAXS pattern obtained for copolymer ERE-12 before stretching. The two concentric rings represent random orientation and are attributable to the (111) and (200) planes for a polyethylene orthorhombic crystal arrangement. Upon stretching at 21°C to 588%, these rings are transformed to equatorial arcs (Fig. 2), indicating orientation of the crystallites, presumably in the polyethylene end blocks. An elongation of 588% corresponds to a draw ratio of ~6.9. Polyethylene at a draw ratio of even 4 shows much higher orientation, indicating that the block copolymer has elasticity.

As the Et₂AlCl-TiCl₃(AA) catalyst is known to give "blocky" random ethylene-propylene copolymers,⁵ there may be some increased crystallization on stretching owing to the crystallization of ethylene sequences in the random or B block. This "blockiness" is demonstrated by Figure 3, which is the ¹³C spectrum of ERE-14. The αδ⁺ signal at 35.9 ppm downfield from TMS is clearly evident. This signal is due to the carbon at the junction between a propylene and ethylene sequence.⁶

WAXS patterns before and after stretching copolymer PRP-6 at 21°C to 262%

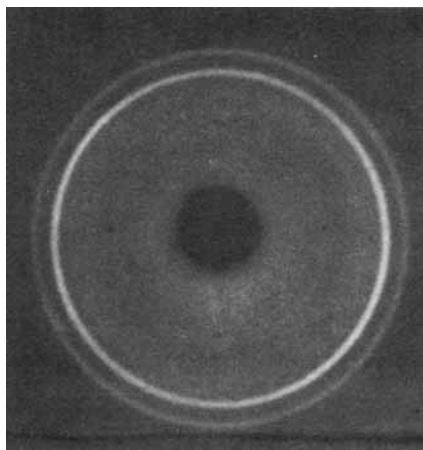


Fig. 1. WAXS pattern for ERE-12 copolymer before stretching.

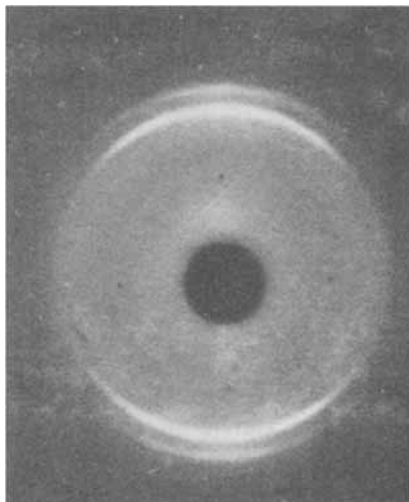


Fig. 2. WAXS pattern for ERE-12 copolymer after stretching 588% at 21°C.

elongation (Figs. 4 and 5, respectively) show essentially the same random orientation of polypropylene crystallites. On the other hand, isotactic polypropylene elongated 260% (draw ratio ~ 3.6) shows considerable orientation⁷ demonstrating that the random ethylene-propylene blocks in the PRP copolymer are deforming.

The three inner rings (measured from inside to outside) in Figures 4 and 5 are attributed to reflections from the polypropylene (110), (040), and (130) planes, respectively, in a monoclinic crystal arrangement. The outermost ring is a coalescence of the reflections from the (13 $\bar{1}$ -041) and (111) planes. This assignment is based on a measure of the intensity and proximity of reflections in isotactic polypropylene by Natta, Corradini and Cesari.⁸

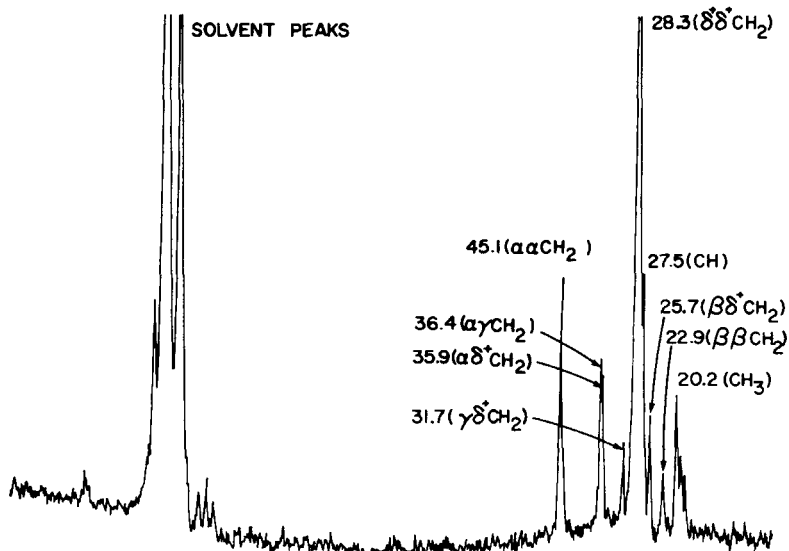


Fig. 3. ^{13}C -NMR spectrum for ERE-14 copolymer, 20K scans, 1.5 sec. repetition time. Numbers are chemical shifts downfield from TMS.

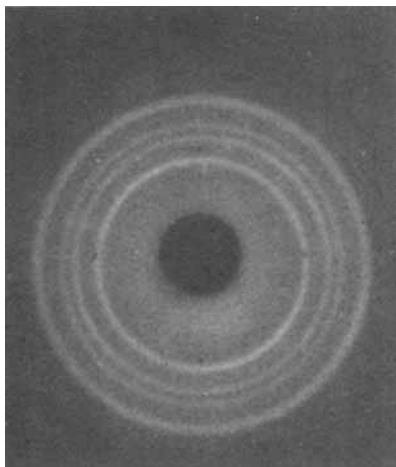


Fig. 4. WAXS pattern for PRP-6 copolymer before stretching.

Balta-Calleja and Peterlin⁹ have shown that at an annealing temperature of 155°C, the WAXS patterns of polypropylene, held in a stretched condition, show a highly oriented fiber structure in which the (13 $\bar{1}$ -041) and (111) reflections are resolvable. When copolymer PRP-6 was stretched at an elevated temperature ($\sim 75^\circ\text{C}$), it was possible to elongate the sample 495%. The resulting WAXS pattern (Fig. 6) showed characteristic arcs representative of oriented crystallites of isotactic polypropylene and presumably due to the polypropylene end blocks. Thus, the comparison of the behavior of PRP-6 at 21 and 75°C indicates that the chain mobility of the polypropylene in the end blocks is impeded at the lower temperature, but facilitated at the higher temperature resulting in orientation and increased possible deformation. The low chain mobility in the end blocks at 21°C suggests that the 262% elongation observed at that temperature is due to the random central block. This indicates that these polymers are true block copolymers. Further, the polypropylene end block orientations at the higher

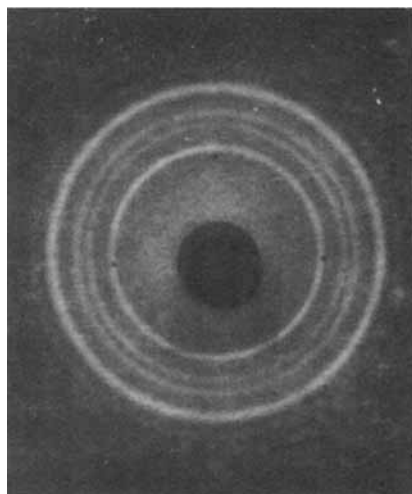


Fig. 5. WAXS pattern for PRP-6 copolymer after stretching 262% at 21°C.

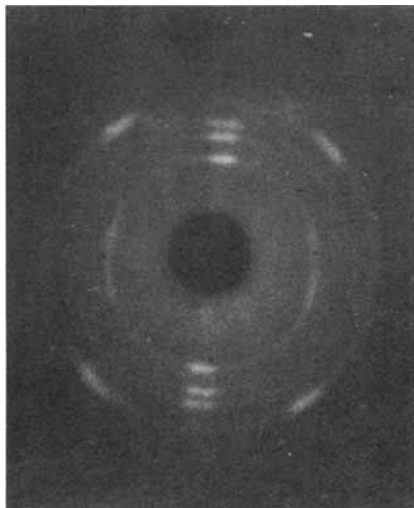


Fig. 6. WAXS pattern for PRP-6 copolymer after stretching 495% at $\sim 75^{\circ}\text{C}$.

temperature suggests that the stress was distributed over these segments. This would only be possible if the end blocks are chemically attached to the random copolymer segment.

During stretching at 21°C , the initially transparent PRP samples developed opacity. Whether this was due to spherulite growth or void formation was not determined. At the elevated temperature ($\sim 75^{\circ}\text{C}$) the samples remained translucent. The initially translucent ERE-12 sample developed transparency upon stretching at 21°C . The WAXS patterns for another ABA block copolymer PRP-7, obtained before stretching and after elongating 473% at $\sim 75^{\circ}\text{C}$, are shown in Figures 7 and 8, respectively, for comparison to the corresponding patterns for PRP-6 (Figs. 4 and 6, respectively).

Neither of the patterns for the undeformed samples (Figs. 4 and 7, respectively) show any indication of homopolyethylene. Upon stretching PRP-7, two outer equatorial arcs (Fig. 8) that are due to reflections from polyethylene are evident.

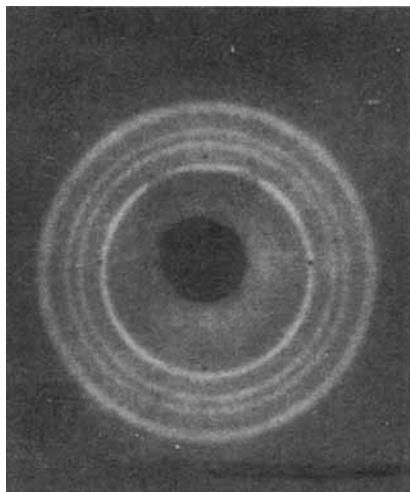


Fig. 7. WAXS pattern for PRP-7 copolymer before stretching.

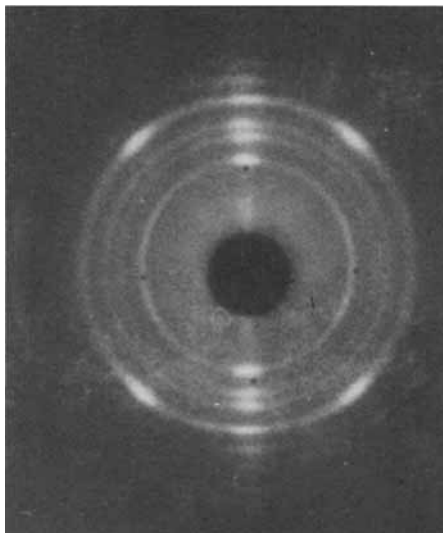


Fig. 8. WAXS pattern for PRP-7 copolymer after stretching 473% at $\sim 75^{\circ}\text{C}$.

There is no indication of crystallized polyethylene in the WAXS pattern of the stretched sample of PRP-6 (Fig. 6). The length of the random B block is approximately the same for both PRP-6 and -7 (Table I). However, the feed ratio of ethylene to propylene in the random block is 1:2 for PRP-6 versus 3:1 for PRP-7. Given the tendency for the catalyst used here to produce a "blocky" microstructure,⁵ it is quite likely that crystallizable polyethylene segments are present in the random block of PRP-7. Thus, the segments will crystallize and orient under deformation and this is evident in the WAXS pattern (Fig. 8). This provides additional confirmation that ABA block copolymer may be prepared by the alternate addition of propylene and ethylene to a Ziegler-Natta catalyst using a gas-phase polymerization technique.

The data presented here also demonstrates that different combinations of mechanical properties are possible for ABA block copolymers by varying the type and length of the A blocks and by adjusting the ratio of comonomers in the random B block.

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