Rheo-Optics and X-ray Scattering Study of Elastomeric Polypropylene^{*}

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INTRODUCTION

Elastomeric polypropylenes (ePP) have been known since the early history of polypropylene. Elastomeric polypropylenes were first synthesized by Natta using heterogenous Ziegler-type catalysts; he attributed the elastomeric behavior to their low crystallinity and stereoisomer blocks consisting of alternating isotactic crystalline and atactic amorphous segments.¹ Subsequent to Natta's work, there have been a number of reports of the production of related materials produced with different catalysts,ⁱⁱ with notable advances by Collette,ⁱⁱⁱ Chien,^{iv} and Collins.^V Recently, we reported that metallocene catalysts derived from 2-arylindene ligands produce elastomeric polypropylenes which can be separated into fractions differing in tacticity and crystallinity.^{vi,vii} Studies of the elastomeric polypropylenes using rheological and optical-polarimetry methods reveal evidence of a physical network in contrast to the blend of atactic and isotactic fractions.^{viii,ix,x} Dynamic infrared (IR) polarimetry studies provide evidence of co-crystallization of solvent fractions of the materials subjected to step-shear flows.^{xi}

In the current study, we examine the tensile flow properties of elastomeric polypropylene and its solvent fractions derived from 2-arylindene metallocenes catalysts. The origin of tensile set is studied by simultaneously measuring the tensile stress and optical birefringence. The birefringence follows the flow-induced anisotropy arising from amorphous chain orientation and oriented crystallites. Wide Angle and Small Angle X-ray Scattering (WAXS and SAXS, respectively) were performed to investigate the crystallite orientation as well as strain-induced crystallinity.

EXPERIMENTAL

Materials. The elastomeric polypropylene (PP-22010) was synthesized by BP Amoco Chemical Company in liquid propylene at 50°C with bis(2-(3,5-di-tbutylphenyl)indenyl) hafnium dichloride.^{xii} Fractionation was carried out by successive extraction of PP-20010 with boiling diethyl ether and heptane under a nitrogen environment following the procedure reported previously.^{vii,ix} The blend material was obtained by blending the lowest isotacticity (ES) and the highest isotacticity (HI) fractions to match the isotacticity of the parent ePP sample. Table 1 shows the characterization of the elastomeric polypropylene PP-20010 together with its solvent fractions.

sample	% wt	$Mw(K)^{a}$	PDI ^a	mmmm (%) ^b	$m\left(\% ight)^{b}$
ePP 20010	100	201	2.3	34	73
ES	48	147	2.1	21	67
HS	42	220	2.3	44	79
HI	10	432	2.5	76	92
Blend	-	-	-	34	73

^a Determined by GPC (waters 150°C) at BP Amoco Chemical Co ^b Determined by ¹³C NMR

Table 1. Polymer Characterization

Tensile Test. Tensile test was measured with a Miniature Material Tester, MiniMat 2000 (Rheometric Scientific, Inc.), at room temperature using ASTM D- 1708 dumbbell specimens with a gauge length of 2.2 cm. Specimens were diecut from compression-molded sheets (about 0.5 mm thickness) pressed at 180°C and slowly cooled to room temperature followed by annealing for at least one day. The crosshead separation rate for elongation and contraction was 1 and 0.1 mm/min, respectively. Tensile stress was calculated as the ratio of tensile force to the instantaneous cross-sectional area (measured by a caliper at different strains and interpolated between). Strain was computed as the ratio of the change in separation distance between two lines drawn at the middle of the specimen to its original separation distance ($\Delta I/I_0$).

Dynamic Birefringence. The dynamics of the materials were probed with optical polarimetry that follows the birefringence of a deformed sample using an optical train setup identical to the one reported previously.^x In the optical setup, monochromatic HeNe light passes through a polarizer (0°) and a photoelastic modulator (PEM, 45°) before it is transmitted through a sample with a normal incidence. The transmitted light then passes through an analyzing polarizer (45°) and impinges upon a photodiode detector where the signals are demodulated using lock-in amplifiers.

Wide Angle and Small Angle X-ray Scattering (WAXS and SAXS). WAXS and SAXS experiments were performed at the Stanford Linear Accelerator Center (SLAC) on beamline 1-4 of the Stanford Synchrotron Radiation Laboratory (SSRL). The X-ray source is focused with a flux ~10¹⁰ photons and monochromated by a (111) Si crystal to a wavelength of $\lambda = 1.488$ Å. A CCDbased area detector (Photonic Science) with a 1024x1024 array of 25µm square pixels was used to collect the 2-D diffraction data. Images were assembled from the summation of 1000 consecutive frames, and the portion of reciprocal space was calibrated with a Lupolen standard. Data analysis was performed using 1-D profiles summed either azimuthally or radially from the 2-D patterns and corrected for background scattering and scattering from windows associated with the optics.

RESULTS and DISCUSSION

The results of the simultaneous tensile stress and birefringence of the parent elastomeric polypropylene are shown in Figure 1. During the uniaxial elongation deformation (rate of 1 mm/min), both the tensile stress and birefringence increased to positive values. Since polypropylene has a positive stress-optical coefficient, a positive birefringence corresponds to polymer chains oriented along the flow direction.^{xiii} Once the desired strain was attained, the sample was held for 14 hrs to follow the relaxation of the tensile stress and birefringence. Both stress and birefringence relax to positive values. However, the birefringence relaxes faster than the tensile stress as observed from the fitting of the relaxation, specimens were contracted at a rate of 0.1 mm/min until a zero stress was reached. The strain was then adjusted automatically to maintain zero stress for 14 hrs (to allow complete relaxation). The residual strain (tensile set) and residual birefringence suggest that complete recovery is not achieved during relaxation after the deformation. The time held at strain affects the recovery:

longer time at strain increases frozen-in deformation, and therefore increases tensile set and residual birefringence.



Figure 1. Simultaneous tensile stress and birefringence response of elastomeric polypropylene PP-20010 in uniaxial tensile flow under various strains.

The simultaneous tensile stress and birefringence data for the lowest isotacticity (ES) fraction are displayed in Figure 2. During uniaxial deformation, both the stress and birefringence rise to positive values. Holding the specimen at strain, the stress and birefringence have very different relaxation responses. The stress relaxes to a positive plateau; at low strain (10%) stress relaxes completely after about 2 hours. On the other hand, the birefringence relaxes to a negative plateau, the magnitude of which increases with increasing strains. The negative birefringence indicates that the chains are oriented perpendicular to the flow direction after deformation.



Figure 2. Simultaneous tensile stress and birefringence response of the lowest isotacticity (Ether Soluble) fraction at various strains.

Similar negative birefringence relaxation response was observed for the lowest isotacticity (ES) fraction deformed under shear flow using a Linkam shearing apparatus. Following a 250% step-strain at room temperature, birefringence increased to a positive value and relaxed to a negative plateau. The negative birefringence decreased as temperature was raised and disappeared completely at 75°C. Applying a step-shear at 80°C, the birefringence relaxes completely to zero birefringence. These observations suggest negative birefringence arises from crystallites which melt at 75°C.

(a). Lowest isotacticity (ES) (b). Medium Isotacticity (HS)



Figure 3. WAXS images at 300% strain (top) and azimuthal plots (bottom) for (a). ES fraction; (b). HS fraction. Uniaxial deformation is along the vertical axis. Successive azimuthal plots have been shifted vertically for clarity.

The WAXS images and the azimuthal plots of the lowest (ES) and medium isotacticity (HS) fractions are shown in Figure 3. Before deformation, the ES fraction shows an isotropic halo scattering pattern typical of an amorphous polymer. Upon uniaxial deformation, crystalline arcs appear at the meridional axis, the axis parallel to the direction of strain. Integrating a narrow annulus containing the crystalline scattering of the first-order reflections gives the 1-D plots shown in Figure 3a. These plots show the strain-induced crystallinity as a function of strain; which increases as the strain increases and shows the primary crystalline axis orthogonal to the applied strain. After 1 day of releasing from strain, the ES fraction relaxes, as observed from the decreased peak intensity.

The medium isotacticity (HS) fraction shows radically different flow behavior than the ES fraction. Before deformation, the HS fraction exhibits isotropic crystalline rings typical of the α -phase of i-PP. As the HS sample was strained, relatively bright spots of intensity developed on the equatorial axis, indicating a molecular-scale alignment parallel to the applied strain direction – contrasting to the response of the ES fraction. These bright spots are characteristic of highly aligned crystalline materials (molecules). SAXS, which probes larger distances than WAXS, displays an intensity increase at the meridional planes for the deformed HS fraction. Longer order orientation in the order of 10 nm is evident which suggests lamellae oriented along the flow direction.

The flow behavior of the blend of the lowest and highest isotacticity fractions reflects both phenomena of the lowest isotacticity and the medium isotacticity fractions. As the sample was deformed to 300%, the intensity increased both in the direction parallel and orthogonal to the flow direction. Crystalline arcs appear

at the meridional axis similar to the ES fraction, while relatively bright spots appear at the equatorial axis similar to the HS fraction.

Conclusions

Rheo-optics and X-ray scattering methods provide significant insight into the flow behavior of semi-crystalline polymers. Deformation of ePP induces orientation of crystallinity which remains after the stress is released, suggesting the origin of tensile set. Relaxation of the ES fraction (lowest isotacticity) held at a constant strain causes the birefringence to relax to a negative plateau, indicative of a perpendicular orientation of crystallites to the flow direction. The disappearance of the negative birefringence with heating to 75°C suggests a crystalline contribution to the negative birefringence. This is collaborated by WAXS data which show perpendicular crystallite orientation. Furthermore, strain-induced crystallization was also observed by WAXS. To investigate the component contribution, WAXS analysis of the blend sample showed crystalline orientation both along and perpendicular to the flow direction, in contrast to the parent ePP.

Natta, G.; Crespi, G. U.S. Patent 3,175,999, 1965.

ⁱⁱ. Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143-1170.

[.] Collette, J. W.; Tullock, C. W. (Dupont) U.S. Patent 4,335,225, 1982.

^{iv}. Llinas, G. H.; Day, R. O.; Rausch, M. D.; Chien, J. C. W. Organometallics **1993**, *12*, 1283-1288.

^v. Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000-1009.

^{vi}. Coates, G.W.; Waymouth, R.M. *Science* **1995**, 267(#5195), 217-219.

 ^{vii}. Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. M.; Waymouth, R. M. *Macromolecules* 1998, *31*, 6908-6916.

viii. Hu, Y.; Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 3334-3340.

^{ix}. Carlson, E. D.; Krejchi, M. T.; Shah, C. D.; Terakawa, T.; Waymouth, R. M.; Fuller, G. G. *Macromolecules* **1998**, *31*, 5343-5351.

^x. Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 8094-8099.

^{xi}. Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *3*2, 8100-8106.

^{xii}. Waymouth, R.M. et al. *manuscript in preparation*.

xⁱⁱⁱ. Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer-Verlag: Berlin, 1983.