Transient Birefringence of Elastomeric Polypropylene Subjected to Step Shear Strain

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ABSTRACT: The step shear strain behavior of elastomeric polypropylene (ePP) synthesized from an unbridged metallocene catalyst is studied using polarimetry. The elastomeric nature of ePP is presumed to arise from a multiblock structure of isotactic (iPP) and atactic (aPP) polypropylene blocks. At lower temperatures stereoregular blocks of iPP are able to crystallize while stereoirregular blocks of aPP remain amorphous. The flow behavior of ePP is compared with homopolymer blends of iPP and aPP that have the same isotactic content as ePP as well as solvent fractions of the parent ePP sample. Step shear strain experiments carried out on crystallized samples show that ePP does not completely relax from an applied strain and that a cross-linked network has formed. Imperfections in the network structure are revealed by birefringence measurements that show a partial relaxation of the polymer orientation. In contrast, crystallized homopolymer blend samples are able to completely relax after the application of a step shear strain. Step shear strain experiments of the solvent fractions of ePP suggest that the elastomeric behavior results from a combination of fractions that are able to cocrystallize to form a physically cross-linked network.

Introduction

The microstructure of polypropylene is greatly responsible for the physical properties of the material. Atactic polypropylene has no stereoregularity and is an amorphous gum elastomer. Syndiotactic and isotactic polypropylene are rigid thermoplastics with stereoregular structures able to form helices and pack into crystals. Elastomeric polypropylene was first produced by Natta and co-workers, who suggested that its behavior was the result of a block structure in which isotactic crystallites physically cross-link amorphous atactic polypropylene segments.[1−3] Polypropylene of this form displays elastic behavior, yet softens and flows upon heating, characteristic of a thermoplastic elastomer.[4] The isotacticity of a sample is typically reported in terms of the fraction of isotactic pentads, [mmmm], which is generally determined by ^{13}C solution NMR measurements. Elastomeric polypropylenes typically possess moderate [mmmm] values.

Elastomeric polypropylenes have been prepared and isolated with a variety of techniques, and the materials have been studied in terms of both their microstructure and macroscopic behavior.[5−13] We have prepared unbridged metallocene catalysts derived from bis(2-phenylindenyl)zirconium dichlorides designed to produce a multiblock structure by interconverting between chiral, isospecific and achiral, aspecific catalytic forms.[14−16] These catalysts are capable of synthesizing polypropylenes with a wide range of tacticities, including atactic samples, moderately isotactic, elastomeric samples, and highly isotactic samples. Recently, we have reported the thermal and linear rheological behavior of an elastomeric polypropylene (ePP) synthesized from an unbridged metallocene catalyst.[17] Our previous work showed that ePP crystallizes at lower temperatures and melts over a broader temperature range than homopolymer blends of matching isotactic content. Small-amplitude, oscillatory mechanical measurements revealed that ePP has fewer monomers between equivalent point constraints than an atactic/isotactic blend of matching isotactic content; however, comparison of the small-amplitude rheological results with large-amplitude tensile strength and stress relaxation shows that small-amplitude rheology offers limited predictions of large-amplitude behavior.[17,18]

In the present study we used large-amplitude step-relaxation experiments to exaggerate the differences between the ePP system assumed to have a stereoblock structure and a blend system that lacks connectivity between sequences. The response of ePP to a large-amplitude step in shear strain was monitored using a transient birefringence experiment that follows the flow-induced anisotropy arising from amorphous chain orientations and macroscopically oriented crystallites. We also examined the rheo-optical response of the solvent fractions of ePP. Our previous work established that ePP is a heterogeneous material in terms of isotacticity.[17,18] Elastomeric behavior has been induced in other polypropylene systems by blending isotactic homopolymer with low-tacticity, ether-soluble polypropylene fractions.[19] Since ePP is a blend of components that differ in tacticity, we are motivated to study the effect of composition on elastomeric behavior. The use of optical techniques affords the opportunity to study samples in small quantities (approximately 100 mg) and to compare the response of the ePP parent sample with its isolated solvent fractions.

Experimental Section

Materials. An elastomeric polypropylene sample (ePP) was prepared at Amoco Chemical Co. using an unbridged metallocene catalyst derived from bis(2-phenylindenyl)zirconium dichloride. The sample was fractionated by successive extraction with boiling diethyl ether and heptane under a nitrogen environment. Full characterization and details of the prepara-

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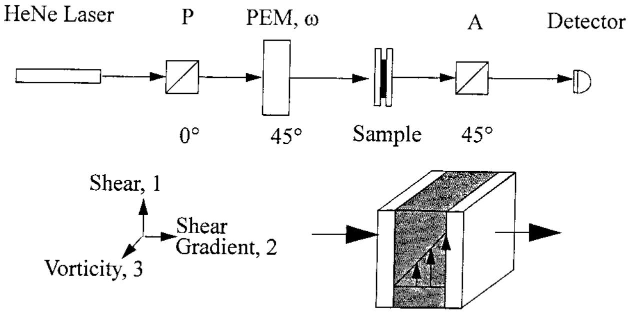

Figure 1. Optical setup for transient birefringence measurements flow−vorticity plane.

Table 1. Sample Microstructure

sample	wt % of ePP	[mmmm]	M_w ($\times 10^3$)	M_w/M_n
ePP	100	0.32	455	2.7
ES	36	0.18	339	2.5
HS	43	0.33	367	2.4
HI	21	0.51	598	3.1
PP41		0.85	41.4	2.4
APP495		0.10	495	2.1
B41 (PP41/aPP496)		0.31	(41.4/495)	

tion, purification, and characterization of this sample have been reported previously.[17,18] An atactic polypropylene homopolymer was prepared with a metallocene catalyst to have an [mmmm] = 0.10, a M_w = 496 000, and an M_w/M_n = 2.7. The fraction of isotactic pentads, [mmmm], was determined by ^{13}C NMR measurements and is a measurement of the sample's isotacticity.[20−22] A metallocene isotactic polypropylene (PP41) was prepared to have an [mmmm] = 0.86, a M_w = 41 400, and an M_w/M_n = 2.7. An atactic/isotactic polypropylene homopolymer blend (B41) was prepared to match the tacticity of ePP by dissolving 0.89 g of PP41 and 2.11 g of an atactic polypropylene homopolymer (aPP496) in boiling xylene and reprecipitating the blend with the addition of acidified methanol. Details of the preparation and characterization of these samples have also been reported previously.[17] Gel permeation chromatography measurements of molecular weight were carried out at Amoco Chemical Co. on a Waters 150C in trichlorobenzene at 145 °C and are referenced against polypropylene standards. Samples used in this study are listed with their microstructural information in Table 1.

Dynamic Birefringence. The dynamics of polypropylene were probed using a polarimetry experiment that follows the birefringence of a deformed sample. Figure 1 shows the optical train used to monitor the time-dependent birefringence in these experiments. In this apparatus, monochromatic light is provided by a HeNe laser. The light passes through a polarizer (0°) and photoelastic modulator (PEM, 45°) to provide elliptically polarized light. The polarization modulated beam is transmitted at normal incidence through a sample under parallel plate deformation. Deformation and flow are provided at 0° in the laboratory frame using a Linkam CSS 450 shearing apparatus. Light thus passes along the shear gradient axis. The transmitted beam then passes through an analyzing polarizer (45°) and impinges upon a photodiode detector. The signals are demodulated using lock-in amplifiers. The intensity of the transmitted light, I, has the following form:[23]

$$I = \frac{I_0}{4}[1 + 2J_1(A)\sin(\omega t)\sin(\delta')]; \quad \delta' = \frac{2\pi d \Delta n'_{13}}{\lambda} \tag{1}$$

where I_0 is the incident intensity, $J_1(A)$ is an calibration constant experimentally determined using elements of known retardation, ω is the modulation frequency of the PEM, δ' is the retardation of the sample, d is the sample thickness, λ is the wavelength of light, and $\Delta n'_{13}$ is the birefringence of the sample in the flow−vorticity plane.

The samples were held in a Linkam shearing apparatus modified to contain a nitrogen environment. A rotational displacement voltage transducer was used to measure applied strains. Samples of thickness 200−500 μm were deformed in a parallel plate geometry with light propagating down the shear gradient axis. Polypropylene has a positive stress−optical coefficient, so a positive birefringence signal signifies polymer chains oriented in the flow direction.[24] Positive shear strain is applied at time t_1 by a clockwise displacement of the bottom window. At time t_2 a negative deformation is applied by a counterclockwise displacement of the bottom window. All samples were prepared with the same thermal history. Samples were heated to 200 °C under nitrogen in the flow cell and held for 10 min to erase any thermal or strain history. Samples were then cooled at 20 °C/min to 25 °C. Samples were allowed to age for 20 h to allow slow crystallization processes to take place. For experiments carried out at above 25 °C samples were subsequently heated at 20 °C/min and allowed to equilibrate for 10 min.[25]

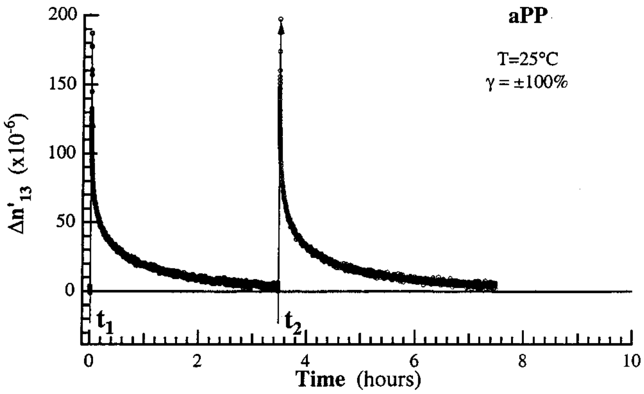

Figure 2. Birefringence response of the atactic homopolymer aPP496 to reversed step deformation (100% shear strain; T = 25 °C).

Mechanical Stress Measurements. Mechanical stress measurements were carried out on a Rheometrics dynamic analyzer (RDAII) using parallel plate geometry. Samples were heated and pressed in the rheometer under a N_2 environment at 200 °C and held for 10 min to erase all thermal history. Samples were then cooled at 20 °C/min to 25 °C and held for 20 h to provide a common thermal history for all samples. Step-relaxation experiments were performed at 0.5, 1.0, 2.0, and 3.0% average shear strain on 25 mm parallel plates.

Results and Discussion

Figure 2 shows the birefringence response of the atactic homopolymer aPP496 plotted against time for a reversed step deformation carried out at 25 °C and 100% shear strain. Deformation caused the birefringence signal to make an instantaneous jump followed by a monotonic decay back to zero as the polymer relaxed. At time t_2 the deformation was reversed, causing an identical birefringence response. The birefringence in this atactic sample arises strictly from oriented amorphous segments that are able to relax past chain entanglements. Because it relaxes back to an isotropic state, the aPP496 system yielded a symmetric response from both step deformations in a reversed step shear strain protocol. Figure 3 shows the birefringence response of the atactic/isotactic homopolymer blend B41 ([mmmm] = 0.33) under the same deformation conditions. The B41 sample yielded a qualitatively similar response to that of aPP496. B41 was also able to relax its chain orientations back to an isotropic configuration. The presence of isotactic crystallites increases the relaxation time of the system; however, like aPP496 this sample yielded a symmetric response from both step deformations since it relaxed back to an isotropic state between deformations.

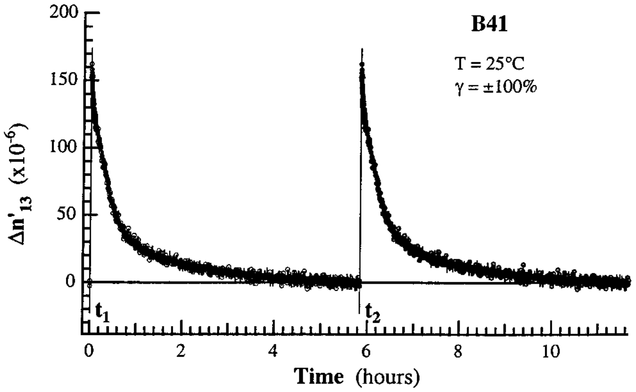

Figure 3. Birefringence response of the isotactic/atactic homopolymer blend B41 under reversed step deformation (100% shear strain; $T = 25$ °C).

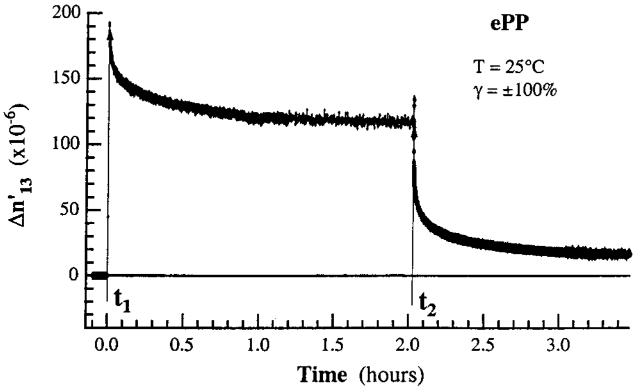

Figure 4. Typical birefringence response of the elastomeric sample ePP under reversed step deformation (100% shear strain; $T = 25$ °C).

Figure 4 shows a typical response for ePP ([mmmm] = 0.32) subjected to a reversed step-deformation experiment (25 °C, 100% shear strain). The birefringence response to deformation for this sample was significantly different from that of the samples discussed above. From an initially quiescent, zero-birefringence state, deformation caused the birefringence of ePP to step up to a large value and relax to a plateau value. Reversed deformation allowed the birefringence signal to relax toward zero. The observation of a plateau in the birefringence following step deformation reveals polymer orientations that were not able to relax at long times due to physical cross-links and provides clear evidence for an elastomeric network.

While rheo-optical investigation allows the study of small samples (ca. 100 mg), direct birefringence measurements of the stress within these elastomeric samples are difficult because semicrystalline polymers can have additional contributions to the optical anisotropy. The Kuhn and Grün model for polymer polarizability only accounts for "intrinsic" optical anisotropy that arises from the anisotropy of the segmental polarizability.[26] In general, a system's polarizability can also have anisotropic "form" contributions. In addition, polymeric crystallites contain highly ordered polymer segments that do not produce stress in the system. In general, the birefringence for an elastomeric polypropylene sample has three contributions:[27]

$$\Delta n' = (1 - \phi_c)C\sigma + \phi_c \Delta n'^{\circ}_{c} f_c + \Delta n'_{\text{form}} \qquad (2)$$

where ϕ_c is the volume fraction of crystallinity, C is the stress–optical coefficient of the amorphous phase, σ is the stress, $\Delta n'_c{}^{\circ}$ is the intrinsic birefringence of the crystallites, f_c is degree of orientation of the average crystallite optical axis, and $\Delta n'$ form is the form birefringence. Form contributions are generally accompanied by an anisotropic scattering of light. The elastomeric polypropylenes in this investigation are not turbid and do not scatter light anisotropically under the experimental conditions employed, and thus, we neglect the form term; this assumption has been found to be valid for many crystalline polyethylene and polypropylene systems.[28] Estimates of ϕ_c are available from wide-angle X-ray measurements on ePP;[29] however, ePP is known to contain both the α and γ crystal phases of polypropylene,[29] and each phase has its own intrinsic birefringence. While these complications make the determination of stress from optical data prohibitive, the optical data do reveal orientations of amorphous strands and crystalline structures within elastomeric polypropylene that evolve and relax over time.

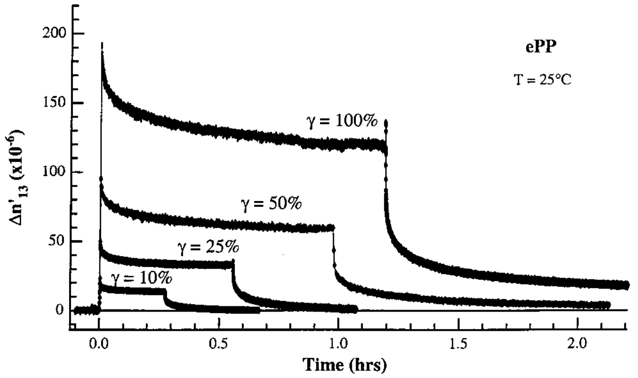

Figure 5. Birefringence response of the elastomeric sample ePP. Sample deformed at $T = 25$ °C at 10, 25, 50, and 100% shear strain.

As shown in Figure 5, room temperature ePP has an initial relaxation following shear strain, but after the first few thousand seconds, further relaxation becomes very slow (with an apparent time constant of 10 000 s or more) and was not recorded further. In addition to this elastomeric behavior, these strain studies revealed network imperfections in the ePP sample. After deformation, the samples exhibited some relaxation, indicating that the physical network was unable to fix the orientations of all deformed chains. Furthermore, larger strain experiments (50 and 100%) induced an irreversible anisotropy in the ePP system.

In an effort to probe strain dependence, the nontrivial relaxation behavior was investigated by fitting the relaxations to a double exponential of the form

$$\Delta n'_{13} = A_1 + A_2 \exp\left(\frac{-t}{\lambda_{\text{short}}}\right) + A_3 \exp\left(\frac{-t}{\lambda_{\text{long}}}\right) \qquad (3)$$

where A_1 is the nonrelaxing, residual birefringence, A_2 and A_3 are preexponential factors, λ_{short} is the shorter relaxation time, and λ_{long} is the longer relaxation time. While only offered as an empirical fit, the double-exponential form was chosen to capture the essentials of temporary network models that have one time scale related to amorphous chain relaxation and one time scale associated with the lifetime of temporary network junctions.[30,31] For ePP λ_{short} ranged from 14 to 78 s and λ_{long} ranged from 1300 to 1700 s; the two modes were similar in magnitude.

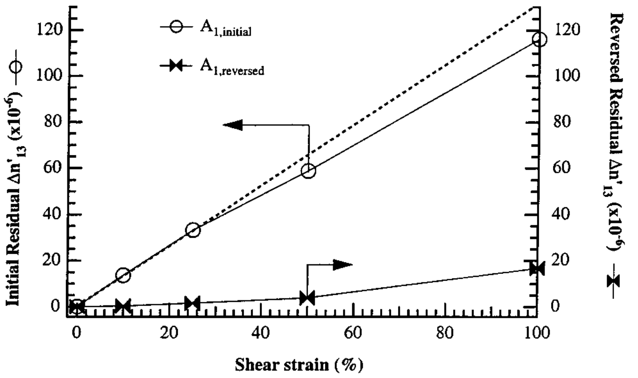

Figure 6. Residual birefringence of ePP following step deformation as a function of shear strain. Open circles show the residual birefringence following initial deformation, and the solid bow ties show the residual birefringence following reversed deformation.

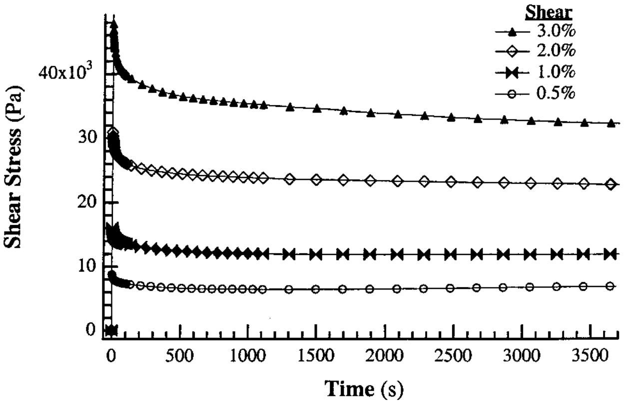

Figure 7. Mechanical stress measurement of relaxation following step deformation for the ePP system at 25 °C (shear strain = 0.5, 1.0, 2.0, and 3.0%).

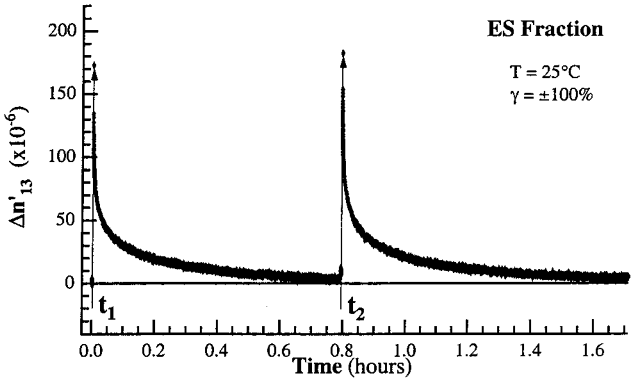

Figure 8. Birefringence response of the ether-soluble fraction of the elastomeric sample ES under reversed step deformation (100% shear strain; $T = 25$ °C).

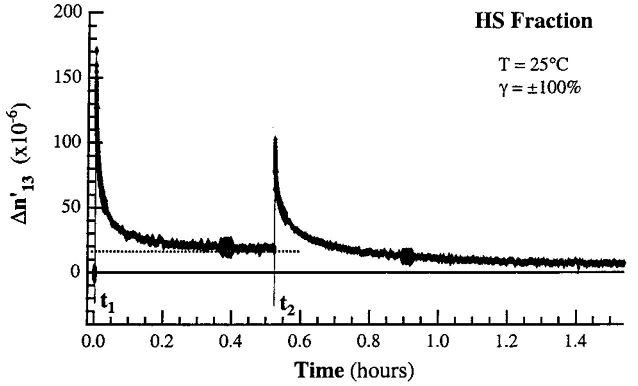

Figure 9. Birefringence response of the heptane-soluble fraction of the elastomeric sample HS under reversed step deformation (100% shear strain; $T = 25$ °C).

Figure 6 plots A_1 from the fit of the relaxation following the initial deformation (open circles) as a function of shear strain. The figure shows that for 0, 10, and 25% shear strain the level of the residual birefringence ($A_{1,\mathrm{initial}}$) scaled with the amount of shear strain as one would expect for an elastic solid.[32] As shown in Figure 7, mechanical stress measurements indicate that for shear strain up to 3.0% the stress scaled with the amount of shear strain. The stress relaxation plateau is due solely to oriented polymer segments. Mechanical stress measurements at higher amounts of strain were unavailable due to the torque limitations of the rheometer's transducer. Optical data show that the $A_{1,\mathrm{initial}}$ values from 50 and 100% shear strain fall below the linear trend extrapolated from the lower strain values. In addition to the larger amount of relaxation, higher strains led to an irreversibility in the ePP sample revealed by a residual birefringence following the reversed deformation ($A_{1,\mathrm{reversed}}$). Figure 6 also plots $A_{1,\mathrm{reversed}}$ from the fit of the relaxation following the reversed deformation (solid bow ties) as a function of shear strain. In Figure 6 the solid bow ties show that for low strains $A_{1,\mathrm{reversed}}$ approached zero as shear strain approaches zero.[33] At 50 and 100% shear strain the $A_{1,\mathrm{reversed}}$ of the relaxed system reveals a significant amount of residual birefringence. These results suggest that high shear strain may be able to rupture some of the weak links of the elastomeric network. A ruptured network would show increased relaxation following deformation. In addition, weakly formed crystallites (thinner lamellae, γ vs α phase, high degree of regio/stereoerrors held near lamellae surface, etc.) may be able to melt, re-form, and anneal while the sample is held in a strained state, resulting in a network oriented in the flow direction. Such a network would have a nonzero f_c (from eq 3) and consequently a nonzero birefringence, even in the stress-free state. Stress-induced melting—recrystallization has been reported in polyethylene samples using SANS.[34] While polyethylene samples are not elastomeric, these findings suggest that deformation may allow for a mechanism of melting—recrystallization within ePP samples.

Motivated to examine the different types of physical cross-links that form within the ePP sample, we probed the step shear strain response of the individual solvent fractions of ePP. The ePP polymer is a compositionally heterogeneous system in terms of tacticity. ePP can separated into an ether-soluble fraction (ES, [mmmm] = 0.18), a heptane-soluble fraction (HS, [mmmm] = 0.33), and a heptane-insoluble fraction (HI, [mmmm] = 0.51).[17] We monitored the birefringence response of individual solvent fractions in order to probe the compositional dependence of the large-amplitude elastomeric behavior of ePP.

The neat ES sample had a response similar to that of aPP496, in which deformation led to a step in birefringence and a complete monotonic decay of the signal (Figure 8). While the HS fraction did exhibit a residual birefringence following initial deformation, the plateau was of much lower magnitude than the one exhibited by the ePP parent sample (Figure 9). This plateau showed that there were physically cross-linked chains in this fraction that could not relax imposed

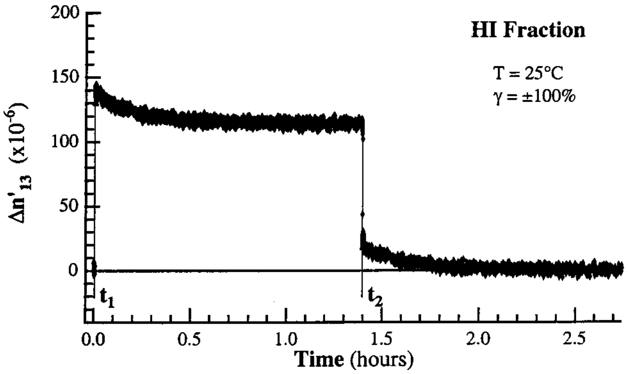

Figure 10. Birefringence response of the heptane-insoluble fraction of the elastomeric sample HI under reversed step deformation (100% shear strain; $T = 25$ °C).

stress; however, the lower value shows that it relaxed more of its flow imposed anisotropy. This result is consistent with the HS fraction having a lower crystallinity and thus being able to form fewer physical cross-links.[17] The HI fraction was more difficult to deform without having the sample slip on the glass of the flow cell than the previous sample. However, 100% shear strain deformation of this fraction was achieved, and when deformed the HI sample behaved like an elastic solid (Figure 10). After a sharp rise in the birefringence signal, indicating chain alignment, there was only a slight and fairly slow relaxation of the birefringence signal. Most of the chain orientation was fixed and unable to relax. When the deformation was reversed at time t_2, the signal stepped back and recovered to a zero-birefringence, isotropic state. The ability to deform this fraction at 100% shear strain contrasts studies of the heptane-soluble fractions isolated from stereoblock systems prepared from alumina-supported Zr and Ti alkyls; these heptane-insoluble fractions have been shown to be semicrystalline plastic materials possessing a yield point.[19] Little relaxation in the birefringence following a step shear strain deformation indicates that almost all of the chains in the HI fraction are incorporated into an elastomeric network. The fact that the birefringence relaxes completely to zero upon removal of strain could indicate that there are few weak links in the network formed by this sample. A network formed from isolated crystalline platelettes is consistent with previous work which found that neat, semicrystalline fractions of ePP do not form spherulites in their semicrystalline state under these experimental conditions.[17]

The dynamics of the isolated solvent fractions offer insight into the role of composition in ePP. The results suggest that the elastomeric nature of ePP arises from the ability of the HI fraction to form cross-links and the ability of the HS fraction to stretch and deform. This is significant since it has been found that the neat fractions display kinetics, crystalline contents, and crystalline phases.[17,18] Cocrystallization has also been reported in other stereoblock systems. Collette and co-workers have induced elastomeric behavior by blending a highly isotactic homopolymer with an ether-soluble polypropylene fraction that was incapable of crystallizing on its own.[19]

Conclusions

Large-amplitude step shear strain experiments reveal that crystallized ePP samples contain semipermanent physical cross-links. In contrast to the blend of atactic and isotactic polypropylene which lacks any segmental connectivity, the ePP sample was not able to relax all of its imposed stress. This type of cross-linking shows that there are chains that are permanently tethered in an network and provides strong evidence that ePP contains an atactic/isotactic multiblock microstructure. The results also suggest that large amounts of shear strain ($\geq 50\%$) are able to rupture the ePP physical network at weak tie points formed by small crystals or crystals far from equilibrium. The effect of deformation on nonequilibrium crystals is also shown by the development of an irreversible anisotropy at higher strains in which the ePP sample cannot return to an isotropic state upon reversal of deformation.

Step shear strain data on the solvent fractions show that the behavior of the parent ePP sample results from being composed of fractions differing in isotacticity. The segments of low isotacticity are not completely included in the physical network and allow a partial relaxation of the ePP system. Chains of moderate isotacticity found in the heptane-soluble fraction HS are able to form some physical cross-links, but the isotactic segments have difficulty crystallizing on their own, as exhibited by its low elastomeric plateau. The heptane-insoluble fraction HI behaves as an elastic solid by itself and is evidently able to cocrystallize with fractions of lower isotacticity, providing a larger cross-link density to the ePP sample. While cocrystallization between fractions is likely a significant contributor to the physical cross-link density, the study of the HS fraction points to the presence of an atactic/isotactic connectivity. The HS fraction is a homogeneous, inseparable polymer fraction with a moderate isotacticity. It can crystallize alone, and this fraction exhibits cross-linking by maintaining an elastomeric plateau. The cooperative role that the fractions play in the elasticity of the ePP material has been studied by following the dynamics of deuterium-labeled fractions in situ and is presented in our accompanying paper .[35]

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