Component Stress-Strain Behavior and Small-Angle Neutron Scattering Investigation of Stereoblock Elastomeric Polypropylene [*]

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Abstract

Elastomeric polypropylene (ePP) produced from unbridged 2-arylindene metallocene catalysts was studied by uniaxial tensile and small-angle neutron scattering (SANS) techniques. The ePP can be separated into three fractions by successive boiling-solvent fractionation method to yield: a low-tacticity fraction soluble in ether (ES), an intermediate-tacticity fraction soluble in heptane (HS), and a high-tacticity fraction insoluble in heptane (HI). Tensile properties of ePP were compared to its solvent fractions, and the role of each solvent fraction residing within ePP was investigated by blending 5 weight % deuterated fraction with ePP. The tensile properties of each fraction vary considerably, exhibiting properties from a weak gum elastomer for ES, to a semi-crystalline thermoplastic for HI. The intermediate-tacticity HS fraction exhibits elastic properties similar to the parent elastomer (ePP). In the melt at 160 °C, SANS shows that all deuterated fractions are homogeneously mixed with ePP in a one-phase system. At 25 °C upon a slow cooling from the melt, the low-tacticity fraction is preferentially segregated in the amorphous domains induced by different crystallization temperatures and kinetics of the deuterated ES and high-tacticity components. The high-tacticity component within ePP (dHI-ePP) retains its plastic properties in the blend. Despite its low crystallinity ($\leq 2\%$), the low-tacticity fraction can co-crystallize with the crystalline matrix. The dES-ePP shows little or no relaxation when held under strain and recovers readily upon the release of stress.

Keywords

elastomeric polypropylene; neutron scattering; polymer deformation; SANS; elongation; polymer structure; tacticity fractions

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Introduction

Isotactic polypropylene (i-PP) is a low-cost semi-crystalline thermoplastic exhibiting excellent mechanical properties with a world-wide production exceeding 20 million metric tons.[1] The crystallinity of isotactic PP is a consequence of the regular structure of the stereogenic centers along the polymer backbone; in contrast atactic polypropylene is an amorphous material. Elastomeric semi-crystalline polypropylenes are also known; Natta was the first to isolate an elastomeric form of polypropylene and attributed the elastomeric properties to a multiblock microstructure comprising alternating sequences of stereoregular isotactic and random atactic sequences.[2,3]

Elastomeric polypropylenes (ePP) can be produced by a number of different synthetic strategies as reported by Collette and coworkers at Dupont[4-9] and Job at Shell.[10,11] More recently, several classes of metallocene catalysts have been developed for the production of elastomeric polypropylenes,[12-20] notably those developed by Chien,[21-25] Collins,[26-28] Rieger,[29,30] Erker,[31] and our group.[32-51] Our group has investigated a family of elastomeric polypropylenes produced from unbridged 2-arylindene metallocene catalysts.[32-51] Investigations of the structures and properties of the elastomeric polypropylenes produced from these catalysts reveal that they are compositionally heterogeneous and can be separated into fractions of different tacticity, crystallinity, and molar mass.[33,39] Successive boiling-solvent extraction yields three fractions: a low-tacticity ether-soluble fraction, an intermediate-tacticity heptane-soluble fraction, and a high-tacticity heptane-insoluble fraction.

In this study we report the tensile properties of a sample of ePP and its solvent fractions at room and elevated temperatures. The deformation behavior of the individual fractions residing in the ePP matrix was studied by labeling individual solvent fractions with deuterium and doping these materials into protonated ePP. Small-angle neutron scattering (SANS) was used to probe the arrangement and deformation behavior of the labeled chains under strain.[52-54] The miscibility of the deuterated components in ePP was examined in the melt and in the crystalline state. The molecular orientation observed allowed us to relate the chain orientation level as a function of both the chain tacticity and the applied deformation. The current experiments complement previous studies on the dynamic response of each solvent fraction under a tensile deformation using rheo-optical and X-ray scattering methods.[46,55]

Experimental

Sample Preparation. Elastomeric polypropylene (ePP-10) was synthesized at BP Chemical Co. in liquid propylene at 50 °C with bis(2-(3,5-di-t-butylphenyl)indenyl) hafnium dichloride / MAO catalyst systems, as reported elsewhere.[56] Boiling-solvent fractionation was carried out following the procedure described earlier[33,39,56] with boiling diethyl-ether and heptane to yield a low-tacticity ether-soluble (ES) fraction, an intermediate-tacticity heptane-soluble (HS) fraction, and a high-tacticity heptane-insoluble (HI) fraction. Table 1 shows the physical properties of the materials.

Deuterated polypropylene was prepared following conditions as closely as possible to those of PP1 reported previously.[39] Deuterated monomer (C_3D_6) from Cambridge Isotopes was purified by condensing about 30 ml of deuterated monomer into a lecture bottle containing 2 g of solid Methylaluminoxane (MAO), obtained by vacuum drying of a toluene MAO solution (Akzo MAO type 4). The deuterated propylene was then re-condensed into the original container and the process repeated to remove all impurities. Polymerization was carried out in a 300-ml Parr reactor equipped with a mechanical stirrer equilibrated at 20 °C with an ethylene glycol / water cooling-loop. The reactor was flushed three times with argon and toluene, and half of the MAO was injected as a toluene solution under argon. The reactor was cooled with a dry-ice / acetone bath and the purified deuterated propylene condensed into the reactor. The reactor was warmed slowly to room temperature and a catalyst solution of bis-(2-phenylindenyl)-zirconium dichloride,[39] previously activated with the remaining half of the MAO, was injected as a toluene solution under argon pressure. A total of 25 ml of toluene and 25 ml of propylene were used for each polymerization with catalyst concentration of 5×10^{-5} M and the [MAO]/[Zr] ratio of 3,500. Polymerization was run for 1 hour and the excess deuterated monomer recondensed into the lecture bottle. Polymer from the reactor was precipitated into acidified methanol with 5% HCl. After stirring for 1 day, the polymer was washed with pure methanol for another 12 hours, and the polymers were collected and dried in a vacuum oven at 40 °C for at least 1 day. GPC analysis of molecular weight indicated $M_n = 129$ kg/mol and $M_w/M_n = 5.5$. ^{2}H-decoupled ^{13}C NMR analysis indicated an isotacticity content of [mmmm] = 30 %.

Samples for SANS experiments were prepared by blending 5% (by weight) deuterium labeled fraction with protonated ePP-10. The perdeuterated polymer (d-ePP) sample was

fractionated by successive extraction with boiling diethyl-ether and heptane under a nitrogen atmosphere following the same procedure as for the protonated ePP-10. Each deuterated fraction (d-ePP, d-ES, d-HS or d-HI) and protonated ePP-10 were dissolved in boiling xylene (300 ml) in the presence of 0.2% wt antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT). Polymer blends were precipitated into methanol with vigorous stirring. The resulting blends were dried at 40 °C in vacuum and hot-pressed to a thickness of 0.5-1.0 mm at 180 °C between two teflon sheets (Mechanical Grade PTFE, McMaster-CARR), and ambiently cooled to room temperature.

Material Characterization. Number and weight average molecular weights (M_n and M_w) were obtained at BP Chemical Co. using a Waters 150C high-temperature chromatograph. The solvent used was 1,2,4-trichlorobenzene at 139 °C using two Polymer Laboratories PL GEL Mixed-B columns at a flow rate of 1 ml/min. Calibration was done against polypropylene standards.

The ^{2}H-decoupled ^{13}C NMR spectra of the perdeuterated polypropylene were obtained at the Varian Applications Lab. For protonated polypropylenes, ^{13}C NMR spectra were recorded at 75.425 MHz on a Varian UI 300 spectrometer at 100 °C using 10 mm sample tubes. Samples were prepared in 1,1,2,2-tetrachloroethane containing about 0.5 ml of 1,1,2,2-tetrachloroethane-d2.[55]

Thermal analysis was performed using a Perkin-Elmer DSC 7 with indium as a calibration standard. Polymer samples (about 0.01 g) were melt-pressed between two Teflon sheets (Mechanical Grade PTFE, McMaster-CARR) at 180 °C using a light pressure (≤ 250 psig).

Disk-like samples were punched from films cooled with liquid nitrogen using a standard one-hole paper punch. These samples were weighed and sealed into an aluminum DSC pan supplied by Perkin-Elmer. Samples were pretreated from room temperature to 200 °C at 20 °C/min, held at 200 °C for 10 min, cooled to room temperature at 20 °C/min, and then aged at room temperature for 24 hours. The melting temperature and the heat of fusion were measured by heating from -50 °C to 200 °C at 20 °C/min. Crystallinity was calculated by normalizing the heat of fusion (ΔH_f) from the endotherm scans by a theoretical value of a completely crystalline sample of 209 J/g.[57]

Tensile Tests. Tensile tests were performed with ASTM D-1708 dumbbell specimens (2.2 cm gauge length) die cut from compression-molded sheets with a thickness of about 0.5 mm. Room-temperature tensile tests were performed in the lab of Charles L. Myers at BP Chemical Co. with a crosshead separation rate of 25.4 cm/min. Temperature-dependent tensile tests were conducted with a Miniature Material Tester, MiniMat 2000 (Rheometric Scientific, Inc.) with a crosshead separation rate of 10 mm/min. Tensile modulus of elasticity was determined as the tangent slope at the lowest strain. Hysteresis cycle tests were performed by elongating the specimen to 100% elongation (2 × original gauge length) in three successive cycles, with 30 s hold at 100% elongation and 60 s hold after crosshead recovery between cycles. Stress relaxation is measured as the decrease in stress during extension at 100% elongation for 30 s. Retained force was measured as the ratio of stress at 50% elongation during the recovery step to the initial stress at 100% elongation in the second cycle. A three-cycle recovery test was performed by elongating the specimen to 300% elongation (4 × original gauge length) with no hold time imposed at extension; crosshead direction was immediately reversed after reaching 300% elongation. The

elongation at which stress returned to the baseline identified a tensile set for the first cycle.

A tensile set for the second cycle was the elongation at which stress exceeded the baseline

during the extension. Hysteresis-to-break tests were conducted by successive cycles of

increasing elongations to 300%, 500%, 700%, and finally to the break of the specimen; in

each cycle, the specimen followed a recovery step with no holding at strain.

Small-Angle Neutron Scattering (SANS). SANS was performed at the National

Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in

Gaithersburg, MD. SANS for samples in the melt at 160 °C and under strain at room

temperature were carried out at beamlines NG1 and NG3, respectively. The neutron beam

was ~ 6 mm in diameter and of incident wavelength $\lambda = 6$ Å in the case of the strain

experiments and 9 Å in the case of the melt experiments. The energy resolution of the

source was $\Delta\lambda / \lambda \sim 0.15$. For the experiments conducted in the molten state at 160 °C, the

samples were placed in a cell with copper windows; and for the room temperature

experiments under strain, samples were held with a tensile testing device and had an initial

active path length of 1.0-1.2 mm. Data were collected on a 2-D multiwire detector

providing a q range: 0.002 Å^{-1} $< q <$ 0.05 Å^{-1}, (where q is the scattering vector: $q = 4\pi \sin\theta$

$/ \lambda$ for a radiation of wavelength λ scattered through an angle 2θ). Each exposure was

collected over a 20-min period. These data were corrected for background scattering and

scattering from the relevant windows, and normalized for the change in scattering volume

present in the probe beam before and after extension. Incoherent background scattering

was subtracted from scattering of the fully protonated sample. In addition, the data from

the stretched, tagged polypropylene samples were normalized with the SANS pattern from

the untagged matrix at the same extension ratio in an effort to counteract any incoherent scattering. True strain (ε) was calculated from the ratio of the change in separation distance between two lines drawn at the middle of the specimen ($\Delta l = l - l_o$) to its original separation distance (l_o): $\varepsilon = \Delta l / l_o$. The tensile testing device was repositioned in the beam so that the probe beam always impinged on the vertical center of the sample after each stretching.

Data Analysis

Analysis of SANS. Analysis of polymer compatibility of the deuterated fraction within ePP was derived from the Zimm analysis of polymer blends originally developed for light and small-angle X-ray scattering. The coherent cross section ($d\Sigma/d\Omega$) of a homogenous blend of two polymer species, one of which is deuterium labeled, is[58-60]

$$\frac{d\Sigma}{d\Omega} = \left(a_H/v_H - a_D/v_D\right)^2 S(q) \tag{1}$$

where a_D and a_H are the scattering lengths of the repeat units (monomers) of the labeled and unlabeled species, which have the specific molar volumes of v_H and v_D, respectively. Assuming that the polymer chains form ideal (Gaussian) conformation which are unperturbed by the weak interactions between monomers, the structure factor $S(q)$ based on the random phase approximation (RPA) is[61]

$$\frac{1}{S(q)} = \frac{1}{v_H N_{w,H} \phi_H P_H(q^2 R_{g,H}^2)} + \frac{1}{v_D N_{w,D}(1-\phi_H) P_D(q^2 R_{g,D}^2)} - \frac{2\chi_{HD}}{v_0} \tag{2}$$

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where $N_{w,D}$, $N_{w,H}$, $R_{g,D}$, and $R_{g,H}$ are weight-averaged degree of polymerization and

z-average radii of gyration of the labeled and unlabeled species, respectively. The volume

fraction of the unlabeled species is denoted by ϕ_H and the reference volume is defined as

$v_o = (v_H v_D)^{\frac{1}{2}}$. The Flory-Huggins interaction parameter between segments of the labeled

and unlabeled species is represented by χ_{HD}. The intrachain functions $P_H(q^2 R_{g,H}^2)$ and

$P_D(q^2 R_{g,D}^2)$ are represented by a z-averaged Gaussian (Debye) function.[62,63]

At small scattering vector q, eqns 1 – 2 reduce to the Ornstein-Zernike or Zimm form:[64,65]

$$\frac{d\Sigma}{d\Omega}(q) = \frac{\frac{d\Sigma}{d\Omega}(0)}{1 + q^2 \xi^2} \tag{3}$$

$$\frac{d\Sigma}{d\Omega}(0) = \frac{\left(\frac{a_H}{v_H} - \frac{a_D}{v_D}\right)^2}{(v_H N_{w,H} \phi_H)^{-1} + (v_D N_{w,D} \phi_D)^{-1} - 2\,\chi_{HD}/v_0} \tag{4}$$

where ξ is the composition fluctuation correlation length. The correlation length is a

measure of distance over which the concentration fluctuations remain correlated and can be

obtained from the slope and extrapolated intercept of the graph $(d\Sigma/d\Omega)^{-1}$ vs. q^2.

We describe molecular anisotropy following the approach outlined by Mitchell and

Windle.[66] Molecular orientation is described by the azimuthal coherent cross section

averages of the second spherical harmonic component of a uniaxial distribution function:

$$P_2(\cos\alpha) = \frac{3\cos^2\alpha - 1}{2} \tag{5}$$

where α is the angle between the polymer coil and the orientation director vector (uniaxial extension axis). The orientational parameter (S) is represented in terms of the normalized amplitudes of the spherical harmonics:

$$S = \frac{\left\langle P_2(\cos\alpha)\right\rangle_{sample}}{\left\langle P_2(\cos\alpha)\right\rangle_0} \tag{6}$$

where $\left\langle P_2(\cos\alpha)\right\rangle_{sample}$ is computed by:

$$\left\langle P_2(\cos\alpha)\right\rangle = \frac{\int\limits_0^{\pi/2} \frac{d\Sigma}{d\Omega}(q,\alpha)P_2(\cos\alpha)\sin\alpha\, d\alpha}{\int\limits_0^{\pi/2} \frac{d\Sigma}{d\Omega}(q,\alpha)\sin\alpha\, d\alpha} \tag{7}$$

where $\frac{d\Sigma}{d\Omega}(q,\alpha)$ is the scattering cross section azimuthal average of the scattering patterns.

The model for a single unit is assumed to be an infinitely long rod, (in physical terms, assumes as stiff chain with an infinitely high M_w), so that the orthogonal components of the scattering model are $< P_2(\cos\alpha) >_0 = -\frac{1}{2}$. It should be noted that a complete description of the orientation function can be obtained from the scattering data from any of the four quadrants available, for instance $0 \le \alpha \le \pi/2$. The results presented here, determined from the complete azimuthal range of $0 < \alpha \le 2\pi$, are averaged over the four quadrants.

Results and Discussions

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Mechanical Properties. The physical properties of ePP-10 are tabulated in Tables 1−3.[56]

Figures 1−2 display the tensile behavior of ePP-10 and its solvent fractions, whose results

are summarized in Tables 2-3. Elastomeric polypropylene (ePP-10) exhibits tensile

properties characteristic of a polyolefin thermoplastic elastomer: a high (1300%)

elongation at break, a tensile strength of 8 MPa, good elastic recoveries as measured by a

moderate tensile set of 58% elongation (after stretching the sample to 300% elongation),

and stress-strain hysteresis. Hysteresis can be quantified in several ways; in Table 2 we

report the percentage of stress relaxation for a sample held at 100% elongation for 30 s. For

ePP-10, 47% of the engineering stress decays within 30 s when held at 100% elongation.

As described previously, the elastomeric polypropylene can be fractionated in boiling

solvents to extract fractions with increasing molecular weight, tacticity, and crystallinity

(Table 1). The tensile properties of the fractions obtained from boiling-solvent extraction

vary considerably, exhibiting properties from a weak gum elastomer for the ether-soluble

(ES) fraction to a semi-crystalline thermoplastic for the heptane-insoluble (HI) fraction

(Figure 1).[6] The heptane-insoluble fraction exhibits properties typical of a semi-crystalline

thermoplastic, deforming irreversibly with necking behavior typical of isotactic PP (Table

1). The heptane-soluble (HS) fraction is elastomeric and exhibits a higher tensile strength

and modulus than the whole polymer; this is consistent with its higher tacticity, density,

and heat of fusion of the heptane-soluble fraction (Tables 1−3, Figures 1−2).[67] The

ether-soluble fraction exhibits properties of a weak gum elastomer with a low tensile

modulus and strength, but a tensile set comparable to ePP-10 (Table 2). The stress

relaxation for both the ether-soluble (42%) and heptane-soluble fractions (39%) are similar

to that of ePP-10.

To investigate the effect of thermal history on the mechanical properties, a compression-molded sample of ePP-10 was annealed isothermally at 160 °C, 155 °C, and 150 °C for 24 hours successively, and then annealed for 12 hours subsequently at progressively lower temperatures in 10 °C increments. The tensile properties of this sample were compared to a compression-molded sample cooled slowly from the melt (approx. 5 °C/min). The tensile properties did not appear to be strongly influenced by these different thermal treatments.[68] The tensile properties of annealed ePP-10 are similar to the non-annealed compression molded sample; the elongation to break is somewhat less (1100%) and the retained force at 50% recovery is lower, but other tensile properties are not significantly different from the compression molded sample (Table 2). These results are surprising since in studies reported elsewhere,[56,69] we have shown that both the melting profiles (Figure 3) and the crystalline morphologies of ePP-10 (studied by tapping mode AFM) depend sensitively on the thermal history. The melting profile of the non-annealed sample reveals a broad melting range extending up to 160 °C, with two melting peaks centered at 40 °C and 150 °C, whereas the annealed sample shows a narrow high-temperature melting peak centered at 149 °C, as well as a distribution of melting peaks from 40 °C to 100 °C. While the distribution of melting peaks is quite different, the degrees of crystallinity are not strongly influenced by annealing, as manifest in similar heats of fusion (Table 1). Morphological studies reveal large hierarchical hedritic morphologies for samples annealed at 120 – 130 °C.[69] While morphological studies were not carried out on annealed samples used for tensile tests, these results imply that the tensile properties are determined to first order by the total degree of crystallinity rather than

the specific morphological features observed. Further studies are warranted to interrogate the influence of thermal history and morphology on the properties of these materials.

Stress-strain hysteresis is a characteristic feature of polyolefin thermoplastic elastomers. In Table 2, hysteresis is reported as tensile stress relaxation and retained force. Tensile stress relaxation is reported as a percentage decrease of engineering stress when held at 100% elongation for 30 s, whereas retained force is the ratio of the stress at 50% elongation to that at 100% elongation on the second cycle (Table 2). The stress relaxation of $47 - 48\%$ is similar for annealed and non-annealed samples of ePP-10 at 100% elongation, whereas the retained force is lower for the annealed sample. A tensile recovery test on ePP-10 and the heptane-soluble fraction (HS) reveals a higher degree of hysteresis for HS (Table 2 and Figure 2). We had envisioned that the presence of a significant amount (48%) of the low-crystallinity ES fraction in ePP-10 might be a source of the stress relaxation in ePP-10. However, the higher degree of hysteresis for the heptane-soluble fraction (from which all the ether-soluble fraction has been removed) relative to ePP-10 implies that the ether soluble fraction is not the sole or even primary source of stress relaxation in ePP-10. Our current hypothesis, which is partially supported from rheo-optical studies of the relaxation properties,[47,55] is that one of the primary sources of stress relaxation is amorphous segments of chains partially tethered with the crystallites. Since there is no reason to believe that every chain ends or begins with a crystallizable isotactic sequence, it is likely that these materials contain atactic chain sections that are only partially constrained in only one crystal and are thus free to relax following a deformation.

A series of tensile measurements were carried out at both 25 °C and 50 °C in a thermostated Minimat Tensile Testing device to assess the temperature dependence of tensile properties (Table 3). These experiments were carried out with a crosshead separation of 10 mm/min, different than those reported in Table 2, but the moduli and tensile sets of ePP-10 and HS-ePP10 are roughly comparable to those reported in Table 2. Temperature-dependence experiments reveal that both ePP-10 and HS retain elastomeric properties at 50 °C, although the moduli decrease by a factor of 2 and the tensile sets increase by approx. 60% at 50 °C. It should be noted that the tensile set in these temperature-dependent studies is measured after 100% elongation, different than those reported in Table 2 using 300% elongation.

Deuterated ePP. A sample of deuterated ePP was prepared and fractionated in order to probe the molecular orientation of deuterated ePP chains under strain. The synthesis of deuterated polypropylene was carried out under conditions optimized to match ePP-10. The characterization of deuterated ePP and its solvent fractions is given in Table 4. The tacticity of deuterated ePP (d-ePP), reported as the fraction of isotactic [mmmm] pentads, is [mmmm] = 30 %, similar to that of ePP-10 ([mmmm] = 34 %).[56,69] The number average molecular weights are comparable (d-ePP M_n = 129 kg/mol vs. ePP-10 M_n = 87 kg/mol), but the molecular weight distribution of the deuterated d-ePP was broader at M_w/M_n = 5.5. The melting point and heat of fusion of d-ePP are T_m = 128 °C and ΔH = 13 J/g, respectively. These values are lower than those of the protonated samples, but within the range of elastomeric polypropylenes we have tested previously.[39,56,69] Fractionation of d-ePP was carried out under similar conditions to that of ePP-10; the properties of the deuterated fractions are comparable, although not identical to those of ePP-10 (Tables 1

and 4). Fractionation of d-ePP generated slightly less weight percent of an ether-soluble fraction, comparable amounts of the heptane-soluble fraction and slightly more of a heptane-insoluble fraction compared to ePP-10 (Tables 1 and 4).

Small-angle neutron scattering (SANS) was carried out on a series of samples of ePP-10 doped with 5 wt% of a deuterated ePP or its fractions. Shown in Figure 4 is the 1-D SANS coherent cross section profiles of ePP-10 doped with the deuterated high-tacticity fraction (dHI-ePP) in the melt at 160 °C and crystalline states at 25 °C. The scattering profiles at 160 °C and 25 °C are comparable over the range of scattering vector q investigated. The cross sections in the crystalline state are slightly lower than those at 160 °C at high q region. Fitting the data with eqns $1 - 2$, assuming a Random Phase Approximation (RPA) function, yields a good data regression. The similarity of the scattering profiles and their conformance to the RPA model imply that deuterated heptane-insoluble fraction is miscible and well-dispersed in ePP-10 and there is only a slight change in the conformation of the dHI-ePP fraction upon crystallization from the melt.

Similar experiments carried out with ePP-10 doped with 5 wt% deuterated ES fraction (dES-ePP) revealed quite a different behavior. The scattering profiles of ePP-10 doped with deuterated low-tacticity fraction (dES-ePP) at 160 °C are similar to those of dHI-ePP and conform reasonably well to the RPA model, indicating that in the melt, the deuterated ether-soluble fraction is well-dispersed in ePP-10 (vida infra). In contrast, the scattering profile for this deuterated fraction at 25 °C is quite different (Figure 5). At 25 °C, the cross sections decay steeply with q in the low q region ($q \leq 0.015$ Å), and at higher scattering vectors, $q \geq 0.01$ Å, the cross sections at 25 °C are much lower than those at 160 °C. The

lower cross sections at high scattering vector suggest that at 25 °C the deuterated chains are not homogeneously mixed. For mixtures with the same composition, Alamo and co-workers calculated that scattering cross sections for a two-phase polymer melt are lower than those of a one-phase system at high q range.[70]

Analysis of the scattering data of the deuterated samples according to the Ornstein-Zernike (OZ) or Zimm analysis (eqns 3−4) in a low q region provided further information. As shown in Figure 6, all labeled fractions within ePP show a linear dependence of $(d\Sigma/d\Omega)^{-1}$ vs. q^2 at low scattering vector ($q \leq 0.02$ Å). In the melt at 160 ºC, the OZ plots of dHI-ePP and dES-ePP extrapolate to positive intercepts. The positive intercepts suggest a homogeneous one-phase system indicating that the deuterated fractions are miscible with ePP in the melt.[64,65] Extrapolation of the OZ plots to $q = 0$ yields cross sections $d\Sigma/d\Omega(0)$ of 765 and 185 cm^{-1} for dHI-ePP and dES-ePP, respectively. The calculated cross sections for an ideal mixing case ($\chi_{HD} = 0$) are 533 and 167 cm^{-1} for dHI-ePP and dES-ePP, respectively. The Flory-Huggins interaction parameters calculated from the OZ plots are identical for both systems, $\chi_{HD} = 1.4 \times 10^{-4}$, but smaller than the critical interaction parameter χ_s (Table 5). The interaction parameter for a regular homogeneously mixed polyolefin blend is usually between the athermal limit and stability limit: $0 \leq \chi \leq \chi_s$;[61] the stability limit is given by

$$\chi_s = \frac{v_0}{2}\left(\frac{1}{v_H N_{w,H}\phi_H} + \frac{1}{v_D N_{w,D}\phi_D}\right)$$

(8)

The OZ plot analysis indicates that both dHI-ePP and dES-ePP are homogeneously mixed in the melt at 160 ºC without clustering / aggregation of the labeled chains.

In the crystalline state at 25 ºC, the Ornstein-Zernike plots yield positive extrapolated intercepts for dePP-ePP, dHS-ePP, and dHI-ePP (Figure 6) that suggest a homogeneous one-phase system. The OZ plot of the low-tacticity deuterated fraction (dES-ePP), on the other hand, extrapolates to a negative intercept. The negative intercept suggests that the d-ES chains are not homogeneously well-mixed within the ePP matrix. This suggests that slow crystallization of dES-ePP induces an inhomogeneity of the deuterated low-tacticity chains and high-tacticity chains of ePP. There are two possibilities: either the d-ES fraction does not co-crystallize at all or it participates only in secondary crystallization and is thus not homogeneously dispersed in the crystalline phase. Since we have shown in other studies that the ether soluble fraction ES-ePP can crystallize (albeit to a very low degree) [55,69] we attribute the inhomogeneous distribution of the dES-ePP to a differential partitioning of the dES-ePP chains in the amorphous and crystalline domains due to a large mismatches in crystallization temperatures and kinetics of the d-ES and ePP chains.[38]

This segregation is likely not a consequence of an isotope effect since the Flory-Huggins interaction parameter between the labeled and unlabeled chains is small, $\chi_{HD} = 1.4 \times 10^{-4}$ in the melt and the product of the interaction parameter with number of repeat units is below the isotope-driven segregation limit, $\chi N \leq 2$. Nevertheless, we do not observe a distinct inter-phase boundary: the coherent cross sections decay with an exponent of -2.2 in the whole q range; the Porod region with q-dependence of $d\Sigma/d\Omega \sim q^{-4}$ is not seen. Furthermore, the cross section data fail to yield a straight line when fitted to a two-phase system proposed by Debye and co-workers in a plot of $d\Sigma/d\Omega^{-1/2}$ vs. q^2 in the low q region.[71,72] The negative intercept of the OZ plot and the absence of a sharp phase

boundary suggest that there is not strong phase segregation, but rather, following a slow crystallization from the melt, the low tacticity d-ES chains, which consist of non-crystallizable atactic sequences, are excluded from the highest melting crystalline domains.

Similar crystallization-induced phase separation has also been observed by Wignall and co-workers on the blends of linear (high-density) and branched (low-density) polyethylenes investigated by DSC, SANS, and small angle X-ray scattering (SAXS).[73,74] In the molten state, the blends were homogeneous. At room temperature following a slow cooling (0.75 °C/min), the components phase segregated due to melting point (~20 °C) and structural differences. Rapid quenching from the melt to −78 °C resulted in extensive co-crystallization to produce a miscible one-phase system. In addition, Seki and co-workers have observed similar behavior for isotactic polypropylene / ethylene-propylene blends by SANS and transmission electron microscopy (TEM).[75] In the molten state, the polymer blends were in a homogeneous single-phase mixture, but at room temperature following a slow crystallization from the melt, the polymer blends were phase separated due to crystallization of the isotactic polypropylene. The ethylene-propylene copolymer, which lacks crystallizability, was excluded from the crystalline phase of the polypropylene chains.

SANS of ePP-10 under Strain. The tensile properties of the various solvent fractions are reported in Table 2. In an effort to establish the role of the various fractions in the tensile properties of ePP-10, small angle neutron scattering was carried out with a variety of deuterium-labeled ePP-10s under strain. SANS measurements were taken *in situ* at 100%

and 300% strain, and after releasing the samples from strain to monitor the deformation of the tagged chains. The experimental protocol for SANS was as follows: the sample was elongated to 100% strain, a SANS image *in situ* was collected under strain, and then the sample was elongated to 300% strain and a second SANS image was taken. The stress relaxation of the labeled chains was measured as well after 1 – 1.5 hour at 300% strain. Permanent deformation was monitored from samples held at 300% strain for 1 – 1.5 hour and then released and allowed to relax for one day. No induced anisotropy was seen in the SANS patterns in the (control) case of the undoped (fully protonated) ePP sample, even for strains up to 300%.

Shown in Figure 7 are 2-D SANS images of ePP-10 labeled with 5 wt% of d-ES component at room temperature (dES-ePP). Prior to uniaxial tensile stretching, the SANS image shows an isotropic scattering pattern. Upon stretching, the labeled chains within ePP exhibit an anisotropic SANS pattern. Bright spots develop along the equatorial axis, which indicate molecular alignment along the direction of the strain axis. The molecular anisotropy can be represented by azimuthal plots of coherent cross section over a scattering vector range of 0.0106 Å^{-1}< q < 0.0140 Å^{-1}. This is shown in Figure 8 for the dES-ePP system. The q-range, which represents structure on ~500 Å length scale, corresponds to the most intense signal in the scattering cross section. The molecular anisotropy is reported in terms of an orientation parameter <P$_2$>, calculated according to eqns 5 – 7, and is reported in Table 6. The results of these experiments (Table 6) reveal that both the deuterated heptane-insoluble fraction (dHI-ePP) and the deuterated ether-soluble fraction (dES-ePP) show considerable anisotropy when ePP-10 labeled with these fractions are held at 100% or 300% strain. In addition, when released from a 300% strain, all samples show evidence of

residual anisotropy, revealing a permanent deformation of the material when subjected to a 300% strain. The final state of the sample retains both macroscopic distortion to the eye and residual molecular orientation in the SANS profiles.

The degree of orientation of the deuterium labeled fractions under strain, as measured by the orientation parameter $<P_2>$, increases with increasing strain for both the d-HI and d-ES fractions. The orientation parameter for dHI-ePP blend under deformation is rather modest; $<P_2> = 0.09 \pm$ at 100% strain and $<P_2> = 0.24 \pm 0.02$ at 300% strain. Molecular orientations after 1–1.5 hours stress relaxation under 300% strain do not change appreciably. Similar results were obtained from the d-ES fraction within ePP-10.[76] For the d-ES fraction the molecular anisotropy increases with increasing strain with values of $<P_2>$ = 0.28 ± 0.02 at 100% strain and $<P_2> = 0.45 \pm 0.03$ at 300% strain. Significantly after 1-hour at 300% strain, the labeled ether-soluble fraction in dES-ePP does not show appreciable relaxation despite its low tacticity and crystallinity. One day after release 1 hour of straining at 300% the orientation parameter reduces to $<P_2> = 0.17 \pm 0.02$.

The fact that the d-HI fraction is oriented and retains its orientation at 300% strain is expected, since this highly crystalline fraction is expected to co-crystallize with ePP-10; the scattering data for dHI-ePP at 25 °C are consistent with this interpretation. Thus, under strain, the d-HI chains are constrained in the crystalline elastomeric network of ePP-10 and some fraction of these chains retain their orientation when held at 300% strain. More surprising perhaps is the observation that the deuterated ether-soluble fraction also remains anisotropic when held at 100% or 300% strain. Despite its low crystallinity, (≤ 2 % by DSC and WAXS, Table 1) the d-ES chains remain oriented when held under strain. These data

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suggest that at least some segments of the deuterated ether-soluble chains remain oriented under strain. Thus, while the ES fraction by itself exhibits the properties of a weak gum elastomer (Figure 1 and Table 2), when a deuterated ether-soluble fraction of polypropylene elastomer is blended into ePP-10, this fraction does not relax completely, as might be expected if this fraction were incapable of crystallizing. Rather, this fraction remains anisotropic under strain. We attribute this residual orientation of the deuterated fraction to the co-crystallization of the d-ES chains with the more highly tactic components of ePP-10. This result is corroborated by morphological studies and wide-angle X-ray diffraction (WAXD) that the ES fraction of ePP-10 crystallizes by itself and also co-crystallizes with more highly tactic components of ePP-10.[55,69] These data taken together imply that the physical properties of ePP-10 are not simply predicted from the properties of the individual components as described in Figure 1 and Table 2, but rather that the various fractions contribute cooperatively.

At this point, it is important to point out that in contrast to a deuterated sample of ePP (d-ePP) or the deuterated heptane-soluble and heptane-insoluble fractions (d-HS and d-HI), which appear to be homogeneously distributed within ePP-10 at 25 °C, the d-ES fraction is not homogeneously distributed within ePP-10 in its semi-crystalline form at 25°C. Thus, we cannot directly compare the order parameters of dES-ePP to that of dHI-ePP. Nevertheless, the fact that the d-ES does not relax reveals clearly that there is some constraint that prevents the deuterated ether-soluble fraction from relaxing when held at strain.

Upon removal of the stress field, permanent anisotropy is observed in all deuterium labeled samples; the final state of the sample retains both macroscopic distortion to the eye and residual molecular orientation in the SANS profiles. The non-zero orientation parameters after releasing from stress signify that the labeled chains are permanently oriented. The orientation parameters of the permanent anisotropy (Table 6) are similar for the doped whole polymer (dePP-ePP) and the intermediate-tacticity fraction (dHS-ePP) with value of $\langle P_2 \rangle = 0.13 \pm 0.02$. The permanent anisotropy in the high-tacticity fraction (dHI-ePP) yields an orientation parameter $\langle P_2 \rangle = 0.20 \pm 0.01$. Compared to $\langle P_2 \rangle = 0.24 \pm 0.02$ at 300% strain, the doped high-tacticity chains experience only a small decrease in anisotropy upon releasing from stress; the small relaxation of molecular anisotropy suggests that the high-tacticity fraction are a primary source of the plastic deformation observed even when it blended with lower-tacticity fractions. The plastic deformation of the high-tacticity fraction is analogous to that seen in the tensile properties of the neat HI fraction (Figure 1).

Conclusions

Polypropylene synthesized by unbridged 2-arylindene metallocene / MAO catalyst system is a thermoplastic elastomer. The material retains its elastomeric properties even at elevated temperature of 50 °C. The tensile properties are a consequence of combination of chain sequences that are both crystalline and amorphous; the amorphous sequences are oriented readily under strain, and the crystalline sequences provide a physical network for elastic recovery. The elastomeric polypropylene (ePP) is compositionally heterogeneous and made up of polypropylene chains of varying tacticity, crystallinity, and molecular

weight. Each fraction has quite different properties: the high-tacticity HI fraction exhibits tensile behavior typical of a thermoplastic; the intermediate-tacticity HS fraction exhibits quite good elastomeric properties similar to ePP, while the low-tacticity ES fraction acts like a gum elastomer.

Small-angle neutron scattering (SANS) has been used to study the behavior of each deuterated solvent fraction residing within ePP in the melt and crystalline states. In a liquid state, all deuterated fractions within ePP are well-mixed in a one-phase system. In the crystalline state at 25 °C following a slow crystallization from the melt, all deuterated doped fractions (dePP-ePP, dHS-ePP, and dHI-ePP) are homogeneously mixed except the low-tacticity fraction (dES-ePP). The slow crystallization from the melt induces a partitioning of the d-ES chains into the less crystalline domains.

The role of each fraction residing within ePP under tensile deformation was studied using SANS. The highest-tacticity fraction within ePP (dHI-ePP) shows a plastic deformation with a very little molecular anisotropy relaxation upon releasing from stress. The intermediate-tacticity fraction (dHS-ePP) exhibits similar permanent anisotropy behavior as the whole d-ePP (dePP-ePP); this suggests that the elasticity in ePP may be dominated by the intermediate-tacticity fraction. The low-tacticity fraction (dES-ePP), despite its low crystallinity, can co-crystallize with the crystalline matrix. SANS shows that the molecular anisotropy of d-ES chains within ePP does not relax appreciably when held under strain.

Acknowledgements

Figure Captions

Figure 1. Tensile properties of ePP-10 and its solvent fractions.

Figure 2. Hysteresis curves of ePP-10 and the intermediate-tacticity heptane-soluble (HS) fraction.

Figure 3. Effect of thermal history on the melting profile of elastomeric polypropylene ePP-10 as measured by DSC. Reprinted from Ref [56].

Figure 4. 1-D SANS coherent cross section profiles of high-tacticity heptane-insoluble fraction within ePP (dHI-ePP) in the melt (160 °C) and crystalline (25 °C) states.

Figure 5. 1-D SANS coherent cross section profiles of low-tacticity ether-soluble fraction within ePP (dES-ePP) in the melt (160 °C) and crystalline (25 °C) states.

Figure 6. Ornstein-Zernike or Zimm plots of deuterated fractions within ePP in the melt (160 °C) and crystalline (25 °C) states.

Figure 7. 2-D SANS patterns of d-ES within ePP (dES-ePP): (a). unstretched, and (b). at 300 % strain along the vertical direction.

Figure 8. 1-D azimuthal SANS cross section profile of dES-ePP averaged over a q-range of 0.0106 Å^{-1} $\leq q \leq$ 0.0140 Å^{-1} ($\phi = 0°$ and 180° along the equatorial axis).

Table 1. Polymer Characteristics and Physical Properties

sample	wt %	M_n^a (kg/mol)	M_w/M_n^a	[mmmm] %[b]	[m] %[b]	IR index[c]	T_m (°C)[d]	ΔH (J/g)[d]	Crystallinity% (DSC)	(XRD)
ePP-10	100	87	2.3	34	73	0.34	42-149	22	11	8
ES-ePP10	48	70	2.1	21	67	0.19	41-45	2	1	2
HS-ePP10	42	96	2.3	44	79	0.38	42	32	15	11
HI-ePP10	10	173	2.5	76	92	0.70	47-155	82	39	37
ePP-10 annealed							50-160	27	14	

[a] determined by GPC (waters 150 °C) at BP Chemical Co.
[b] determined by ^{13}C NMR, [mmmm] is fraction of five contiguous isotactic sequences
[c] determined by the ratio of absorbance intensity A_{998}/A_{975}
[d] determined by DSC endotherm scan from 0 °C to 200 °C at 20 °C/min

Table 2. Tensile Properties of ePP-10 and its Solvent Fractions

Sample	ePP-10	ES-ePP10	HS-ePP10	HI-ePP10	ePP-10 (annealed)
density (g/cm^3)	0.863	0.859	0.877	0.913	0.862
tensile strength (MPa)	8.01	0.81	18.2	26.1	6.07
tensile modulus (MPa)	6.28	1.73	19.5	259	8.94
elongation to break (%)	1,305	>3,000	994	690	1,100
tensile stress relaxation[a] (%)	47.3	41.6	38.7	n.o.[b]	48.2
retained force, 50% recovery[c] (%)	10.6	18	26.5	n.o.[b]	5.4
recovery tests[d]					
tensile set first cycle[e] (%)	58	53	35	n.o.[b]	65
tensile set second cycle[f] (%)	17	6	15	n.o.[b]	29

[a] decrease in stress (or force) during 30 s the specimen is held at 100% elongation
[b] not observed, exhibits plastic deformation
[c] ratio of stress at 50% elongation during recovery to stress at 100% elongation at the 2nd cycle
[d] three extension cycles to 300% with no holding time at extension
[e] elongation at which stress returns to the baseline after 300% elongation
[f] elongation at which stress increases above the baseline

Table 3. Temperature-dependent Tensile Properties

Sample	[mmmm] %	temperature (°C)	tensile modulus (MPa)	tensile set[a] (%)
ePP-10	34	25	11.8 ± 0.8	17.1 ± 1.0
ePP-10	34	50	5.8 ± 1.1	28.3 ± 1.1
HS-ePP10	44	25	19.6 ± 0.6	12.2 ± 0.1
HS-ePP10	44	50	7.4 ± 0.2	19.6 ± 0.9

[a] elongation at which stress returns to the baseline after 100% elongation

Table 4. Polymer Characteristics in SANS Studies

sample	wt%	M_n[a] (kg/mol)	M_w/M_n[a]	[mmmm] %[b]	T_m (°C)[c]	ΔH (J/g)[c]
d-ePP	100	129	5.5	30	30-147	13
d-ES	34	87	3.6	18[d]	-	0
d-HS	42	129	3.7	33[d]	35-140	18
d-HI	24	186	6.3	51[d]	30-155	50

[a] determined by high-temperature GPC at BP Chemical Co.
[b] determined by ^{13}C NMR, fraction of five contiguous isotactic sequences
[c] determined by DSC, endotherm scans from −50 °C to 200 °C at 20 °C/min
[d] values estimated from protonated fractions prepared and fractionated under similar conditions.[39]

Table 5. SANS Molecular Characteristics in Melt at 160 °C

sample	χ_{HD}[a] 10^4	$\chi_{HD\text{-critical}}$[a] 10^4	$d\Sigma/d\Omega(0)_{exp}$ (cm^{-1})	$d\Sigma/d\Omega(0)_{calc}$[a,b] (cm^{-1})
dES-ePP	1.4	14.4	185	167
dHI-ePP	1.4	4.7	765	533

[a] specific molar volumes of deuterated fractions are estimated from those of protonated fractions
[b] ideal mixing system with Flory-Huggins interaction parameter $\chi_{HD} = 0$

Table 6. SANS Molecular Anisotropy in Crystalline State at 25 °C

sample	orientation parameter $\langle P_2 \rangle$ 0%	100%	300%	released[a]
dePP-ePP	0 ± 1	-	-	14 ± 1
dES-ePP[b]	0 ± 1	28 ± 2	45 ± 3	17 ± 2
dHS-ePP	0 ± 1	-	-	12 ± 1
dHI-ePP	1 ± 1	9 ± 1	24 ± 2	20 ± 1

[a] after 1-day released from 300% strain for 1−1.5 hour
[b] crystallization-induced non-homogeneous mixture; data not to be compared with other fractions

References

(1) Jebens, A. *Polypropylene Resins*; SRI International: Menlo Park, CA, 1997.

(2) Natta, G.; Mazzanti, G.; Crespi, G.; Moraglio, G. *Chim. Ind.* **1957**, *39*, 275-283.

(3) Natta, G. *J. Polym. Sci* **1959**, *34*, 531-549.

(4) Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858-3866.

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

(6) Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrel, J. R.; Mulhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851-3858.

(7) Tullock, C. W.; Tebbe, F. N.; Mulhaupt, R.; Ovenall, D. W.; Setterquist, R. A.; Ittel, S. D. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3063-3081.

(8) Ittel, S. D. *J. Macromol. Sci. Chem.* **1990**, *A27*, 9-11.

(9) Tullock, C. W.; Mulhaupt, R.; Ittel, S. D. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 19-23.

(10) Job, R. C.; Haas, D. F. U.S. Patent 5,118,768, 1992.

(11) Job, R. C. U.S. Patent 5,089,573, 1992.

(12) Chen, R.; Xie, M. R.; Wu, Q.; Lin, S. G. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 411-415.

(13) Kuhl, O.; Koch, T.; Somoza, F. B.; Junk, P. C.; Hey-Hawkins, E.; Plat, D.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *604*, 116-125.

(14) Longo, P.; Amendola, A. G.; Fortunato, E.; Boccia, A. C.; Zambelli, A. *Macromol. Rapid Commun.* **2001**, *22*, 339-344.

(15) Mansel, S.; Perez, E.; Benavente, R.; Perena, J. M.; Bello, A.; Roll, W.; Kirsten, R.; Beck, S.; Brintzinger, H. H. *Macromol. Chem. Phys.* **1999**, *200*, 1292-1297.

(16) Nedorezova, P. M.; Tsvetkova, V. I.; Bravaya, N. M.; Savinov, D. V.; Optov, V. A. *Polym. Sci. Ser. A* **2000**, *42*, 573-579.

(17) Schmidt, R.; Alt, H. G. *J. Organomet. Chem.* **2001**, *621*, 304-309.

(18) Yoon, J. S.; Lee, Y. S.; Park, E. S.; Lee, I. M.; Park, D. K.; Jung, S. O. *Eur. Polym. J.* **2000**, *36*, 1271-1275.

(19) Resconi, L.; Piemontesi, F.; Lin-Chen, Y. U.S. Patent 5,747,621, 1998.

(20) Sassmannshausen, J.; Bochmann, M.; Rosch, J.; Lilge, D. *J. Organomet. Chem.* **1997**, *548*, 23-28.

(21) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 2601-2617.

(22) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030-2031.

(23) Llinas, G. H.; Dong, S. H.; Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242-1253.

(24) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G. Y.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 8569-8570.

(25) Cheng, H. N.; Babu, G. N.; Newmark, R. A.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 6980-6987.

(26) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771-3778.

(27) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779-3786.

(28)   Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000-1009.

(29)   Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelae, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348-4355.

(30)   Kukral, J.; Lehmus, P.; Feifel, T.; Troll, C.; Rieger, B. *Organometallics* **2000**, *19*, 3767-3775.

(31)   Dreier, T.; Erker, G.; Froehlich, R.; Wibbeling, B. *Organometallics* **2000**, *19*, 4095-4103.

(32)   Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217-219.

(33)   Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586-11587.

(34)   Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174-11182.

(35)   Kravchenko, R.; Masood, A.; Waymouth, R. M. *Organometallics* **1997**, *16*, 3635-3639.

(36)   Petoff, J. L. M.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909-5916.

(37)   Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707-2715.

(38)   Carlson, E. D.; Krejchi, M. T.; Shah, C. D.; Terakawa, T.; Waymouth, R. M.; Fuller, G. G. *Macromolecules* **1998**, *31*, 5343-5351.

(39)   Hu, Y. R.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908-6916.

(40)   Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 2039-2046.

(41)   Kravchenko, R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 1-6.

(42)   Lin, S.; Hauptman, E.; Lal, T. K.; Waymouth, R. M.; Quan, R. W.; Ernst, A. B. *J. Mol. Catal. A: Chem.* **1998**, *136*, 23-33.

(43)   Petoff, J. L. M.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316-11322.

(44)   Waymouth, R. M.; Kravchenko, R.; Bendig, L. L.; Moore, E. J.; Myers, C. L.; Quan, R. W.; Ernst, A. B. U.S. Patent 6,160,064, 2000.

(45)   Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147-4155.

(46)   Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 8100-8106.

(47)   Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 8094-8099.

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

(49)   Lin, S.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 8283-8290.

(50)   Petoff, J. L. M.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 7984-7989.

(51)   Tagge, C. D.; Kravchenko, R. L.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 380-388.

(52)   Boue, F. *Adv. Polym. Sci.* **1987**, *82*, 47-101.

(53)   Lohse, D. J. *Rubber Chemistry and Technology* **1994**, *67*, 367-383.

(54) Zirkel, A.; Urban, V.; Richter, D.; Fetters, L. J.; Huang, J. S.; Kampmann, R.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 6148-6155.

(55) Wiyatno, W.; Pople, J. A.; Gast, A. P.; Waymouth, R. M.; Fuller, G. G. *submitted to Macromolecules* **2002**.

(56) Wiyatno, W.; Chen, Z.-R.; Liu, Y.; Waymouth, R. M.; Krukonis, V.; Brennan, K. *submitted to Macromolecules* **2002**.

(57) Wunderlich, B. *Macromolecular Physics, Vol. 2: Crystal Nucleation, Growth, Annealing*, 1976.

(58) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; Gennes, P. G. D. *Macromolecules* **1975**, *8*, 804-818.

(59) Maconnachie, A.; Richards, R. W. *Polymer* **1978**, *19*, 739-762.

(60) Hayashi, H.; Flory, P. J.; Wignall, G. D. *Macromolecules* **1983**, *16*, 1328-1335.

(61) De Gennes, P. G. *Scaling Concepts in Polymer Physics*, 1979.

(62) Glatter, O.; Kratky, O.; Editors. *Small Angle X-ray Scattering*, 1982.

(63) Debye, P. *J. Phys. & Colloid Chem.* **1947**, *51*, 18-32.

(64) Wignall, G. D. *Encycl. Polym. Sci. Eng.* **1987**, *10*, 112-184.

(65) Alamo, R. G.; Londono, J. D.; Mandelkern, L.; Stehling, F. C.; Wignall, G. D. *Macromolecules* **1994**, *27*, 411-417.

(66) Bassett, D. C.; Editor. *Developments in Crystalline Polymers-2*, 1988.

(67) Myers, C. A.; Allen, C.; Ernst, A.; Naim, H. *Society of Plastics Engineers (SPE) Conference Proceedings* **1999**, *55*, Session M10.

(68) The tensile properties were also tested on compression-molded samples retained for one year at room temperature. The tensile properties of the year-old samples were very similar to those tested one day after compression molding.

(69) Schonherr, H.; Wiyatno, W.; Pople, J. A.; Frank, C. W.; Fuller, G. G.; Gast, A. P.; Waymouth, R. M. *Macromolecules* **2002**, *35,* 2654-2666.

(70) Alamo, R. G.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J.; Londono, J. D.; Mandelkern, L.; Stehling, F. C.; Wignall, G. D. *Macromolecules* **1997**, *30*, 561-566.

(71) Debye, P.; Anderson, H. R., Jr.; Brumberger, H. *J. Appl. Phys.* **1957**, *28*, 679-683.

(72) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518-525.

(73) Wignall, G. D.; Alamo, R. G.; Londono, J. D.; Mandelkern, L.; Kim, M. H.; Lin, J. S.; Brown, G. M. *Macromolecules* **2000**, *33*, 551-561.

(74) Wignall, G. D.; Londono, J. D.; Lin, J. S.; Alamo, R. G.; Galante, M. J.; Mandelkern, L. *Macromolecules* **1995**, *28*, 3156-3167.

(75) Seki, M.; Nakano, H.; Yamauchi, S.; Suzuki, J.; Matsushita, Y. *Macromolecules* **1999**, *32*, 3227-3234.

(76) The order parameters of dES-ePP are not to be compared with other deuterated fractions that are homogeneously mixed with the ePP.