Conformational Asymmetry in Poly(vinylcyclohexane) Containing Diblock Copolymers

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Received December 9, 1993; Revised Manuscript Received March 31, 1994[●]

ABSTRACT: Three types of compositionally symmetric and nearly monodisperse diblock copolymers, poly(1,2-butadiene)–poly(styrene) (1,2-PB–PS), poly(*cis*-1,4-isoprene)–poly(styrene) (1,4-PI–PS), and poly(1,4-butadiene)–poly(styrene) (1,4-PB–PS), were anionically synthesized and subsequently catalytically saturated, yielding poly(vinylcyclohexane)–poly(ethylethylene) (PVCH–PEE), poly(ethylenepropylene)–poly(vinylcyclohexane) (PEP–PVCH), and poly(ethylene)–poly(vinylcyclohexane) (PE–PVCH). The order–disorder transition temperature, T_{ODT}, was determined for the unsaturated and saturated diblock copolymers using dynamic mechanical spectroscopy. Changes in T_{ODT} with saturation are dependent on the resulting polyolefin microstructure. PVCH–PEE has a much lower T_{ODT}, while PEP–PVCH and PE–PVCH display higher ones, relative to the unsaturated precursor materials. Group contribution analysis qualitatively anticipates the PVCH–PEE behavior but fails to account for the PEP–PVCH and PE–PVCH results. Entropic arguments based on differences in the conformational characteristics of each block appear to be correlated with the associated variations in the segment–segment interaction parameter, χ. These findings support earlier speculation regarding the role of conformational asymmetry in the thermodynamics of polymer–polymer systems.

Introduction

Model polyolefins, developed with controlled microstructure and architecture through the catalytic hydrogenation of unsaturated precursor polymers, are attractive materials for conducting fundamental studies related to a variety of topics in polymer science and engineering.[1–13] These saturated compounds possess certain physical properties that can be superior to the unsaturated precursors, such as enhanced thermal and oxidative resistance. Furthermore, anionically polymerized precursor molecules can be designed with specific molecular architectures and conformational characteristics not accessible using other currently available methods such as Ziegler–Natta catalysis. Such compounds have been especially useful in elucidating the underlying molecular factors contributing to the thermodynamics and phase behavior of diblock copolymer systems.

One of the earliest systematic studies of catalytically hydrogenated polydiene block copolymers was reported by Halasa.[5] He exploited the versatility of lithium-catalyzed anionic polymerization along with the high efficiency of certain homogeneous saturation reactions in producing a host of model polyolefins. Subsequent collaborations with Cohen and co-workers[6,7] revealed a rich spectrum of thermodynamic and structural properties in these materials, particularly regarding the crystallization behavior in the microphase-separated state. Poly(styrene)-based triblock copolymers that contain a hydrogenated (rubbery) polyolefin center block constitute an important sector of the commercial block copolymer market, finding applications in adhesives, footware, and other items of commerce where long-term stability is an issue. Owens et al.[8] have studied the effect of hydrogenation on the thermodynamic properties of a model poly(1,2-butadiene)–poly(styrene) diblock copolymer using small-angle X-ray scattering (SAXS) measurements. As might be expected from rudimentary solubility parameter considerations, saturation of poly(1,2-butadiene) to poly(ethylethylene) influences the Flory–Huggins χ parameter and accordingly shifts the order-to-disorder phase transition temperature. These authors also encountered an anomalous peak position in the SAXS profiles which was attributed to the asymmetry in statistical segment lengths between the block components. Such "conformational asymmetry" is of central importance to the work reported here. However, we will relate this feature to variations in χ, not the microdomain periodicity, which has been considered in previous publications.[3,9]

Extensive experimentation in our laboratory with poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymers has revealed the importance of composition fluctuations on the phase behavior of this class of materials near the order–disorder transition (ODT).[9,10] In the disordered state, large-amplitude composition fluctuations lead to significant deviations from mean-field behavior as revealed by small-angle neutron scattering (SANS) and rheological measurements. At compositions close to $f_{\mathrm{PEP}} = 0.65$ (f_{PEP} refers to the volume fraction of PEP) we have discovered modulated and perforated hexagonal-layered phases between the classical lamellar and hexagonally packed cylindrical phases;[11] in some cases all four ordered phases, and the disordered state, can be accessed in a single material through changes in temperature. Most recently, we have expanded our study of asymmetric polyolefin diblock copolymers to include systems composed of poly(ethylene) (PE) and poly(vinylcyclohexane) (PVCH) along with PEP and PEE, i.e., PE–PEE, PE–PEP, PVCH–PEE, PEP–PVCH, and PE–PVCH diblock copolymers. Our work with these materials have revealed a rich polymorphism that contains certain elements of universality (e.g., hexagonally modulated and perforated layered phases) and a striking asymmetry in phase behavior with respect to the composition, f.[12] These discoveries leave little doubt that block copolymer thermodynamics is not universal in the classical parameters f and χN alone, where N is the degree of polymerization. We have concluded that at least two additional factors play an important role: conformational asymmetry and fluctuation effects. In this paper we examine the effects of conformational asymmetry on the order–disorder transition in compositionally symmetric

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[●] Abstract published in *Advance ACS Abstracts*, May 15, 1994.

0024-9297/94/2227-3611$04.50/0

polyolefin diblock copolymers that contain a PVCH block, i.e., $f_{\mathrm{PVCH}} \cong 0.5$.

Recently, we have shown[13] that a conformational asymmetry parameter, a_1/a_2 (where a_i is the Gaussian coil statistical segment length based on a common reference volume), is strongly correlated with the observed χ parameter for a number of polyolefin systems. This parameter accounts for two fundamentally different ways that large polymer coils occupy space. The volume of the molecule, V, is determined by the degree of polymerization N and the segment volume v_0, $V = v_0N$, while the conformational size of a polymer coil in the melt state is related to the unperturbed radius of gyration, $R_g^2 = b^2(N/6)$ (here we note the b refers to the statistical segment length of a repeat unit, while a is associated with a segment of a specified volume). In the limit $N \rightarrow 1$ there is only one space-filling criterion, the molecular volume V. Classical regular solution theories for polymer–polymer mixing ($N \gg 1$) fail to account explicitly for conformational differences (i.e., variations in a), leading to combinatorial entropy terms that are linear in N^{-1}.[14,15] Excess entropies of mixing necessarily appear as corrections to the classical heat of mixing, i.e., in the well-known Flory–Huggins χ parameter. In order to make the parametrization of conformational asymmetry more transparent, we will adopt a notation introduced by Helfand and Sapse[16] 2 decades ago to describe the effects of segment length asymmetry on interfacial properties in polymer blends. Fortuitously, those *local* (i.e., segment length scale) effects can be characterized using the same reduced parameters as the *nonlocal* (i.e., over length scales between b and R_g) properties described here.

Recognizing that conformational asymmetry effects should be defined in an N-independent way, we can combine the volume (V) and space-filling (R_g) parameters into a single parameter

$$\beta^2 = R_g^2/V = b^2/6v_0 \tag{1}$$

and define conformational asymmetry between two different species by

$$\epsilon = (\beta_1/\beta_2)^2 \tag{2}$$

Vavasour and Whitmore have relied on this same parametrization and notation while incorporating the effects of broken conformational symmetry ($\epsilon \neq 1$) into the theoretical mean-field phase diagram for diblock copolymers.[17] Also, if v_0 is fixed at a constant value and the b parameters are rescaled appropriately (and renamed a), then $\epsilon = (a_1/a_2)^2$, making direct contact with our earlier treatment of conformational asymmetry.[13] A more complete description of these concepts is presented elsewhere.[18]

Here we must emphasize that there may be other excess free-energy contributions to χ that derive from *local* structural asymmetry effects. These can be associated with finite compressibility and nonideal packing effects as discussed by Schweitzer[19] or variations in the segment shape (or local architecture) as described by Dudowicz and Freed.[20] A basic thrust of our experimental work in this area is to design and investigate polymer–polymer systems that will aid in establishing the relative importance of both *local* and *nonlocal* contributions to the excess free energy of mixing.

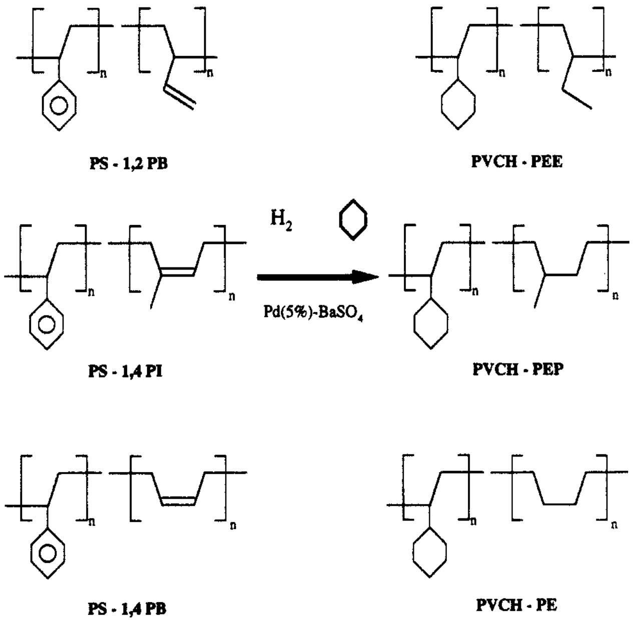


Figure 1. Reaction schematic for the synthesis of poly(vinylcyclohexane) containing diblock copolymers.

A new set of polyolefin diblock copolymers has been designed with these objectives in mind. Poly(vinylcyclohexane) (PVCH) has been combined with other polyolefins, PEE, PEP, and PE, by anionic polymerization and heterogeneous hydrogenation as shown in Figure 1. PVCH was selected based on its rather different physical and structural properties as compared with PEE, PEP, and PE. PVCH possesses a glass transition temperature (T_g) of about 140 °C,[21] compared with T_g's of less than −20 °C for the other polyolefins.[22] The density of PVCH is about 10% greater than that of the other polyolefins which leads to a modest enthalpic contribution to the χ parameter. Nevertheless, PVCH is a saturated hydrocarbon that lacks specific interactions and possesses conformational properties that result in both asymmetric ($\epsilon \neq 1$) and symmetric ($\epsilon = 1$) states when combined with other polyolefins. In the current presentation we report the successful synthesis and thermodynamic characterization of several compositionally symmetric PVCH-containing diblock copolymers. Dynamic mechanical spectroscopy was utilized to characterize the order–disorder transition temperature, T_{ODT}, of each diblock copolymer. Group contribution analysis does not account for the thermodynamic behavior observed for each of these systems. However, a strong correlation between ϵ and the measured χ_{ODT} supports earlier conjectures regarding the influence of conformational asymmetry on polyolefin phase behavior.

Experimental Section

Three types of symmetric monodisperse diblock copolymers, poly(1,2-butadiene)–poly(styrene) (1,2-PB–PS), poly(1,4-*cis*-isoprene)–poly(styrene) (1,4-PI–PS), and poly(1,4-butadiene)–poly(styrene) (1,4-PB–PS), were anionically synthesized in cyclohexane using a lithium counterion.[23] The PS blocks were polymerized at 40 °C for approximately 3 h, yielding atactic, predominantly head-to-tail PS. The poly(1,2-butadiene) block was polymerized for 12 h at 20 °C following the addition of a 5:1 molar ratio of 1,2-dipiperidinoethane, resulting in >99%, 1,2 addition as confirmed by ^{1}H NMR.[22] The poly(1,4-butadiene) block was polymerized at 40 °C for 12 h, yielding 93% 1,4 addition and 7% 1,2 addition as confirmed by ^{1}H NMR analysis.[23] The 1,4-PI–PS diblock copolymer was kindly provided by Dr. Jimmy Mays and has been described earlier;[21] the poly(1,4-*cis*-isoprene) block contains 75% *cis*-1,4, 20% *trans*-1,4, and 5% 3,4 repeat units.

Hydrogenation reactions were accomplished using a BaSO$_4$-supported palladium catalyst (5% Pd, Strem) suspended in cyclohexane under 500 psi of hydrogen. Reaction temperatures were 120 °C with a polymer solution concentration and catalyst loading of 8 g/L and 2.5 g of catalyst/g of polymer, respectively. All the hydrogenation reactions were completed in newly designed

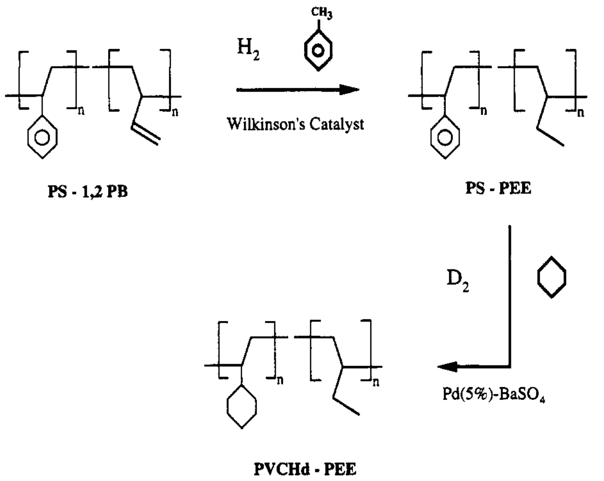


Figure 2. Schematic of the two-step hydrogenation–deuteration labeling technique used to obtain neutron contrast in PVCHd–PEE-2.

0.1- or 0.5-L reactors with vigorous mixing (2000 rpm) for 12 h.[21] A report describing the hydrogenation reactor will be provided elsewhere.[24] Here we note that reactor design plays an important role in the heterogeneous catalytic hydrogenation of polymers, most notably through its effect on the mass-transfer aspects of these reactions.

Small-angle neutron scattering (SANS) experiments have been used to characterize the morphological state of the saturated diblocks. A two-step hydrogenation–deuteration labeling technique was developed in our laboratory based on selectivity differences between homogeneous and heterogeneous catalysts. The method is shown schematically in Figure 2. In the first step the poly(diene) double bonds are hydrogenated using a well-known homogeneous hydrogenation catalyst, $RhCl(PPh_3)_3$, often referred to as Wilkinson's catalyst (99.9% Strem).[25,26] These reactions were conducted at 100 °C under 100 psi hydrogen for 30 min in toluene with a polymer concentration and catalyst loading of 30 and 0.8 g/L, respectively. Triphenylphosphine (PPh_3; 99% Strem) was added as a cocatalyst at concentrations of 0.8 g/L (3:1 molar ratio). The catalyst was then extracted by several reverse precipitations using methanol as the nonsolvent. The second deuteration step was conducted using the heterogeneous catalyst Pd(5%)–$BaSO_4$ in either cyclohexane (for PS–PEE or PEP–PS) or decalin (for PE–PS), in the 0.5-L reactor at 120 °C under 500 psi of deuterium (99% Cambridge) with vigorous stirring (2000 rpm). Polymer solution concentrations and catalyst loadings were identical to those indicated previously. The resulting diblock copolymers, PVCHd–PEE-2 and PE–PVCHd-1, contain a deuterium-labeled PVCH block with hydrogenous PEE or PE blocks. This combination provides excellent neutron contrast; separate experiments with PS homopolymers demonstrate a PVCH isotopic makeup of $-(C_8H_{5.5}D_{8.5})-$.

Gel permeation chromatography (GPC) traces of the unsaturated and noncrystalline saturated diblock copolymers were obtained from a Waters 150C instrument fitted with Phenogel columns operated at 25 °C with tetrahydrofuran as the mobile phase. Calibration was accomplished using a set of monodisperse polystyrene (Pressure Chemical Co.) standards. The polydispersity index, M_w/M_n, was measured for each diblock copolymer with respect to the poly(styrene) calibration standards and found to be 1.05–1.06. The volume fraction of PS in each diblock copolymer is reported based on the polymerization reaction stoichiometry; this was also verified by ^1H NMR. ^1H NMR (Varian VXR-300) spectra were obtained at 25 and 90 °C from 10% solutions in $CDCl_3$ with TMS as the internal reference. These spectra were primarily used to characterize the polydiene microstructure and the saturation efficiency of the hydrogenation reactions.[27] Molecular characteristics for the eight polymer blocks prepared in this work are summarized in Table 1. Diblock copolymer characteristics are reported in Table 2.

Table 1. Polymer Physical Properties at 150 °C[a]

polymer	b,[b] Å	ρ,[a] g/cm^3	$10^2\beta$,^{2} Å^{-1}	ref
poly(styrene) (PS)	6.9	0.999	4.6	41
poly(1,2-butadiene) (1,2-PB)	6.2	0.813	5.8	32
poly(1,4-isoprene) (1,4-PI)	6.8	0.825	5.6	36
poly(1,4-butadiene) (1,4-PB)	6.9	0.820	7.3	36, 37
poly(vinylcyclohexane) (PVCH)	7.1	0.913	4.2	38
poly(ethylethylene) (PEE)	5.1	0.807	3.8	32, 39
poly(ethylenepropylene) (PEP)	7.4	0.782	6.1	40
poly(ethylene) (PE)	8.3	0.779	9.6	36, 41

[a] Reported values of b and ρ have been corrected for thermal expansion.[13,36] [b] These b values are associated with the chemical repeat unit of the homopolymer melts as determined by SANS.

Table 2. Diblock Copolymer Characterization Results

polymer	$10^{-3}M_n$	$f_{PS/PVCH}$	$10^2\chi_{calc}$[a]	T_{ODT}, °C	ϵ (150 °C)
1,2-PB–PS-1	22	0.54	23–26	>275	1.3
1,2-PB–PS-2	50	0.46	23–26	>275	1.3
1,4-PI–PS-1	18	0.50	9–17	124	1.2
1,4-PB–PS-1	14	0.50	6–22	98	1.6
1,4-PB–PS-2	20	0.51	6–22	167	1.6
PVCH–PEE-1	23	0.56	0.9–3.1	<80	1.1
PVCH–PEE-2	52	0.48	0.9–3.1	229	1.1
PVCHd–PEE-2[b]	52	0.48	0.9–3.1	212	1.1
PEP–PVCH-1	19	0.52	1.7–2.4	140	1.5
PEd–PVCHd-1[b]	15	0.52	0.02–6.0	235	2.3
PE–PVCHd-1[b]	15	0.52	0.02–6.0	238	2.3
PEd–PVCHd-2	21	0.53	0.02–6.0	>275	2.3

[a] At 300 K based on solubility parameters estimated using methods of Small, Hoy, and Van Krevelen.[34] [b] PVCHd is a deuterium-labeled block with an isotopic composition of $-[C_8H_{5.5}D_{8.5}]_n-$. PEd–PVCHd-1 contains deuterium labeling on both blocks.

Viscoelastic properties were determined for each diblock copolymer using a Rheometrics Solids Analyzer (RSA II). All experiments were performed in the dynamic mode ($0.01 < \omega < 100$ rad/s) with a 0.5-mm shear sandwich test fixture. The sample temperature was controlled to within 1 °C using a thermally regulated nitrogen purge. Two types of viscoelastic experiments were performed on each diblock copolymer. The order–disorder transition temperature, T_{ODT}, was determined by measuring G' at a fixed frequency and strain amplitude (ω = 0.1–0.5 rad/s, γ = 10%) while slowly heating (1 °C/min) the specimens. Isothermal frequency scans for 1,4-PB–PS, and PEd–PVCHd-1 were also collected at various temperatures throughout the ordered and disordered states using a 10% strain amplitude.

Small-angle neutron scattering (SANS) experiments were performed on oriented samples prepared in a specially designed oscillatory shearing apparatus described elsewhere.[28] Thin sheets (1 mm) of block copolymer were subjected to a 100% amplitude oscillatory strain at a shear rate of $|\dot{\gamma}| = 0.57\ s^{-1}$ at 175 °C for 3 h while under a nitrogen purge. Strips were then cut in the three orthogonal directions defined in Figure 3 and placed between two $^1/_{16}$-in. quartz windows. SANS experiments were conducted at the 12-m SANS facility at Risø National Laboratory, located in Roskilde, Denmark, using λ = 6.0 Å neutrons with a spread of $\Delta\lambda/\lambda = 0.09$. Scattering patterns were recorded on a 60 × 60 cm^2 area detector located 3 m from the sample and are reported in arbitrary units of intensity.

Results

All the symmetric poly(styrene)–poly(diene) diblock copolymers were essentially completely saturated with hydrogen or deuterium using the heterogeneous hydrogenation and homogeneous techniques described above. ^1H NMR spectra show that >99.5% of the olefinic and aromatic resonances in the unsaturated precursors are converted to aliphatic and cyclic resonances. GPC traces obtained following the hydrogenation are indistinguishable from the diblock copolymer precursors, which demonstrates that chain scissions or detrimental side reactions have not occurred.[21]

Each block copolymer was synthesized with approximately 50% by volume PVCH (i.e., $f_{PVCH} \approx 0.5$). Con-

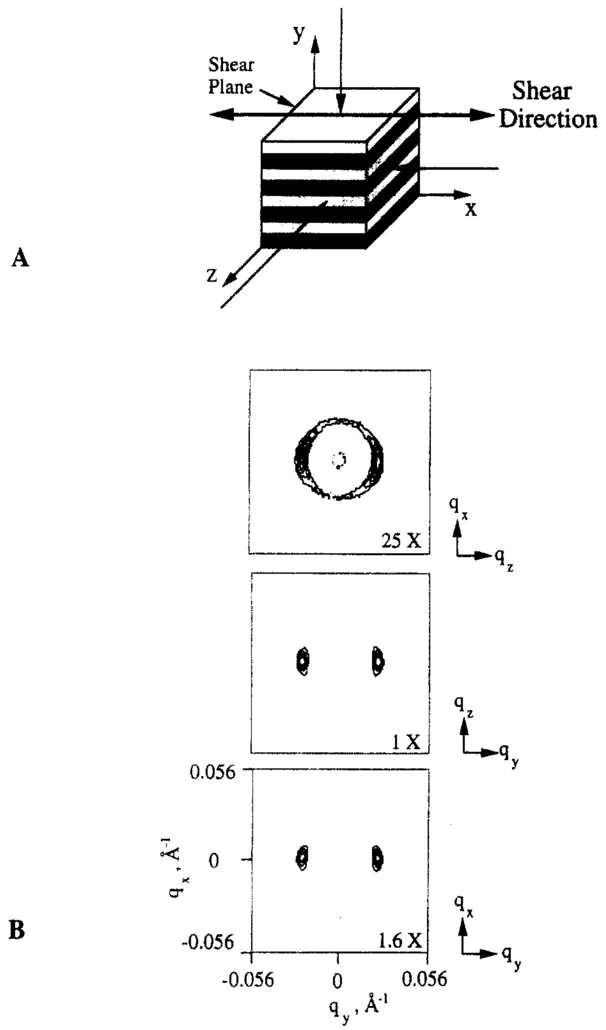


Figure 3. (A) Coordinate system used in describing the oscillatory shear orientation and small-angle neutron scattering (SANS) experiments. The arrows identify the neutron beam access used in the SANS experiments. The lamellar morphology indicated is referred to as the "parallel" orientation. (B) SANS patterns obtained from shear-oriented PVCHd–PEE-2. Intensity contours have been multiplied by the factor indicated in each plot. Strong reflections in the y–z and x–y scattering planes and weak scattering in x–z indicate the parallel lamellae orientation shown in A.

sequently, the ordered morphology should be lamellar. Utilizing the two-step labeling process, shown in Figure 2, and a specially designed shearing device, the morphology of PVCHd–PEE-2 and PE–PVCHd-1 was established using SANS measurements. Figure 3 depicts a cube of material subjected to shear with the three orthogonal directions defined with respect to the shear field. SANS results for PVCHd–PEE-2, obtained with the neutron beam directed along these three directions, are also shown in Figure 3. These SANS data are consistent with a lamellar morphology arranged in what is now referred to as a parallel orientation;[29] i.e., the unit normals of the lamellae are perpendicular to the flow direction and parallel to the velocity gradient direction. In the x–y and y–z scattering planes strong reflections are apparent at scattering wavevectors $|q_y| = q^* = 0.0253$ Å^{-1} ($|q| = 4\pi/\lambda \sin\theta$, where 2θ is the scattering angle), with higher order reflectiosn at $2q^*$ and $3q^*$. This result, along with the weak, nearly isotropic pattern in the x–z scattering plane, establishes a lamellae morphology with parallel orientation. For the PE–PVCHd-1 specimen strong reflections in the x–y and y–z directions at $|q_y| = q^* = 0.035$ Å^{-1}, with a blank pattern in the x–z direction, also confirm a parallel orientation of lamellae (not shown) for this specimen. We presume that the unsaturated precursors, and PEP–PS materials, are also lamellar based on numerous publications that deal with these materials and evidence provided by mechanical spectroscopy (see below).

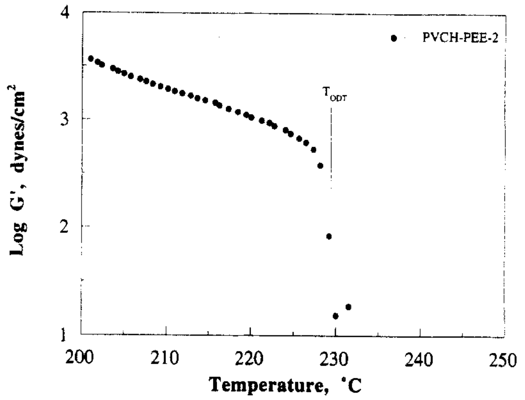


Figure 4. Temperature dependence of the low-frequency dynamic elastic modulus for the PVCH–PEE-2 diblock copolymer (10% strain amplitude, $\omega = 0.2$ rad/s, heating rate = 1 °C/min). The order–disorder transition temperature, T_{ODT}, is identified with the discontinuity in G' at 229 ± 2 °C.

Order–disorder transition (ODT) temperatures were determined following the procedures established in earlier reports.[30,31] Low-frequency isochronal ($\omega < \omega_c$) dynamic elastic shear moduli were obtained as the specimens were slowly heated. In the ordered state the structured morphology (lamellae for all cases reported here) leads to a nonterminal low-frequency response, (typically $G' \sim G'' \sim \omega^{0.5}$). At the ODT the ordered morphology "melts" into a fluctuating disordered fluid, causing G' to drop discontinuously and producing a terminal response ($G' \sim \omega^2$, $G'' \sim \omega^1$).

1,2-PB–PS-1 and 1,2-PB–PS-2 display rheological behavior characteristic of microscopically ordered lamellar material, over the rheologically accessible temperature window (25 °C < T < 275 °C). In contrast, PVCH–PEE-1 showed rheological behavior characteristic of microscopically disordered material at temperatures above the glass transition temperature: for this specimen $T_g \approx 80$ °C (for pure PVCH, $T_g \approx 140$ °C).[21] $T_{ODT} = 229 \pm 2$ °C was established for PVCH–PEE-2 based on the isochronal temperature sweep shown in Figure 4. Isothermal frequency scans at 227 and 232 °C show rheological behavior characteristic of the ordered and disordered states, respectively. T_{ODT} for PVCHd–PEE-2, the deuterium-labeled version of this material, was determined similarly, with the discontinuity in G' occurring at 212 ± 2 °C. This 17 °C difference in the measured T_{ODT} values reflects the well-known isotope effect that can be traced to small variations in the polarizability and length of C–H and C–D bonds.[32] These results confirm that T_{ODT} increases with increasing molecular weight, as anticipated by the N-dependence of the classical combination entropy of mixing.[14,15]

Isochronal temperature scans were also obtained for 1,4-PI–PS-1/PEP–PVCH-1 and 1,4 PB–PS-1/PEd–PVCHd-1 and are shown in Figures 5 and 6, respectively. 1,4-PI–PS-1 is characterized by $T_{ODT} = 124 \pm 2$ °C, while the saturated homologue PEP–PVCH-1 displays $T_{ODT} = 140 \pm 2$ °C. 1,4-PB–PS-1 shows a discontinuous decrease in G' at 98 ± 2 °C, signaling the ODT, while PEd–PVCHd-1 is characterized by an ODT at 235 ± 2 °C; the deuterium-labeled PE–PVCHd-1 disorders at 238 ± 2 °C. In both cases the discontinuity in G' occurs over a 2 °C temperature window. The dynamic mechanical properties of 1,4-PB–

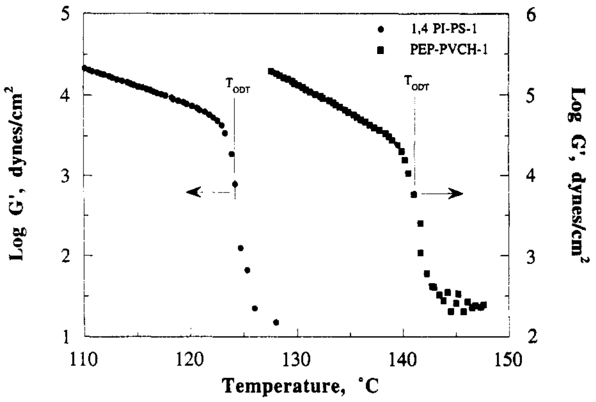


Figure 5. Temperature dependence of the low-frequency dynamic elastic modulus for the 1,4-PI-PS-1 and PEP-PVCH-1 diblock copolymers (2% strain amplitude, ω = 0.2 rad/s). Order–disorder transition temperatures occur at T_{ODT} = 124 ± 2 and 140 ± 2 °C, respectively. Upon saturation T_{ODT} increases by 16 °C due to a modest increase in the χ parameter.

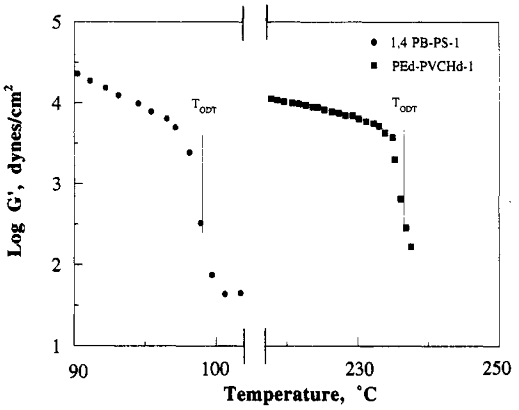


Figure 6. Temperature dependence of the low-frequency dynamic elastic modulus for 1,4-PB-PS-1 (ω = 0.2 rad/s) and PEd-PVCHd-1 (ω = 1.0 rad/s) (10% strain amplitude, heating rate = 1 °C/min) where T_{ODT} = 98 ± 2 and 235 ± 2 °C, respectively. Upon saturation T_{ODT} increases by 137 °C due to a dramatic increase in the χ parameter.

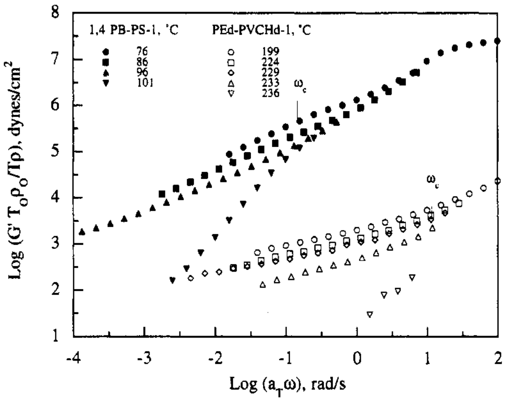


Figure 7. Reduced frequency plot for dynamic elastic data obtained from the 1,4-PB-PS-1 and PEd-PVCHd-1 diblock copolymers. The G' data have been temperature and density corrected and time–temperature superpositioned (T_0 = 76 and 199 °C for 1,4-PB-PS-1 and PEd-PVCHd-1, respectively). T_{ODT} lies between 96 and 101 °C for 1,4-PB-PS-1 and between 233 and 236 °C for PEd-PVCHd-1 based on the $\omega < \omega_c$ behavior, which confirms the assignments made based on the results shown in Figure 6.

PS-1 and PEd-PVCHd-1 were also investigated using isothermal frequency scans. In Figure 7 we present representative dynamic elastic (G') moduli for 1,4-PB-PS-1 and PEd-PVCHd-1. These data have been temperature and density corrected and time–temperature superpositioned[33] using high-frequency branches ($\omega > \omega_c$) of the spectra based on a common reference temperature (T_0 = 76 °C for 1,4-PB-PS-1, T_0 = 199 °C for PEd-PVCHd-1). The critical crossover frequency is noted on the figure as ω_c which separates the high- and low-frequency viscoelastic regimes. At high frequencies, $\omega > \omega_c$, the response is dominated by chain-entanglement effects that are not affected by the microdomain characteristics. At low frequencies ($\omega < \omega_c$) the rheological response is governed by microdomain structure. For 1,4-PB-PS-1 and PEd-PVCHd-1 the low-frequency regimes display both ordered ($G' \sim \omega^{0.5}$, $G'' \sim \omega^{0.5}$) and disordered ($G' \sim \omega^2$, $G'' \sim \omega^1$) behavior. 1,4-PB-PS-1 exhibits a sharp change in the low-frequency response between 96 and 101 °C which confirms the assignment of T_{ODT} = 98 ± 2 °C from the isochronal temperature scan (Figure 6). PEd-PVCHd-1 displays a similar change in its low-frequency behavior between 233 and 236 °C, which also confirms the previous assignment of T_{ODT} = 235 ± 2 °C. 1,4-PB-PS-2 shows a discontinuous decrease in G' at 167 °C, while PEd-PVCHd-2 displays behavior characteristic of the ordered state up to 275 °C. In all cases the rheological characteristics of these samples in the ordered state are consistent with a lamellar morphology.

Discussion

The results given in the previous section can be summarized as follows. 1,2-PB-PS-1 and 1,2-PB-PS-2 exhibit microstructurally ordered behavior up to at least 275 °C. After complete saturation T_{ODT} is reduced to <80 °C for PVCH-PEE-1 and 229 ± 2 °C for PVCH-PEE-2. Therefore, since N remains constant and a lamellar morphology is present before and after saturation, the χ parameter must decrease significantly. In the case of 1,4-PI-PS-1 the discontinuity in G' occurs at 124 ± 2 °C, while the saturated homologue, PEP-PVCH-1, shows a modest increase in T_{ODT} to 140 ± 2 °C. The 1,4-PB-PS-1 sample is characterized by T_{ODT} = 98 ± 2 °C, while the saturated homologue, PEd-PVCHd-1, displays a dramatically higher value, T_{ODT} = 235 ± 2 °C. For 1,4-PB-PS-2 T_{ODT} = 167 °C, while PEd-PVCHd-2 displays microscopically ordered behavior up to 275 °C. In contrast to the PVCH-PEE system, T_{ODT} for PEP-PVCH and PE-PVCH increases with respect to the unsaturated precursors, indicating an increase in the χ parameter. Therefore, depending on the microstructure of the polydiene precursor, the χ parameter may increase or decrease upon hydrogenation.

The PVCH-based diblock copolymers reported here are all saturated hydrocarbons than are governed by simple van der Waals interactions. Therefore, a crude estimate of segment–segment interactions can be obtained using cohesive energy density calculations based on the group contribution technique,[34]

$$\chi = V_0(\delta_1 - \delta_2)^2/RT \tag{3}$$

where V_0 is a common reference molar volume, δ_1 and δ_2 are the solubility parameters of components 1 and 2, R is the gas constant, and T is the absolute temperature. For 1,2-PB-PS, 1,4-PI-PS, and 1,4-PB-PS the χ parameters were calculated at 300 K using Hoy, Small, and Van Krevelin's method[34] with V_0 = 65 cm³/mol. The resulting χ parameters are between 0.06 and 0.26 (Table 2). Similarly, χ parameters were estimated for PVCH-PEE, PEP-PVCH, and PE-PVCH and found to vary between 0.0002 and 0.06 (Table 2). Thus, in all three systems we would expect a sizable decrease in χ with saturation.

The group contribution calculations are in qualitative agreement with the experimental findings for the 1,2-PB–PS/PVCH–PEE diblock copolymer system which shows a decrease in T_{ODT} upon saturation. However, for the other two systems, 1,4-PI–PS/PEP–PVCH and 1,4-PB–PS/PE–PVCH, the χ parameter is predicted to decrease by an order of magnitude, in direct contradiction with the results reported here. On the basis of the group contribution analysis, we would expect these systems to be disordered viscous liquids at room temperature. Similar calculations have led at least one group[35] to dismiss PVCH-based block copolymers as commercially useless, since these predicted thermodynamic effects (i.e., the anticipated decrease in χ) would necessitate commercially intractable molecular weights to insure microphase separation. However, our experimental observations demonstrate that the χ parameter increases slightly for PEP–PVCH and increases significantly for PE–PVCH. These results indicate that other factors must be considered in attempting to rationalize polyolefin block copolymer phase behavior.

Recently, Bates and Fredrickson[18] have shown that a new parameter, related to the space-filling nature of homopolymer melts, results in an additional entropic contribution, χ_ϵ, to the classical segment–segment interaction parameter χ,

$$\chi = \chi_0 + \chi_\alpha + \chi_\beta + ... + \chi_\epsilon \qquad (4)$$

where χ_0 accounts for the classical enthalpy of mixing and χ_α, χ_β, ... refer to local excess entropies of mixing, e.g., due to specific interactions and segment packing constraints. χ_ϵ depends on ϵ and composition in a complicated way, and as a result there is not a simple analytical critical condition, as is obtained when $\chi = \chi_0$ (i.e., neglecting excess free-energy contributions to χ_0). Moreover, this analysis is applicable to homopolymer mixtures, although we expect analogous behavior with block copolymers, within the mean-field limit. Therefore, we will not attempt to evaluate our results quantitatively. Instead, only a qualitative correlation between phase behavior and ϵ will be established here.

We have calculated ϵ for the six types of diblock copolymer systems considered in this work. This calculation requires b and the density, ρ, for each block at the temperature of interest. b values have been obtained from SANS data taken from homopolymer melts,[13,32,36–41] while densities have either been measured (density gradient column technique) or taken from the literature.[13,32,36–41] By applying reported thermal expansivities ($\partial \ln R_g/\partial T$ and $\partial \ln \rho/\partial T$), we have estimated β for each block component at 150 °C as given in Table 1. The associated ϵ parameters are listed in Table 2. In the remainder of this section we shall relate these ϵ values to the thermodynamic properties established for the diblock copolymers.

1,2-PB–PS, 1,4-PI–PS, and 1,4-PB–PS possess ϵ parameters of 1.3, 1.2, and 1.6, respectively. Upon saturation the PS and 1,2-PB blocks conformationally "contract", while the 1,4-PI and 1,4-PB blocks conformationally "expand". This leads to both conformational symmetry and asymmetry with saturation, ϵ = 1.1, 1.5, and 2.3 for PVCH–PEE, PEP–PVCH, and PE–PVCH, respectively. These changes in ϵ will be expressed through the ratio ϵ_S/ϵ_U where the subscripts S and U refer to saturated and unsaturated, respectively.

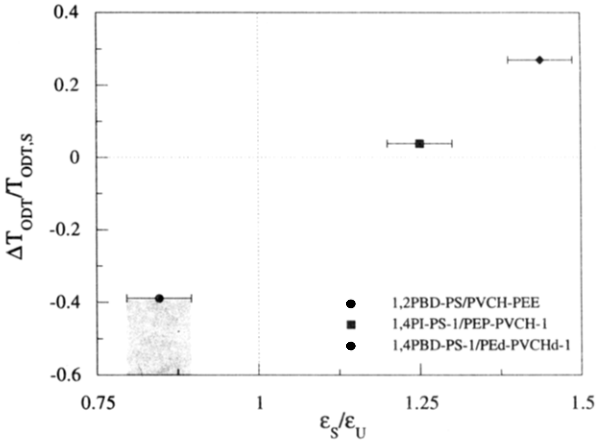
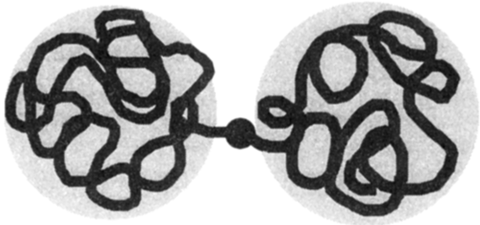


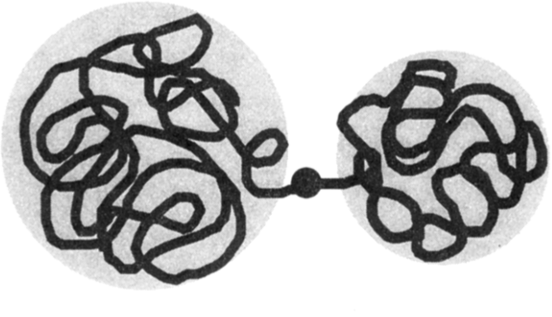
Figure 8. $\Delta T_{ODT}/T_{ODT,S}$ for the three pairs of saturated (S) and unsaturated (U) diblock copolymers as a function of the ratio of conformational asymmetry parameters ϵ_S/ϵ_U, where $\Delta T_{ODT} = T_{ODT,S} - T_{ODT,U}$. ΔT_{ODT} was not quantitatively established for the 1,2-PB–PS/PVCH–PEE system. However, the range of possibilities is limited to the shaded region below the upper limit indicated by the solid symbol. Classical solubility parameter arguments do not anticipate $\Delta T_{ODT} > 0$.

In principle, the quantitative evaluation of our results would rely on a detailed comparison of χ before and after saturation. However, such an analysis would require a complete knowledge of the temperature dependence of χ for each of the six diblock copolymers under consideration, including fluctuation corrections that depend on N.[9] This is clearly beyond the scope of the present work. Therefore, we have opted to present our results in a simple and transparent manner. Although we cannot draw quantitative conclusions from this assessment, we believe that the qualitative deductions are quite compelling. Two parameters have emerged from our experiments: the ratio ϵ_S/ϵ_U and the change in T_{ODT} upon saturation, $\Delta T_{ODT} = T_{ODT,S} - T_{ODT,U}$ which will be expressed in the reduced form $\Delta T_{ODT}/T_{ODT,S}$. Figure 8 shows $\Delta T_{ODT}/T_{ODT,S}$ versus ϵ_S/ϵ_U for the three pairs of systems under investigation. For 1,2-PB–PS/PVCH–PEE ΔT_{ODT} was not established uniquely since neither of the diene-based materials disordered within the experimental temperature window. However, an upper limit of $\Delta T_{ODT} < 195$ °C can be established based on the 1,2-PB–PS-1/PVCH–PEE-1 system. Figure 8 reveals a strong correlation between $\Delta T_{ODT}/T_{ODT,S}$ and ϵ_S/ϵ_U, which translates into a profound entropic contribution to χ that cannot be accounted for by classical arguments. The same conclusion was arrived at in an earlier publication that dealt with other polyolefin block copolymers and homopolymer mixtures.[13] However, in that work the magnitude of χ was smaller and an internal calibration against poly(dienes) (i.e., ΔT_{ODT}) was lacking. By examining the PS-based versus the PVCH-based diblocks, we have provided a firmer basis for concluding that conformational asymmetry plays a significant role when enthalpic effects (i.e., χ_0) become small. This analysis should be complimented by an assessment of the *local* contributions to χ (i.e., χ_α, χ_β, ...) using the theoretical tools provided by Schweizer[19] and Dudowicz and Freed.[20] Because each of the three polyolefin diblock copolymers contain a common block (i.e., PVCH), a relative ranking of the predicted effects should be possible. However, such an assessment is beyond the scope of this publication.

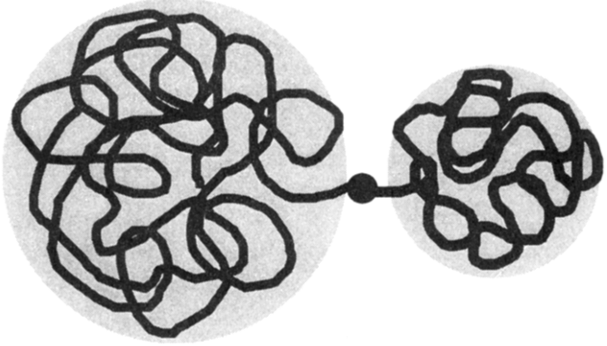
We finish this discussion by presenting a graphic illustration of conformational asymmetry. Three compositionally symmetric (f = 0.5) molecules, that contain blocks of equal molecular volume (V), are depicted in Figure 9. The shaded circles represent R_g^2 for each block, while the thickness of the chains is representative of the projected molecular diameters. Here we note that this perspective is arrived at by considering V and R_g, and therefore it does not reflect the local (monomer-scale)



PVCH - PEE
$\varepsilon = 1.1$



PEP - PVCH
$\varepsilon = 1.5$



PE - PVCH
$\varepsilon = 2.3$

Figure 9. Schematic representation of the space-filling characteristics for PVCH–PEE, PEP–PVCH, and PE–PVCH. The thickness and length of each block reflect a common volume, V. The shaded area represents a cross-sectional view of the coil and is proportional to R_g^2. For PVCH–PEE ($\epsilon = 1.1$) the volume-filling characteristics are comparable, while for PEP–PVCH ($\epsilon = 1.5$) and PE–PVCH ($\epsilon = 2.3$) the conformational asymmetry becomes more apparent, resulting in entropic adjustments to the χ parameter.

architecture of the chain. For PVCH–PEE ($\epsilon = 1.1$) the two blocks fill space nearly symmetrically and by our previous arguments provide little excess entropy (χ_ϵ) to the bare enthalpic parameter, χ_0. In contrast, the pictures that represent the PEP–PVCH and PE–PVCH systems, where $\epsilon = 1.5$ and 2.3, respectively, are clearly asymmetric. For example, the PE block is longer and thinner than the PVCH block. Thus, even though the block volumes are identical, they fill space differently leading to an entropically based increase in χ (see refs 13 and 18 for a more complete discussion of these points). The nonlocal nature of this effect is clearly illustrated by the PVCH–PEE system. Although the local structures of PVCH and PEE are quite different (Figure 1), these two polymers are nearly conformationally symmetric ($\epsilon = 1.1$). We believe that this type of material, which exhibits significant local structural differences but is characterized by nonlocal symmetry ($\epsilon \approx 1$), will provide a basis for discriminating between *local* and *nonlocal* contributions to χ.

Summary

Three compositionally symmetric ($f_{\mathrm{PVCH}} \cong 0.5$) monodisperse diblock copolymers, poly(1,2-butadiene)–poly(styrene) (1,2-PB–PS), poly(1,4-isoprene)–poly(styrene) (1,4-PI–PS), and poly(1,4-butadiene)–poly(styrene) (1,4-PB–PS), were anionically synthesized and subsequently saturated using heterogeneous and homogeneous hydrogenation catalysts. The thermodynamics of the resulting poly(vinylcyclohexane)–poly(ethylethylene) (PVCH–PEE), poly(ethylenepropylene)–poly(vinylcyclohexane) (PEP–PVCH), and poly(ethylene)–poly(vinylcyclohexane) (PE–PVCH) diblock copolymers were investigated using dynamic mechanical spectroscopy and small-angle neutron scattering. PVCH–PEE displayed an order–disorder transition temperature, T_{ODT}, that was at least 195 °C lower than the unsaturated precursor, 1,2-PB–PS. However, for PEP–PVCH and PE–PVCH T_{ODT} was 16 and 137 °C higher than the unsaturated specimens, respectively. Hence, for PVCH–PEE the χ parameter decreases upon saturation, as anticipated by cohesive energy density considerations, while PEP–PVCH and PE–PVCH are characterized by higher χ parameters than the unsaturated homologues, which cannot be accounted for by classical theory. These results are strongly correlated with the relative degree of conformational asymmetry between blocks, $\epsilon = (\beta_1/\beta_2)^2$, $\beta^2 = R_g^2/V$ where R_g is the unperturbed radius of gyration and V is the molecular volume. As ϵ increases or decreases away from unity, entropic contributions to χ increase, leading to a higher than anticipated T_{ODT}. The concept of conformational asymmetry, which leads to a *nonlocal* excess entropy of mixing in polymer–polymer systems, is supported by these findings.

Acknowledgment. Support for this research was provided by Exxon Chemical Co. under contract WGM 9008.20. We are grateful to Jimmy Mays for providing us with the 1,4-PI–PS specimen. Kell Mortensen and Kristoffer Almdal graciously aided us in obtaining the SANS data on the PVCHd–PEE-2 and PE–PVCHd-1 materials.

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