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Notes

Interaction Strengths in Styrene−Diene Block Copolymers and Their Hydrogenated Derivatives

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Introduction

Styrenic block copolymers, such as styrene−isoprene (S/I) and styrene−butadiene (S/B) diblock, triblock, and starblock polymers, have been widely studied due both to their practical utility[1,2] (notably as thermoplastic elastomers) and their importance as model self-assembling systems.[3] Nonetheless, styrene−diene block copolymers have inherent practical limitations, particularly the susceptibility of the diene block to oxidative degradation. Many chemical modifications have been proposed to circumvent these limitations, the simplest of which is catalytic hydrogenation. Saturation of the diene block to yield a polyolefin has been practiced commercially for twenty-five years,[2] vastly improving thermooxidative stability. For elastomers, an amorphous polyolefin is desired, though semicrystalline polyethylene can be prepared via saturation of high-1,4 polybutadiene.[4] Recently, Gehlsen and Bates[5] showed that some catalysts, in addition to saturating the diene block, will also convert PS to poly(vinylcyclohexane) (PVCH).

Hydrogenation can also dramatically affect the interblock interactions. For example, the Flory interaction parameter χ between S and ethylethylene (S/EE) is about 40% larger than between S and the EE precursor, a high-1,2 polybutadiene.[6] Further, it has been suggested that χ increases as the 1,2 content in the B block of the precursor decreases.[7] Comparable increases in χ occur when S/I block copolymers are saturated to yield S/EP (ethylene−propylene).[8] A marked consequence of the increased interblock segregation strength is that the viscosity of an S/B/S triblock (40% 1,2) at low shear rates increases by orders of magnitude upon hydrogenation.[2]

Here, we employ a series of S/I and S/B diblocks and triblocks (high-1,4 diene addition) to examine the effect of saturation on the interblock interaction strength. All block copolymers are of similar composition, allowing for a straightforward comparison between materials of different chemistry. Particular attention is given to the diene-selective saturation products (S/EP and S/E), which are compared both with their unsaturated precursors and with the “dual-saturated” derivatives (VCH/EP and VCH/E).

Experimental Section

Materials. S/I and S/B diblocks and S/I/S triblocks were synthesized by Dexco Polymers; the S/I and S/I/S polymers have been characterized previously.[9] All polymers contain 12.2−13.5 wt % S and vary in molecular weight, with $M_w/M_n < 1.03$. Relevant characteristics appear in Table 1, where f is the volume fraction of S or VCH; samples are denoted by the block chemistry and the molecular weight of the unsaturated polymer in kilograms per mole (e.g., VCH/EP-90). Saturations were conducted in cyclohexane at 8−10 g/L, using a 2-L Parr batch reactor. To selectively saturate the diene block, a homogeneous Ni−Al catalyst[10,11] was prepared by combining 30 mL of 0.1 M nickel 2-ethylhexanoate in cyclohexane (Aldrich) with 10 mL of 1.0 M triethylaluminum in hexanes (Aldrich) in a dry round-bottom vessel previously purged with N_2. This vessel was connected directly to the reactor to inject the catalyst. Hydrogenation conditions were 80−90 °C and 400−500 psi H_2 for 24 h, after which the catalyst was removed by vigorously stirring with 8% aqueous citric acid (heated for the S/E diblock) until the dark catalyst color disappeared. To saturate both blocks, a heterogeneous Pd^0 catalyst supported on $CaCO_3$ or $BaSO_4$ (5% Pd^0; Strem) was used. Catalyst levels (including support) were 50−125% of the polymer mass. Conditions were 90−100 °C and 400−800 psi H_2 for 48 h, after which the catalyst was filtered from the solution. Polymers were precipitated into acetone/methanol. Infrared and ^1H nuclear magnetic resonance spectroscopies showed the level of saturation to be >96% (diene only, for Ni−Al catalyst; both blocks, for Pd^0 catalyst). No detectable saturation (<5%) of the S units occurred with the Ni−Al catalyst. Gel permeation chromatography on the S/I derivatives confirmed that no backbone rearrangements occurred during saturation.

Both rheometry and small-angle X-ray scattering (SAXS) were used to determine T_{ODT}, as previously described.[12] Specimens were compression molded above the PS or PVCH glass transition and annealed[12] to develop the equilibrium morphology: a body-centered-cubic (bcc) lattice of S or VCH spheres in a matrix of polydiene or polyolefin.

Results and Discussion

Figures 1 and 2 show representative rheological and SAXS data for S/EP-48. From the abrupt slope change in G' versus T (Figure 1), $T_{ODT} = 242 \pm 2$ °C. The SAXS data (Figure 2) show a simultaneous decrease in primary peak height and increase in peak width along with the disappearance of the higher-order maximums at $T_{ODT} = 249 \pm 3$ °C. The T_{ODT} values determined from rheometry and SAXS agree to within 9 °C in all cases (see Table 1). The average value of $T_{ODT} = 246$ °C is

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Table 1. Physical Characteristics of Block Copolymers

block copolymer	M_w (kg/mol)	f at T_{ODT}[a]	ρ at T_{ODT} (g/cm^3)[a]	ϵ (140 °C)	T_{ODT} from rheometry (°C)[b]	T_{ODT} from SAXS (°C)[b]
S/I-62	62.6	0.114	0.863	1.23	110 ± 2	111 ± 2
S/I-78	78.4	0.118	0.835	1.23	156 ± 2	161 ± 2
S/I-90	90.6	0.114	0.812	1.23	197 ± 2	202 ± 2
S/I/S-120	120.1	0.116	0.857	1.23	119 ± 3	123 ± 3
S/I/S-149	149.0	0.113	0.831	1.23	164 ± 2	167 ± 2
S/B-62	62.0	0.108	0.861	1.62	103 ± 3	107 ± 3
S/B-81	80.8	0.106	0.819	1.62	176 ± 3	185 ± 3
S/EP-48	49.5	0.106	0.752	1.57	242 ± 2	249 ± 3
S/EP-62	64.2	0.104	0.720	1.57	>310	nd
S/EP/S-90	92.9	0.105	0.755	1.57	238 ± 2	244 ± 3
S/EP/S-107	109.6	0.098	0.741	1.57	266 ± 2	nd
S/E-62	64.0	0.098	0.736	2.26	>310	>260
VCH/EP-90	93.6	0.116	0.755	2.22	233 ± 3	234 ± 3
VCH/E-62	64.5	0.108	0.748	3.20	nd	231 ± 3

[a] Density values are volume-weighted averages of the values for homopolymers of the blocks. Densities at 140 °C taken from ref 32; thermal expansion coefficients from refs 30 (EP), 33 (E, extrapolated below melting point), and 34 (others). [b] nd, not determined by this method. [c] Conformational asymmetry parameter $\epsilon \equiv (\rho\langle R_0\rangle^2/M)_A/(\rho\langle R_0\rangle^2/M)_B$, where $\langle R_0\rangle$ represents the unperturbed end-to-end distance, M is molecular weight, ρ is mass density, and the subscripts "A" and "B" indicate that these parameters correspond to the homopolymers of blocks A and B. Values of $\langle R_0\rangle^2/M$ used in calculating ϵ taken from ref 32.

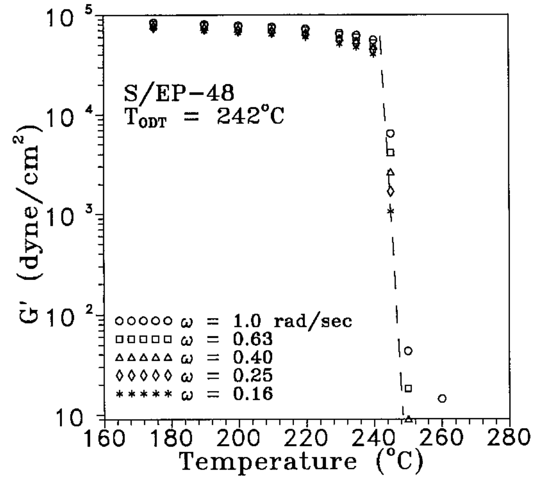

Figure 1. Shear storage modulus G' vs T for S/EP-48 at five different frequencies (as indicated). The abrupt change in slope at 242 °C indicates the order–disorder transition.

an increase of almost 200 °C over that observed for the S/I precursor.[9] Equally dramatic increases in T_{ODT} were observed for the triblocks S/EP/S-90 and S/EP/S-107, while a higher molecular weight diblock (S/EP-62) remained ordered up to its degradation temperature (310 °C). Similarly, while S/B-62 has an ODT of 105 °C, its diene-saturated derivative (S/E-62) remains ordered up to at least 310 °C (where degradation begins to occur).

The ODT temperature also increases dramatically on "dual saturation" of an S/B diblock, from 105 °C for S/B-62 to 231 °C for VCH/E-62. By contrast, the corresponding change for S/I block copolymers is rather modest: S/I-90 has $T_{ODT} = 200$ °C, while VCH/EP-90 has $T_{ODT} = 233$ °C. These changes in T_{ODT} are in good quantitative agreement with those of Gehlsen and Bates[13] for VCH/E and Balsara et al.[14] for VCH/EP.

Values of χ at T_{ODT} can be obtained for each material if χN at the ODT is taken from theory, where N is the degree of polymerization. However, in calculating N from the known molecular weight, the choice of what constitutes a "monomer unit" is somewhat arbitrary (consider the case of polyethylene prepared by saturating polybutadiene). In our case, there is a 20% difference in mass between B and I (and E and EP) repeat units and substantial density variation among materials, which tend to obscure the comparisons. To compensate for these factors, the data are better expressed as an interaction energy density X, which contains no arbitrary reference unit:

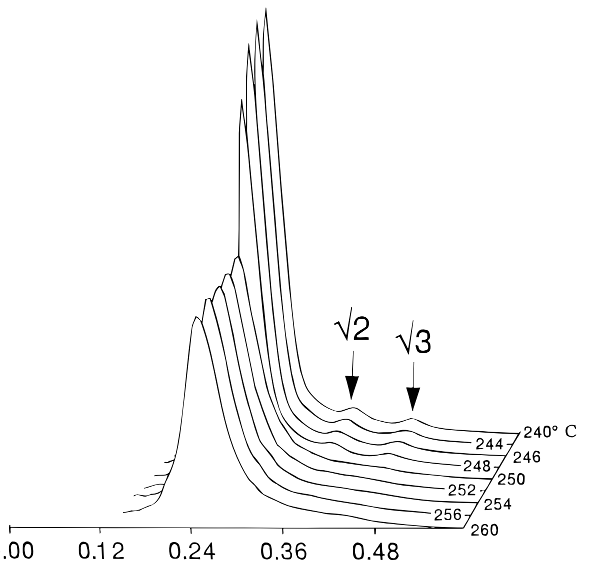

Figure 2. Small-angle X-ray scattering data for S/EP-48 at the indicated temperatures. The scattering vector $q = (4\pi/\lambda) \sin \theta$, where λ is the X-ray wavelength and 2θ the scattering angle. The intensity (vertical) axis is linear. The abrupt drop in primary peak intensity and increase in peak width, as well as the disappearance of the higher-order peaks in a q-ratio of $\sqrt{2}$ and $\sqrt{3}$, all occur at 249 °C and indicate the order–disorder transition.

$$X = \chi(N\rho/M)RT = (\chi N)_{ODT}\rho RT_{ODT}/M \qquad (1)$$

where ρ is the mass density of the material at the ODT (see Table 1) and M is the molecular weight. Note that if χ were based on a temperature-independent exchange energy as originally conceived[15] ($\chi \sim 1/T$), then X would be temperature-independent; experimentally, some temperature dependence of X is typically found. Self-consistent field (SCF) theories[16–18] predict that $(\chi N)_{ODT}$ at a minor component volume fraction $f = 0.11$ (the average for the materials studied here; see Table 1) is approximately 43. For diblocks having the values of f given in Table 1, $(\chi N)_{ODT}$ ranges[18] from 40 to 49 and is

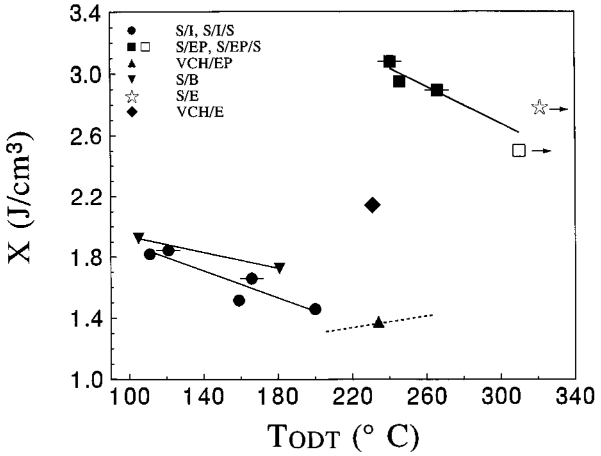

Figure 3. Interaction energy densities X vs temperature for the six chemical systems studied: S/I; S/B; S/EP; S/E; VCH/EP; VCH/E. The open symbols (□, S/EP; ☆, S/E) indicate polymers where T_{ODT} could only be bounded; the arrow indicates the direction in which the true T_{ODT} lies. Points corresponding to triblock copolymers have a horizontal line through the symbol. For S/I, S/B, and S/EP, approximate temperature dependences are indicated by the solid lines. The dashed line for VCH/EP is based on the temperature dependence reported previously by Balsara et al.[14]

scarcely affected by conformational asymmetry.[18,19] Values of $(\chi N)_{\mathrm{ODT}}$ at the appropriate value of f for each polymer were taken from the work of Matsen and Bates.[18] Slightly different values of $(\chi N)_{\mathrm{ODT}}$ would be obtained from different theories, but this would not substantially affect our conclusions; we based our earlier work[9] on the weak-segregation theory of Leibler,[20] for which $(\chi N)_{\mathrm{ODT}} = 60$ at $f = 0.11$.

Figure 3 shows X versus T_{ODT} for the six chemistries examined here. For S/I, S/B, and S/EP, X decreases measurably with increasing temperature. For VCH/E and S/E, only one material of each was examined, so no indication of any temperature dependence of X is available; also, for the S/E, we were only able to put a lower bound on T_{ODT} (>310 °C). To place the triblock copolymers on the same plot, the value for M in eq 1 was divided by 1.95, as discussed previously;[9] a similar factor is obtained from SCF theory for starblocks.[21] On comparing S/I/S with S/I, and S/EP/S with S/EP, the apparent X values for the triblocks are slightly higher than for the diblocks, even with this correction; a factor of 1.87 instead of 1.95 would bring the di- and triblock values into precise agreement. Thus, there may be a slight effect of block architecture on X (and χ), though the magnitude we find here is small (<5%). The magnitudes and temperature dependences of X for S/I and S/B are very similar, as previously reported;[22] the values of χ computed from X and the densities listed in Table 1 are in reasonable quantitative agreement with the range of values reported in the literature for S/I[9,23] and S/B,[24-26] though near the low end.

Figure 3 shows the dramatic effect that saturation can have on the interblock interactions. Extrapolating to 220 °C, we see that X is 2.4 times larger for S/EP than for S/I. Sakurai et al.[8] previously estimated χ for the S/EP system using dioctyl phthalate (DOP) solutions, obtaining $\chi(200\ ^\circ\mathrm{C}) = 0.067$ with a very weak temperature dependence. While this value was also twice that for the precursor S/I diblock, the authors cautioned that the pseudobinary approximation employed in the analysis is questionable for a selective solvent such as DOP. While the value that we estimate for S/EP at 200 °C ($X = 3.3$ J/cm^3 yields $\chi = 0.078$) is similar to that found by Sakurai, we find a very strong inverse temperature dependence for χ. As for measurements in bulk, Koberstein and co-workers reported that for diene-hydrogenated S/B materials, $\chi(200\ ^\circ\mathrm{C}) = 0.050$ when the B precursor contained 95% 1,2 addition,[6] and $\chi(200\ ^\circ\mathrm{C}) = 0.08$ when the B precursor contained 38% 1,2 addition (S/EB).[7] Extrapolating this trend, the χ for S/E would be expected to be even larger; indeed, though we are only able to bound X for S/E, Figure 3 shows that it is at least as large as X for S/EP.

Table 2. Calculated and Experimental Interaction Energy Densities

block copolymer	X calcd from params of Hoy[27] at 25 °C (J/cm^3)	X calcd from params of Coleman[28] at 25 °C (J/cm^3)	range of X obsd experimentally (J/cm^3) [T, °C]
S/I	4.5	8.4	1.4–1.8 [111–202]
S/B	3.0	7.8	1.7–1.9 [107–185]
S/EP	9.8	13.8	2.9 - 3.1 [241–266]
S/E	6.1	9.2	>2.7 [310]
VCH/EP	0.7	3.0	1.4 [234]
VCH/E	0.04	1.1	2.1 [231]

For comparison, values of X were calculated from solubility parameters (δ) obtained from group contribution methods using $X = (\Delta\delta)^2$, where $\Delta\delta$ is the difference in δ between the two block types. Values for δ were calculated using parameters from Hoy[27] and Coleman et al.,[28] ignoring the minor structures from vinyl-type additions in the diene blocks. Table 2 shows the calculated X values at 25 °C; most are significantly larger than observed experimentally. Irregular mixing[29] may contribute to the quantitative differences, so it is more instructive to examine whether the experimental trends are captured. The group contribution estimate reproduces the similarity in X between S/B and S/I and also the increased value of X for styrene–olefin systems over styrene–diene (roughly double). However, the prediction is that X for S/E should be only about $^2/_3$ that for S/EP, whereas experimentally we find the factor to be at least unity.

Also, the values of X calculated for the VCH-containing systems are generally lower than observed experimentally, though the scatter in the calculated values is large (depending on the parameter set chosen). This discrepancy was noted previously by Gehlsen and Bates,[5,13] who attributed it to conformational asymmetry. Calculated values of the conformational asymmetry parameter[19] ϵ are given in Table 1; S and VCH are the monomers forming the more "compact" blocks, and in assigning which block is "A" and which block "B", we choose the convention $\epsilon > 1$ here. While the polymers containing VCH do indeed have some of the largest conformational asymmetries, it is also possible that the group contribution methods generate a δ value for PVCH that is simply much too high, as both sets of parameters yield a value of δ for PVCH which is *larger* than that for PE. Experimentally, Figure 3 shows that X for VCH/E is much larger than for VCH/EP; this result can also be inferred from the data of Gehlsen and Bates,[13] which further indicate that X for VCH/EE is lower still. From a systematic investigation of δ for polyolefins by neutron scattering and equation of state measurements,[30] δ is known to decrease in the order PE > PEP > PEE, implying that δ for PVCH should be lower than for PEP and, perhaps, lower than for PEE. Recently, we attempted to blend a low-molecular-weight

PVCH ($M_w = 3$ kg/mol) with a range of other polyolefins and polydienes to better estimate δ, but no miscible blends could be found.[31]

In summary, the effects of saturating styrene–diene diblocks on the interblock interactions have been quantified. In all the cases examined here and in the literature, selective saturation of the diene block increases X, but the magnitude of the increment in X varies strongly (factor of at least 4) with the chemical structure of the polydiene. This same variability occurs with dual saturation, as noted previously,[13] but the magnitude of the increment is generally smaller. The large increases in interaction strength seen on diene-selective hydrogenation are qualitatively captured by group contribution calculations, but those seen on dual hydrogenations are not, suggesting that the calculated solubility parameter for PVCH may be far from the true value.

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