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Notes

Effect of Nonuniform Deuterium Labeling on Small-Angle Neutron Scattering Results for Polymer Blends

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Introduction

Labeling with deuterium is widely used to provide scattering contrast for small-angle neutron scattering (SANS). Labeled polymers are often made by polymerizing deuterated monomers,[1,2] although we have used a different method of labeling in our SANS studies of thermodynamic interactions in polyolefin blends.[3] The components are made by saturating the double bonds of nearly monodisperse hydrogenous polydienes. Separate aliquots are saturated with D_2 and with H_2 to obtain labeled and nonlabeled model polyolefins of the same molecular structure. The saturation reaction is conducted with a heterogeneous catalyst, palladium on either calcium carbonate ($Pd/CaCO_3$) or barium sulfate ($Pd/BaSO_4$), which produces complete saturation with no discernible chain scission or cross-linking.[4,5] Some H/D exchange occurs as well,[6] which further enhances the scattering contrast between the labeled and nonlabeled blend components. However, it appears that the additional deuterium is distributed nonuniformly within the sample, since even the pure labeled polymers exhibit observable coherent SANS cross-sections.[7] The effect of labeling nonuniformity on the results would appear to be small in most cases,[7,8] but since the thermodynamic interactions in polyolefin blends are themselves rather weak, it is desirable to confirm this by comparing with results obtained with more uniform samples. Here we compare earlier measurements of blend interaction strength for $Pd/BaSO_4$-saturated polymers with those obtained when the saturations are conducted with Wilkinson's catalyst,[9] a more selective homogeneous catalyst. We observe and discuss effects of both the average labeling level and the labeling uniformity.

Experimental Section

The saturated polymers in this study were derived from two samples of polybutadiene, designated PB08 and PB25. Both were made by anionic polymerization, and both have narrow molecular weight distributions ($M_w/M_n < 1.05$). They contain 8 and 25% 1,2 (vinyl) units, respectively; the sequencing of 1,2 and 1,4 units in such polymers is nearly random.[10] Molecular weights were determined by light scattering (M_w = 62 500 for PB08 and 93 000 for PB25) and are expressed in the tables as values of N, the total number of monomeric (C_4) units per chain.

Table 1. Properties of Saturated Polybutadienes

sample code	N	ρ (g cm^{-3})[a]	T_m (°C)[b]	n_D
H08W	1160	0.9171	113	
D08W	1160	0.9505	112	2.00
H08Pd	1160	0.9165	113	
D08Pd	1160	0.9759	113	3.61
H08APd	1180	0.9104	113	
D08APd	1180	0.9680	112	3.48
H25Pd	1720	0.8798	68	
D25Pd	1720	0.9364	67	3.53

[a] Density at 23.0 °C, obtained with a density gradient column[3] after slow cooling of the sample from the melt state. [b] Final melting temperature, obtained with a heating rate of 10 °C/min for samples quenched from the melt.

The polybutadiene precursor PB25 had already been saturated with H_2 and D_2 by $Pd/BaSO_4$ catalysis for use in previous work,[11] and aliquots, designated D25Pd and H25Pd, were used in this study as well. Two aliquots of polybutadiene precursor PB08 were saturated by $Pd/BaSO_4$ catalysis, providing D08Pd and H08Pd, and two others were saturated by the Wilkinson's catalyst, providing D08W and H08W. We also quote and compare results obtained earlier with still another pair of labeled and nonlabeled polymers, designated here D08APd and H08APd, that were derived from another sample of 8% vinyl polybutadiene with slightly different molecular weight (M_w = 63 800).[11]

All saturation reactions were conducted with high-pressure H_2 or D_2 on 1% solutions of the polymer in a 2-L Parr reactor at 100 °C. For the palladium-catalyzed saturations, equal weights of PB08 and $Pd/BaSO_4$ (5% palladium supported on $BaSO_4$; Strem Chemical Co.) were used; the solvent was *n*-heptane, and the pressure was 300 psi. With the homogeneous Wilkinson's catalyst, a preparation consisting of 36.6 mg of tris(triphenylphosphine)rhodium chloride ($(PPh_3)_3RhCl$) and 200 mg of triphenylphosphine (PPh_3) (both from Aldrich Chemical Co.) was used per gram of PB08 (mole ratios of 450:19:1 for double bonds, PPh_3, and $(PPh_3)_3RhCl$[12]). The solvent in this case was toluene, and the pressure was 700 psi.

The reaction conditions were maintained for about 2 days, although, from the pressure changes, the saturation appeared to be essentially complete in a few hours or less. The $Pd/BaSO_4$ reaction product was filtered hot to remove the catalyst, and the polymer was recovered by crystallization as the filtrate cooled. The Wilkinson's catalyst products also crystallized from the reaction mixture as it cooled; several purification cycles—filtration, washing, and crystallization from fresh solvent—were sufficient to remove the catalyst.

Residual unsaturation in all products was less than 1.0% according to FTIR measurements. No indication of chain scission or cross-linking was found in high-temperature size-exclusion chromatography determinations. Melting temperatures of the various H08 and D08 polymers were practically indistinguishable by calorimetry (Perkin-Elmer DSC-7), as can be seen in Table 1. Densities for the various samples at 23 °C are also given in Table 1.

The SANS measurements were made at the NIST Cold Neutron Research Facility in Gaithersburg, MD.[13] The 8 m beam line (NG5) was used with neutron wavelength λ = 9 Å ($\Delta\lambda/\lambda$ = 0.25); the range of scattering vector magnitudes was used, $0.008 \le q$ (Å^{-1}) ≤ 0.085, where q is $(4\pi/\lambda)\sin(\theta/2)$ and θ

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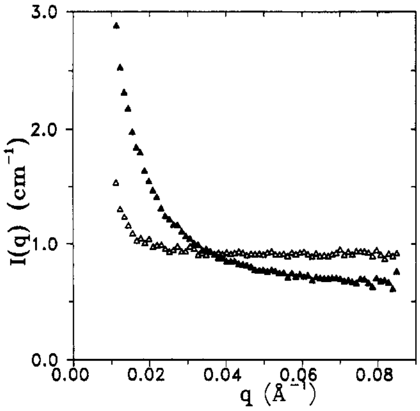

Figure 1. Scattering vector dependence of total SANS intensity at 167 °C for pure labeled polymers saturated with palladium (▲) and Wilkinson's catalyst (△).

is the scattering angle. Sample preparation, experimental procedures, and data analysis are described elsewhere.[3] Scattering measurements were made for pure labeled samples,[7] for equal-volume matched pair mixtures,[3] and for equal-volume blends of the structurally different species.

Results and Discussion

Scattering by Pure Deuterated Components. The number of deuterium atoms per monomeric (C_4) unit in the labeled polymers was calculated from the labeled and nonlabeled polymer densities:[3]

$$n_D = \frac{55.77(\rho_D - \rho_H)}{\rho_H + 0.0139\rho_D} \tag{1}$$

The values are listed in Table 1. Those from Pd-based saturations are significantly larger than the stoichiometric value, $n_D = 2$, indicating H/D exchange in addition to double-bond saturation. However, the labeled product obtained with Wilkinson's catalyst, D08W, has the stoichiometric value within the errors, indicating negligible H/D exchange.

Figure 1 compares the total SANS intensity $I(q)$ for pure D08W and pure D08Pd in the melt at 167 °C. The asymptote at high q is the incoherent contribution I_{inc}, which is proportional to the proton concentration.[1,2] The value of I_{inc} is larger for D08W, which is consistent with the lower deuterium concentration of that sample and accordingly higher proton concentration. The total intensity increases with decreasing q for both, but the upturn begins rather abruptly and at much smaller q for D08W. In fact, $I(q)$ for D08W bears a certain resemblance to the intensity profile for perdeuterated polymers (see, for example, Figure 5 in ref 7), for which, of course, the chains must be labeled uniformly. To our knowledge, at least the cause of this intensity upturn for purely amorphous perdeuterated polymers well above the glass transition is unexplained. Note that the upturn begins at larger q for D08Pd and that the intensity builds gradually with decreasing q through almost the entire range, reaching much larger values of $I(q)$ at small q than does D08W. This behavior is typical for polymers labeled by Pd-catalyzed saturation, and the $I(q)$ characteristics in this case have been shown to be consistent with the existence of differences in labeling level among the various chains in the sample.[7]

Scattering by Matched Pair Mixtures. SANS data for matched pairs[3] were interpreted with the RPA expression for binary blends with $\phi_H = \phi_D = {}^1/_2$:[2]

$$\frac{k_N v}{2I_c(q)} = \frac{2}{NP(q)} - \chi_{HD} \tag{2}$$

in which $I_c(q)$ is the coherent part of the scattering intensity, $I_c(q) = I(q) - I_{inc}$, and k_N is the contrast factor, calculated from n_D.[1,2] Both volume per monomeric unit v and component form factor $P(q)$ are assumed to be independent of labeling. The Debye equation for random coils[2] was used: $P(q) = 2(e^{-u} - 1 + u)/u^2$, where $u = (qR_G)^2$ and R_G is the radius of gyration. Values for R_G (±2%) and the isotopic interaction parameter χ_{HD} ($\pm 1.5 \times 10^{-4}$) were obtained by a nonlinear least-squares fit to eq 2; the results are given in Table 2.

The values of R_G from the H08W/D08W and H08Pd/D08Pd data are the same within the errors, and they agree well with the H08APd/D08APd results reported earlier.[10] However, the values of χ_{HD} for H08W/D08W, which are effectively zero within the errors, are distinctly different from those for the Pd-saturated matched pairs. We attribute that difference mainly to the higher average level of deuterium, and hence larger isotopic contribution to χ in blends,[14] for the polymers labeled by Pd catalysis. The correction for pure labeled component scattering[7] reduces χ_{HD} somewhat (see values in parentheses in Table 2) but cannot account for the entire difference.

Scattering by Blends of Structurally Different Components. SANS data for equal-volume mixtures of the 08 and 25 components were interpreted[3] through the expression

$$\chi = \lim_{q \to 0} E(q) \tag{3}$$

where the excess function $E(q)$ for equal-volume fractions is given by

$$E(q) = v_0\left[\frac{1}{v_1 N_1 P_1(q)} + \frac{1}{v_2 N_2 P_2(q)} - \frac{k_N}{2I_c(q)}\right] \tag{4}$$

in which the $P_i(q)$ were established from the matched pair results for the respective components, and v_0 is the reference volume $(v_1 v_2)^{1/2}$. In past work, we have found $E(q)$ to be insensitive to q in the low-q range,[3] making the extrapolation to evaluate χ relatively unambiguous. The results obtained by this procedure are given in Table 3.

Figure 2 shows examples plot of $E(q)$ for three of the blends at 142 °C: H08W/D25Pd, D08W/H25Pd, and D08Pd/H25Pd. The experimental scatter is largest for D08W/H25Pd, the blend with the labeled component from Wilkinson's catalyst. That blend also has the smallest contrast factor and smallest ratio of coherent to incoherent intensity, so its counting errors are largest. The interaction parameters differ significantly among the three blends: χ(H08W/D25Pd) > χ(D08W/H25Pd) > χ(D08Pd/H25Pd) at all three temperatures (Table 3). This ordering of interaction strengths is consistent with earlier observations on labeling effects for similar blends.[15] It appears to be understandable in terms of solubility parameter ideas, together with the supposition that deuterium substitution always reduces the solubility parameter of saturated hydrocarbons.[11] Thus, H08 has a larger solubility parameter than H25,[10] so χ(H08W/D25Pd) is larger than the "switched-label" χ(D08W/H25Pd). Moreover, D08Pd has a higher labeling level than D08W, so χ(D08Pd/H25Pd) is even smaller than χ(D08W/H25Pd). Notice that, unlike

Table 2. Results from Matched Pair Mixtures

mixture	T (°C)	R_G (Å)	$\chi_{HD} \times 10^4$
H08W/D08W	118	119 (120)[a]	0.0 (−0.5)[a]
	142	120 (121)	0.0 (−0.3)
	167	120 (120)	0.5 (−0.5)
H08Pd/D08Pd	118	119 (121)	2.3 (1.3)
	142	119 (120)	2.1 (1.0)
	167	118 (119)	1.7 (0.5)
H08APd/D08APd[b]	118	118	3.8
	142	116	2.3
	167	115	2.7
H25Pd/D25Pd	83	132	3.0
	121	131	2.7
	167	129	2.3

[a] Values in parentheses are corrected for scattering from the pure labeled component, as described in ref 7. [b] Values reported in ref 11.

Table 3. Flory–Huggins Interaction Parameters for Blends of the 08 and 25 Species

	$\chi \times 10^4$		
blend	118 °C	142 °C	167 °C
H08W/D25Pd	(2 phase)[a]	11.6	9.4
D08W/H25Pd	10.2	8.4	6.6
D08Pd/H25Pd	9.6	6.4	4.3
H08APd/D25Pd	13.4	10.9	8.0
D08APd/H25Pd	9.3	7.4	5.9

[a] $\chi_{\text{critical}} = 14.3 \times 10^{-4}$.

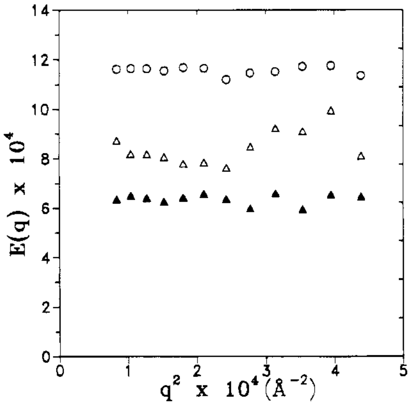

Figure 2. Scattering vector dependence of the excess function $E(q)$ for blends at 142 °C: H08W/D25Pd (○); D08W/H25Pd (△); D08Pd/H25Pd (▲).

deuterium labeling, hydrogenation produces the same properties regardless of catalyst: within the errors χ(H08W/D25Pd) and χ(H08APd/D25Pd) are the same (Table 3).

Summary and Conclusions

A sample of polybutadiene was saturated with D_2 by a heterogeneous catalyst, palladium on barium sulfate, and by a homogeneous Wilkinson's catalyst. The deuterium content of the Wilkinson's catalyst product was that required for double-bond saturation alone. The deuterium content of the product of palladium catalysis was significantly higher, indicating that some H/D exchange had occurred as well. The SANS intensity profile for the Wilkinson's catalyst product resembles those for polymers made with deuterated monomers, indicating uniformity in labeling. The profile for the palladium product is quite different, and its characteristics suggest some nonuniformity in labeling, probably associated with the H/D exchange reaction. The SANS profiles for blends of these two polymers with hydrogenous components were used to obtain values for the Flory–Huggins interaction parameter χ. The results are slightly different, which appears to be caused mainly by the higher deuterium content, and correspondingly larger isotopic interaction, for blends containing the product of palladium catalysis. Labeling nonuniformity *per se* seems to have relatively little effect on the results.

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