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Melt Chain Dimensions of Poly(ethylene−1-butene) Copolymers via Small Angle Neutron Scattering

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ABSTRACT: The radii of gyration for a series of poly(ethylene−1-butene) copolymers of varying ethyl branch content were measured as a function of temperature in the melt via small angle neutron scattering (SANS), and their temperature coefficients, d ln C_∞/dT = κ, changed from negative to positive. The characteristic ratio C_∞ decreased with increasing ethyl branch frequency. When possible, these results were compared with those obtained from Θ solvents and from rotational isomeric (RIS) state theory. The SANS-based chain dimensions were slightly larger than those obtained from Θ solvents. The values of κ differed significantly from those extracted from Θ-solvent measurements. Serious discrepancies with RIS-based calculations were observed.

Introduction

Evaluation of unperturbed polymer chain dimensions, $\langle R^2\rangle_0$, and their response to variations in temperature, d ln $\langle R^2\rangle_0$/dT (κ), has historically been accomplished by dilute solution measurements under Θ conditions. That approach, though, does not always yield unambiguous results. For example, Θ-condition-based measurements on polystyrene produced values of κ that are negative,[1−7] zero,[8−10] or positive,[11] with the negative values being, for the most part, in accord with the predictions of rotational isomeric state (RIS) theory.[12] However, small angle neutron scattering (SANS) for polystyrene in the melt state has shown[13,14] that κ is essentially zero.

A similar result is found for poly(methyl methacrylate) (∼80% syndiotactic) where Θ-condition evaluations[15−21] of κ led to values ranging from +3 to -4×10^{-3} deg^{-1}. Most of these results show general agreement with RIS evaluations,[22] which yield $\kappa \sim 1 \times 10^{-3}$ deg^{-1}. However, melt state force−temperature[23] and SANS[14,24,25] measurements indicate that κ is essentially zero. Θ-solution measurements on isotactic[26−28] and atactic[27−31] (Bernoullian chain statistics) polypropylene indicated that these two forms have different negative values of κ and, at a given temperature, different values for C_∞, the characteristic ratio. The RIS predictions,[32−40] while differing one from the other, tend to at least lend qualitative support to the negative κ inferred from the Θ-solvent assays. Again, however, like the observations on polystyrene and poly(methyl methacrylate)s, SANS measurements[41,42] led to a different conclusion; namely that both forms of polypropylene have, within experimental error, the same C_∞ and that κ is virtually zero for both. Thus, this SANS-based commonality of melt measurements contradicts the Θ-solvent-based values and the RIS predictions.

The same picture was found to hold for atactic poly(1-butene).[42,43] The SANS study[42] in the melt yielded a value for κ of 0.4×10^{-3} deg^{-1}. A parallel probe was done[43] where the radii of gyration, $\langle R_G^2\rangle_0^{1/2}$, were evaluated by SANS in different Θ solvents over the temperature range 10−80 °C. Intrinsic viscosity measurements were also performed, and the values of $[\eta]_\theta$ were found to *decrease* with increasing Θ temperature. However, the Θ-condition SANS data indicated that $\langle R_G^2\rangle_0^{1/2}$ increases with increasing temperature, leading to $\kappa = 0.4 \times 10^{-3}$ deg^{-1}. This latter behavior replicates that found in the melt state via SANS and thermoelastic measurements, in that the findings are contrary to those from intrinsic viscosity measurements,[27,30,31,45] where *negative* values of κ were found over the temperature range −46 to 141 °C.

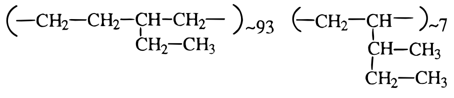
The main objective of both RIS models and the Θ-solvent approach is to determine chain dimensions in the melt. The above-mentioned disagreements between melt state SANS measurements and the RIS predictions, even for chains with relatively simple structures, indicate the presence of a flaw in that model. All current RIS models treat isolated chains in a vacuum. Significant differences may exist between chains in a vacuum and the melt state, as suggested by the recent work of Raphaël, Fredrickson, and Pincus.[46] The Θ-condition approach isolates the macromolecule in low molecular weight solvents where the potential for specific solvent effects exists. Such influences are negligible if solvent discrimination involving the available conformations is absent. In view of these potential problems, we believe SANS is perhaps the preferred tool for measuring chain dimensions. In this paper we present SANS estimates of the temperature dependence of $\langle R_G^2\rangle_0^{1/2}$ for a series of nearly monodisperse poly(ethylene−1-butene) copolymers. These materials can be represented as follows:

PEB-α

$$\left(\mathrm{CH_2{-}CH_2}\right)_{50-\alpha}\qquad \left(\mathrm{CH_2{-}\underset{\displaystyle CH_2{-}CH_3}{\underset{|}{CH}}}\right)_{\alpha}\qquad(1)$$

where 2 ≤ α ≥ 48. An essentially alternating poly(ethylene−1-butene) was prepared via ethyl-1,3-butadiene:

Alt-PEB



$$\left(\mathrm{-CH_2{-}CH_2{-}\underset{\displaystyle CH_2{-}CH_3}{\underset{|}{CH}}{-}CH_2{-}}\right)_{\sim 93}\ \left(\mathrm{-CH_2{-}\underset{\displaystyle \underset{\displaystyle CH_2{-}CH_3}{\underset{|}{CH{-}CH_3}}}{\underset{|}{CH}}{-}}\right)_{\sim 7}\qquad(2)$$

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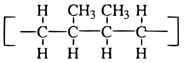
Table 1. Synthesis of Polybutadienes

% vinyl	polar modifier[a]	ratio of modifier/initiator	temperature (°C)	solvent
8[b]	none		25	cyclohexane
17	TEA	10	0	*n*-heptane
25	THF	5	50	*n*-heptane
32	THF	5	30	cyclohexane
35	TEA	500	0	*n*-heptane
38	THF	12.5	30	*n*-heptane
52	THF	37	30	*n*-heptane
66	TMEDA	0.6	30	cyclohexane
78	THF	35	0	cyclohexane
88	TMEDA	5	10	cyclohexane
90	THF	500	0	cyclohexane
97	DIPIP	5	0	cyclohexane
−10[b,c]	none		25	cyclohexane

[a] TEA, triethylamine; THF, tetrahydrofuran; TMEDA, tetramethylethylenediamine; DIPIP, dipiperidinoethane. [b] Initiator, *t*-BuLi. All others *n*-BuLi. [c] % 3,4 content in poly(ethyl-1,3-butadiene).

Temperature coefficients are also reported for head-to-head polypropylene (hhPP) and the hydrogenated materials based on mixed microstructure polyisoprenes.

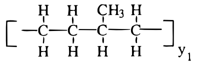
hhPP



plus ~ 3% of other isomers (3)

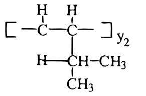
PEP

$y_1=0.93, y_2=0.07, y_3=0$



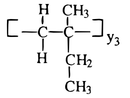
H50SPI

$y_1=0.50, y_2=0.50, y_3=0$



H75SPI

$y_1=0, y_2=0.75, y_3=0.25$



(4)

Experimental Section

The scattering of cold neutrons is a unique tool for the study of the static and dynamic properties of polymers since their accessible q range corresponds to typical intramolecular distances (where q denotes the scattering vector). As a gift from nature, the scattering properties of hydrogen and deuterium are substantially different. Therefore, by isotopic addition and substitution, it is possible to label single polydiene chains, or parts of them, at will. The use of hydrogen or deuterium produces the matched polyolefin pairs, which aside from deuterium labels are chemically identical to each other. This work is based on mixtures of such pairs.

The preparation of samples involved previous strategies.[47−49] 1,3-Butadiene was polymerized using either *n*- or *tert*-butyllithium at 30 °C. Cyclohexane or *n*-heptane was the primary polymerization solvent along with small amounts of a polar cosolvent (triethylamine, tetrahydrofuran, tetramethylethylene diamine, or dipiperinoethane) which was used to control the polybutadiene vinyl content. These materials (Table 1) served as the parent polymers of the random PEB copolymers. Ethyl-1,3-butadiene (Wiley Organics) was used for the preparation of the essentially alternating PEB material. All polydienes, by virtue of the anionic polymerization characteristics, possessed near-monodisperse molecular weight distributions with M_z/M_w and M_w/M_n ratios ≤ 1.05. These heterogeneity indices were evaluated via size exclusion chromatography for the parent polydienes and the room-temperature amorphous polyolefins. The measurement temperature was 30 °C with either four or six 30 cm linear μ-Styragel columns used in a Waters 150 instrument. Absolute molecular weights were determined for the parent polydienes and for the room-temperature soluble polyolefins via low-angle laser light scattering on a Chromatix KMX-6. The details of this characterization step are available elsewhere.[47] The PEB materials derived from 1,3-butadiene are not, strictly spoken, random ethylene−butene copolymers, since the minimum number of ethylene units between 1-butene structures occurs in multiples of two; a consequence of the 1,4-units in the parent polybutadienes.

Table 2. Molecular Characteristics and Physical Properties of Saturated Polybutadienes

sample designation	N	ρ_H (g cm^{-3})	ρ_D (g cm^{-3})	T_g (°C)	r_1r_2
HPB(97), DPB(97)	865	0.8651	0.9074	−25	—
HPB(90), DPB(90)	520	0.8660	0.9011	−34	0.84
HPB(88), DPB(88)	1610	0.8642	0.9108	−34	0.66
HPB(78), DPB(78)	1285	0.8630	0.9002	−45	0.73
HPB(66), DPB(66)	2030	0.8635	0.9146	−54	0.81
HPB(52), DPB(52)	1510	0.8604	0.9053	−61	0.69
HPB(38), DPB(38)	1830	(0.8598)	(0.9072)	(−62)[a]	0.74
HPB(35), DPB(35)	1390	(0.8589)	(0.9132)	(−54)	0.67
HPB(32), DPB (32)	1720	(0.8643)	(0.9079)	(−56)	0.74
HPB(25), DPB(25)	1720	(0.8798)	(0.9364)	(−51)	0.76
HPB(17), DPB(17)	2200	(0.8878)	(0.9359)	(−40)	0.67
HPB(8), DPB(8)	1190	(0.9104)	(0.9680)	(−30)	0.24

[a] The values in parentheses correspond to a secondary thermal transition for the semicrystalline polymers examined.

Saturation was performed under the conditions previously described.[50] Palladium on either calcium carbonate or barium sulfate was the catalyst. ^{1}H-NMR was used to evaluate polydiene microstructure and residual unsaturation. All PEB samples were found to be >99.4% saturated. ^{13}C NMR was used to evaluate the sequence distribution characteristics of the PEB materials. The results were cast in terms of reactivity ratio products, as outlined by Hsieh and Randall.[51] The r_1r_2 values suggest essentially random sequencing with perhaps a slight tendency toward alternation (Table 2).

Densities were determined at 23 °C for the amorphous materials with a density gradient column. These values are given in Table 2 with the densities for the hydrogenous materials in good agreement, when comparisons are possible, with those published elsewhere.[45,47,49] Differential scanning calorimetry (Seiko, Model SSC5200H) was used to determine glass transition temperatures at a scanning rate of 10 °C per minute. Those values are also given in Table 2 and are based on the midpoint of the transition.

The SANS measurements were done at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD, on the 8- and 30-m instruments. Blend preparation (the HPEB and the partially deuterated DPEB components), experimental procedures, and data analysis have been described elsewhere.[47] Data were obtained for a range of scattering vectors $q = 4\pi/\lambda \sin \theta/2$, where θ is the scattering angle and λ is the neutron wavelength over the temperature range 300−440 K for room-temperature amorphous materials. Smaller ranges were used for those ethylene rich samples which exhibited a crystalline fraction. Concentrations of the partially deuterated polyolefins in their corresponding hydrogenous counterparts ranged from 0.04 to 0.50 (volume fraction).

Results and Discussion

SANS. The chain dimension data (Table 3) show that the magnitude of κ decreases as the ethyl branch content increases, changes sign, and then undergoes an increase for ethyl branch content greater than about 25. This behavior is not predicted via RIS theory in that SANS measurements[52] on PEB-2 yielded a value of κ of ca. -1.1×10^{-3} deg^{-1} (which agrees with calculation[53]) while for atactic poly(1-butene) a κ value of -0.1×10^{-3} deg^{-1} was calculated,[38] a value which this work and previous results[42,43] ($\kappa = (0.4-0.5) \times 10^{-3}$ deg^{-1}) fail to support. Typical chain dimension behavior as a function of ethyl branch content is given in Figure 1.

Tonelli[54] has evaluated the influence of ethyl branching on the conformational behavior of polyethylene for branch contents of 5, 10, and 20 per 100 backbone carbons. His RIS-based conclusions led to the finding that $\langle R^2\rangle_0/M$ decreased only slightly for a constant

Table 3. Molecular Parameters for Poly(ethylene−butene) Copolymers

sample[a]	M_w × (10^{-4} g mol^{-1})	$\langle R^2_G\rangle^{1/2}_0$ (Å) at Various Temperatures (°C)								κ (10^3 deg^{-1})
		27	51	83	88	118	121	142	167	
PEB-2.1(8)	6.62					117.7		116.1	115.0	−0.95
PEB-4.6(17)	12.37				159.1	156.5		153.8	151.7	-1.2_8
PEB-7.1(25)	9.65			132.5			131.0		128.9	-0.6_6
PEB-9.5(32)	9.65		131.9	131.2			130.0		129.1	-0.3_8
PEB-10.6(35)	7.80		120.0	119.7			118.1		116.8	-0.5_0
PEB-11.7(38)	10.25		130.0	129.0			128.0		127.0	-0.4_0
PEB-17.6(52)	8.48	114.4	113.8	114.0			113.6		113.5	-0.1_0
PEB-24.6(66)	11.40	123.3	122.9	123.0			123.3		123.2	0
alt-PEB[b]	4.63	74.8	73.4	73.2			73.1		73.0	-0.2_8
PEB-32(78)	7.20	87.7	88.1	89.0			90.3		91.5	0.6_3
PEB-39.3(88)	9.03	96.8	97.5	97.7			98.0		99.3	0.3_2
PEB-40.9(90)	2.92	51.6		53.1			53.7		54.6	0.8_1
PEB-48(97)	4.85	62.6	62.7	63.2			63.6		64.0	0.3_3

[a] Values in parentheses denote vinyl content of the parent polybutadiene. [b] Essentially alternating copolymer of ethylene and 1-butene.

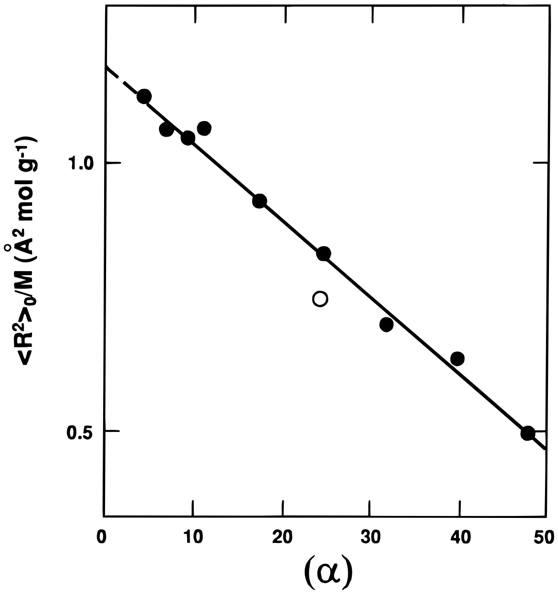


Figure 1. PEB chain dimensions at 356 K for PEB copolymers as a function of ethyl branch content (α). The open symbol denotes alt-PEB.

degree of polymerization (DP) as the frequency of branching (α) increased over the range mentioned. The data of Table 3 support this conclusion, as is seen in Table 4. Within experimental error the RIS based findings are in excellent agreement with the SANS-based data. It can also be seen that $\langle R^2\rangle_0/M$ decreases in a smooth monotonic fashion with increasing α (the extent of branching) over the temperature range 300−440 K. The values of $\langle R^2\rangle_0/M$ for the PEB chains are therefore relatable to α via the expressions given in Table 5. The dependence of $\langle R^2\rangle_0/M$ on α allows the determination of the chain dimensions of polyethylene and poly(ethylethylene). These findings are summarized in Table 6. As can be seen for the case of polyethylene, excellent agreement with the measured[52,55,56] values of $\langle R^2\rangle_0/M$ is obtained. The corresponding comparison with pure poly(ethylethylene) is not possible due to the lack of SANS-based melt chain dimension data.

This conformational behavior has been treated within the RIS framework by Mattice[57] (Table 4 and Figure 2). Therein, that RIS approach seemingly underestimates the chain dimensions as a function of ethyl branchings (Figure 2), while the approach used by Tonelli[54] is well replicated by the SANS results. The noted differences may, in part, be artifactual, since the PEB materials are not strict models for random copolymers. An indication of this is the data point of alt-PEB. Conversely, the ca. 7% content of the articulated *sec*-butyl group is conceivably the cause for the attenuated chain dimensions of alt-PEB.

Θ Conditions. Some random PEB-type copolymers (and alt-PEB) have had their conformational characteristics measured via intrinsic viscosity measurements.[45,58,59] For 300 K generally good agreement was found in terms of C_∞ between experiment and RIS predictions (see Figure 5 of ref 45). As noted the SANS-based values of C_∞ are generally larger than the RIS predictions and hence also larger than those from Θ solvents. This trend can be seen in Table 4. This behavior can be rationalized as due to specific solvent effects where solvent discrimination between conformations is possible.[60,61] This event is one that does not produce additional rotational isomeric states but rather alters the potential energies of the existing states. In other words, the possibility exists where the magnitudes of the various energy minima can be altered by the local solvent−solute interactions. This scenario has previously been used[42] to explain the differences in κ values derived via SANS melt measurements and those from Θ conditions for polypropylene and atactic poly(1-butene). A similar state of play may be invoked to explain similar discrepancies found for polystyrene and poly(methyl methacrylate) (as mentioned in the Introduction).

Chain Dimension Temperature Coefficients. This work has revealed additional materials for which pronounced differences in κ exist with regard to the Θ-condition and SANS-based measurements. A summary of those polymers for which differences exist is given in Table 7. Where appropriate, the RIS and Θ-solvent-based values of κ are generally in semiquantitative agreement, a feature not shared with the SANS-based values. This may be due to the fact that the Θ-condition results have, through the years, served to guide the RIS-based calculations.

The $\langle R_G^2\rangle_0^{1/2}$ data (Table 3) show that as ethyl branch content increases, the magnitude of κ changes, with the sign going from negative to positive. Furthermore, $\langle R^2\rangle_0/M$ decreases as α (the degree of ethyl branching) undergoes an increase (Figure 1). That influence of composition upon $\langle R^2\rangle_0/M$ as a function of temperature is given by the expressions of Table 4.

Obviously polyethylene and poly(1-butene) represent the two compositional extremes, which were not measured in this work. For the polyethylene case good agreement is found[52,63,64] (Table 5) for the calculated values and their measured counterparts, where the

Table 4. Influence of Ethyl Branching on Polyethylene Conformational Characteristics at 298 K

ethyl branches	m_o[a]	$\langle R^2_G\rangle_0/M$ (Å^2 mol g^{-1})		$\langle R^2{}_G\rangle_0$[b] (10^{-4} Å^2)		C_∞		g[c]		
		θ[d]	SANS[e]	θ	SANS	θ	SANS	θ	RIS	SANS
0	28	0.224	0.232	3.136	3.248	8.0_4	8.3_3			
2	29.0	0.198	0.223	2.871	3.234	7.3_6	8.3_3	0.92		1
5	30.8	0.183	0.209	2.818	3.219	7.2_2	8.2_9	0.90	0.95−0.97[f]	0.99
10	33.6	0.159	0.180	2.671	3.024	6.8_5	7.8_8	0.85	0.91−0.95[f]	0.93
15	36.4	0.138	0.162	2.512	2.894	6.4_4	7.4_2	0.80	0.78[g]	0.89
20	39.2	0.120	0.146	2.352	2.842	6.0_3	7.2_8	0.75	0.86−0.91[f]	0.88
25	42.0	0.109	0.131	2.289	2.709	5.8_7	6.9_4	0.73	0.70[g]	0.83
30	44.8	0.102	0.118	2.285	2.576	5.8_6	6.6_0	0.73	0.66[g]	0.79
40	50.5	0.084	0.095	2.117	2.399	5.4_3	5.9_3	0.68	0.61[g]	0.74
50	56.0	0.077	0.077	2.156	2.156	5.5_2	5.2_3	0.69		0.66

[a] m_o denotes the mean molecular weight per two backbone carbons. [b] For DP of 5 × 10^3. [c] $g = \langle R^2_G\rangle_0(\mathrm{PEB})/\langle R^2_G\rangle_0(\mathrm{PE})$ for equal degrees of polymerization. [d] Based on data of ref 49. [e] With the exception of polyethylene and PEB-2.0, values are based on $\langle R^2\rangle_0/M = 1.3393e^{-0.021337\alpha}$. [f] Reference 54. [g] Reference 55.

Table 5. Dependence Of $\langle R^2\rangle_0/M$ on Ethyl Branch Content (α) for PEB Copolymers

temp (°C)	$\langle R^2\rangle_0/M$ (Å^2 mol g^{-1})
27	$1.3393 \times e^{-0.021337\alpha}$
51	$1.3143 \times e^{-0.020532\alpha}$
83	$1.2994 \times e^{-0.019912\alpha}$
121	$1.2684 \times e^{-0.018926\alpha}$
167	$1.2148 \times e^{-0.017221\alpha}$

Table 6. Projected Unperturbed Chain Dimensions for Polyethylene and Poly(ethylethylene)

	polyethylene		poly(ethylethylene)
temp (°C)	$\langle R^2\rangle_0/M$[a] (Å^2 mol g^{-1})	$\langle R^2\rangle_0/M$[b] (Å^2 mol g^{-1})	$\langle R^2\rangle_0/M$[a] (Å^2 mol g^{-1})
27	1.34	1.42	0.46
51	1.31	1.38	0.47
83	1.30	1.33	0.48
121	1.27	1.28	0.49
167	1.22	1.21	0.51

[a] Based on the relations of Table 5. [b] Based on an $\langle R^2\rangle_0/M$ of 1.25 at 140 °C and $\kappa = -1.1 \times 10^{-3}$ deg^{-1}; refs 52, 55, and 56.

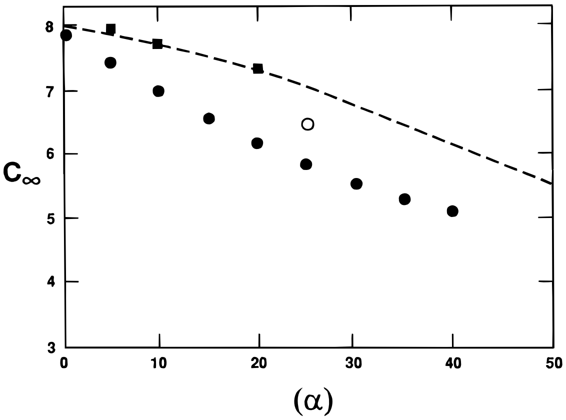


Figure 2. C∞ as a function of ethyl branch content (α) at 300 K. The closed circles are from ref 57. The open symbol denotes alt-PEB. The dashed line is based on the appropriate equation of Table 5. The squares denote the results of ref 54.

Table 7. Temperature Coefficients from RIS, Θ-Conditions, and SANS

	κ 10^3(deg)$^{-1}$			
polymer	RIS	Θ	SANS	refs
polystryene	−0.3 to −1.1	0.4 to −1.1	0	1−14
poly(methyl methacrylate)[a]	∼2.0	0 to 2.4	∼0	15−25
a-polypropylene[b]	0 to −1.8	−1.0 to −3.0	−0.1	26−41
i-polypropylene[c]	−1.0 to −4.0	−1.0 to −4.0	∼0	26−28, 29−40
PEB −11.7		−1.0	−0.4	45, this work
alt-PEB		−0.9	−0.3	43, 45, this work
PEB-40		−1.7	0.5	45, this work
PEB-48	−0.1	−1.0 to −2.7	0.4	43, 45, this work
HHPP			∼0	62
H50SPI			∼0	62
H75SPI			1.2	62

[a] ∼80% syndiotactic. [b] Atactic form. [c] Isotactic form.

$\langle R^2\rangle_0/M$ value determined at 140 °C was corrected for temperature by the SANS and Θ-solvent κ of -1.1×10^{-3} deg^{-1}. The values for poly(1-butene)—Bernoullian chain statistics—are also given. However, a comparison of those results with their directly measured counterparts is not possible due to the lack of those data.

The SANS-based melt values of κ (Table 7) show the influence of frequency and type of side group on the temperature dependence of backbone conformation. Polyethylene and alt-poly(ethylene−polypropylene) share the same κ of -1.1×10^{-3} deg^{-1}. However, H50SPI and polypropylene (head-to-head and head-to-tail) yield κ values of about zero. This shows that the *trans* and *gauche* forms have virtually equivalent energies, as opposed to the parent polyethylene chain, where the more compact *gauche* conformer has a higher energy state (∼500 cal mol^{-1}) than the more extended form. The addition of articulated side groups (see eqs 1 and 4) reverses this order and thus leads to positive values of κ. This is particularly noticeable for the H75SPI sample with articulated and branched groups in alternate backbone carbons. These nonbonded interactions force the favoring of the more extended *trans* conformer as temperature increases.

Conclusions

The temperature dependence of the unperturbed chain dimensions for a series of PEB copolymers in the melt was investigated via SANS measurements of the melt state. In several cases disagreements were found when comparison was made to the corresponding values obtained from Θ-condition intrinsic viscosity measurements. The finding of negative temperature coefficients via intrinsic viscosity while positive values are found in the melt seemingly demonstrates that there is a basic flaw in extracting chain dimensions from intrinsic viscosity measurements. The identity of this masking event remains unknown although nonconstant behavior of the Flory−Fox hydrodynamic parameter is possible.

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