Small-Angle Neutron Scattering Evaluation of the Temperature Dependence of Atactic Polypropylene and Poly(1-butene) Chain Dimensions in the Melt

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Received June 1, 1992; Revised Manuscript Received July 20, 1992

ABSTRACT: Small-angle neutron scattering was used to measure the influence of temperature on the radius of gyration in the melt of atactic polypropylene and poly(1-butene). The chain dimension temperature coefficient, d ln $\langle R^2\rangle_o/dT$, was found to be respectively -0.1×10^{-3} and 0.4×10^{-3} deg^{-1}. These values, with one exception, disagree with the rotational isomeric state predictions as well as with those values obtained via intrinsic viscosity measurements either at Θ conditions or in perceived athermal solvents. Conversely, excellent agreement was obtained with the values available from both thermoelastic and rheological measurements on atactic poly(1-butene).

Introduction

Knowledge concerning the geometrical character of polymers is usually derived from measurements on their dilute solutions in low molecular weight solvents. The modeling of such chain behavior has traditionally been done via the rotational isomeric state (RIS) approach which, in effect, considers and treats an isolated chain in its unperturbed state. Furthermore, a commonly accepted assumption is that Θ-solvent-based behavior, the radius gyration (R_G) and d ln $\langle R^2\rangle_o/dT(\kappa)$, mimics that encountered in the amoprhous melt polymer. The advent of small-angle neutron scattering (SANS) allows the direct measurement of these parameters in the realistic environment of the polymer melt. An added advantage is the capacity to carry out measurements over a much wider temperature range than is usually feasible via the Θ-solvent approach. Generally, though, SANS measurements have been conducted at either a single temperature or over only a narrow range of temperatures.[1–13] An exception is the work of Ballard et al.[14] on isotactic polypropylene (i-PP) which covered the temperature range 23–220 °C, thus embracing both the crystalline and amorphous regimes. Within experimental error R_G for i-PP was found to be *independent* of temperature[15] and yielded the following:

$$R_G = 0.34M_w^{0.50}\ (\text{Å}{\cdot}\text{mol}^{0.50}{\cdot}\text{g}^{-0.50}) \tag{1}$$

The zero value for κ conflicts with values available from recent RIS models.[16–23] However, SANS-based results for polyethylene[24] (PEB-2)[25] and essentially alternating poly(ethylene-propylene)[26,27] (PEP) yielded values of κ in accord with RIS predictions[20,28] and those obtained from dilute solution measurements.[29–34]

The SANS technique has been used to extend these investigations to encompass atactic polypropylene (a-PP) and atactic poly(1-butene) (a-PEE).[35] This work was in part prompted by discrepancies in the RIS polypropylene models and their failure to correctly predict the experimental i-PP κ found via SANS in the melt. a-PP and a-PEE are polymers sharing identical tacticities (meso fractions of 0.50) which allows an unhindered comparison on one hand with the RIS and Θ-solution-based results with those from SANS measurements as well as an intercomparison where the influence of the differing side groups on R_G and κ can be evaluated.

Experimental Section

Sample preparations followed the previous strategies[3,4,8,34,36–38] where polydienes were converted to polyolefins via reduction with either hydrogen or deuterium. a-PP was obtained from poly(2-methyl-1,3-pentadiene) which was polymerized in cyclohexane at 30 °C, with purified *tert*-butyllithium as the initiator. The 1,4-content, via H NMR, was >99.8%. The polybutadiene, ~98% vinyl content, was prepared using dipiperidinoethane as the modifier at 0 °C in cyclohexane. *n*-Butyllithium was the initiator. The parent polydienes served as both the source of the hydrogenous matrix and the partially deuterated target. Thus, the SANS measurements were done on matched polymer pairs differing only in their isotopic content.

Density gradient column measurements showed that the average deuterium/hydrogen (d/h) ratio per a-PP repeat unit was 2.2/3.8 as opposed to the anticipated value of 1/5. a-PEE was found to have a d/h ratio of 2.2/5.8 per repeat unit. Substitution of deuterium, along with the addition event, has been found in the deuteration of hydrogenous 1,4-polybutadiene.[8,39] The polyolefins were at least 99.7% saturated based on ^{1}H NMR measurements.

The polyolefins had Bernoullian chain statistics[36,40] and, as a consequence of the anionic synthesis of the parent polydiene, near-monodisperse molecular weight distributions. The glass transition temperatures of these polyolefins were, via DSC, found to be −5 °C (a-PP) and −27 °C (a-PEE), values in agreement with those previously reported.[36,41–44] The polydispersity question was addressed by using a Waters 150 size exclusion chromatograph (SEC) and calibrations based on a-PP[36] and a-PEE[41] standards. The heterogeneity indices are given in Table I, and the chro-

Table I
Molecular Characteristics of Atactic Polyolefins

sample	dn/dc, mL·g^{-1}	$10^{-4}\bar{M}_w$	$\bar{M}_{z+1}{}^c/\bar{M}_z$	$\bar{M}_z{}^c/\bar{M}_w$	$\bar{M}_w{}^c/\bar{M}_n$	ρ(23.1 °C), g·cm^{-3}
h_6-PP	0.0844	2.33^a	1.01	1.02	1.03	0.8542
$d_{2.2}h_{3.8}$-PP^b	0.0801	2.42^a	1.01	1.02	1.03	0.8996
h_8-PEE	0.0830	3.60^a	1.01	1.01	1.02	0.8654
$d_{2.2}h_{5.8}$-PEE^b		3.57^c	1.01	1.01	1.02	0.9010

^{a} LALLS. ^{b} $M_d - M_h = M_h[\rho_d - \rho_h][\rho_h]^{-1}$ where M_d and M_h denote the average molecular weights of the deuterated or hydrogeneous atactic polyolefin repeat unit. ^{c} via SEC.

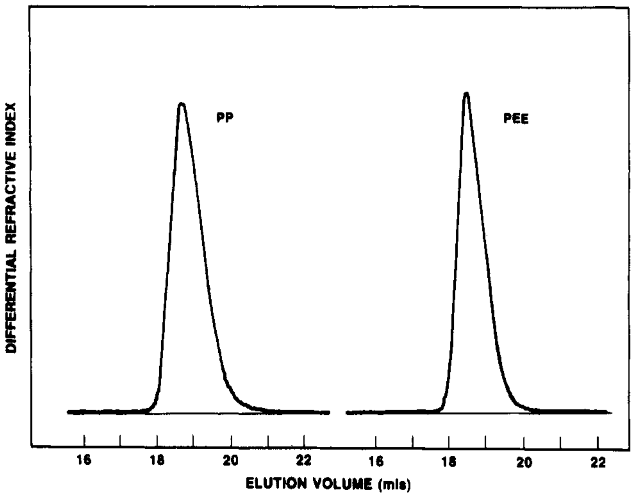

Figure 1. SEC chromatographs of a-PP and a-PEE. The common peak elution count demonstrates that both polyolefins have virtually identical R_G values.

matographs shown in Figure 1. Post-SANS SEC measurements gave no indication of the presence of either branched or degraded material in either polyolefin after the high-temperature portions of the measurements. Analysis[36] of both parent poly(2-methyl-1,3-pentadiene) and the resultant polypropylene has shown that the polydiene possesses only the 1,4-structure which is present in the head-to-tail fashion. Thus, the polypropylene contains no rogue structures.

The weight-average molecular weights (Table I) were determined using a Chromatix KMX-6 low-angle laser-light-scattering (LALLS) instrument (λ = 633 nm) with purified tetrahydrofuran as the solvent. Purification was done by distilling the solvent, under nitrogen, from the sodium:benzophenone complex. The measurements of dn/dc were done using the KMX-16 refractometer at 20 °C (Table I). After consideration of experimental errors and corrections for deuterium content, the matched polyolefin pairs have identical molecular weights. Furthermore, M_w(SEC) and M_w(LALLS) were found to be virtually identical for these polyolefins.

The SANS experiments on a-PP were done using the 8-m instrument at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD, and the FRG-1 research reactor at the Forschungszentrum Geesthacht (GKSS). The wavelength used was about 7 Å and the wavelength spread $\Delta\lambda/\lambda \sim 0.10$ at the GKSS and 0.25 at the NIST. At NIST, the detector distance and collimation were fixed to 3.6 and 4.5 m, respectively, thus covering a Q range of about 0.01–0.11 Å^{-1}. At GKSS, the detector distance was varied to cover a Q range of about 0.01–0.15 Å^{-1}. Position-sensitive two-dimensional He^3 detectors at GKSS and NIST were used. Due to the isotropy of the SANS scattering pattern it was possible to average the data radially in order to improve the signal to noise ratio.

If the interaction of the H and D species is neglected, the scattering per unit volume from a mixture of deuterated and hydrogenated chains is given by[45]

$$\frac{d\Sigma^{-1}}{d\Omega}(Q) = \frac{1}{\phi_H V_{H_w} \Delta^2\rho g_z(Q^2 R_G{}^2{}_{Hz})} + \frac{1}{\phi_D V_{D_w} \Delta^2\rho g_z(Q^2 R_G{}^2{}_{Dz})} \tag{2}$$

Here, Φ_H, R_{GHz}, V_{Hw} and Φ_D, R_{GDz}, V_{Dw}, respectively, denote the volume fractions, z-average radii of gyration, and weight average chain volumes (cm^3) of hydrogenated and partially deuterated materials. $\Delta\rho^2 = [N_A n(b_H - b_d)/\Omega_o]^2$ is the scattering contrast factor; b_H and b_d are the nuclear coherent scattering lengths for hydrogen and deuterium, and n is the number of exchanged hydrogen atoms per monomer. Ω_o is the monomer volume (cm^3·mol^{-1}). $g_z(\xi)$ denotes the z-averaged Debye function with $\xi = R_G{}^2{}_z Q^2/(1 + 2U)$ and $U = M_w/M_n - 1$. The averaging process was performed using a Schultz–Zimm distribution of the molar mass. This yields[46]

$$g_z(\xi) = \frac{2[(1 + u\xi)^{-1/u} + \xi - 1]}{(1 + u)\xi^2} \tag{3}$$

As a consequence of the matching of hydrogenated and (partially) deuterated species, V_{Hw} equals V_{Dw} and $R_{GH} = R_{GD}$. This simplifies eq 1 considerably:

$$\frac{d\Sigma}{d\Omega}(Q) = V_w \Phi(1 - \Phi)\Delta\rho^2 g_z(\xi) \tag{4}$$

where we have omitted the indices H and D. In the Zimm approximation, which is valid in the small Q range the cross section is given by

$$\frac{d\Sigma^{-1}}{d\Omega}(Q) = \frac{1 + Q^2 R_G{}^2{}_z/3}{\Phi(1 - \Phi) V_w \Delta\rho^2} \tag{5}$$

All GKSS data were independently calibrated to a Lupolen standard which had previously been calibrated to a vanadium standard. The NIST data were gauged using a silica standard. A fully protonated sample was measured at several temperatures in order to correct for the incoherent scattering of the matrix. This was subsequently subtracted according to the number of protons per monomer present in the different concentrations. The desired coherent part of the scattering is thus given by

$$\frac{d\Sigma^{coh}}{d\Omega}(Q) = \frac{d\Sigma^{s}}{d\Omega}(Q) - \left(1 - \Phi_D \frac{n}{N_P}\right)(T^s/T^{mat})\frac{d\Sigma^{inc}}{d\Omega}(Q) \tag{6}$$

Here, N_p denotes the number of protons in a monomer unit of the fully protonated material, T^s and T^{mat} are the transmission factor of sample and matrix, respectively. In the limit of the experimental errors, T^s/T^{mat} was found to be equal to unity. From $(d\Sigma^{coh}/d\Omega)(Q)$, the z-averaged radius of gyration is obtained. Since R_G must refer to the weight-average molar mass, R_{Gz} can be changed to R_{Gw} by using eq 7.

$$R_G{}^2{}_w = \frac{U + 1}{2U + 1} R_G{}^2{}_z \tag{7}$$

The SANS measurements yielded molecular weights ranging from 2.0 × 10^4 to 2.22 × 10^4 for the a-PP sample and from 3.81 × 10^4 to 3.99 × 10^4 for the a-PEE sample. These values were in good agreement with those derived from light scattering (Table I). The light-scattering values were used in this work due to the greater precision inherent in those measurements.

Results

In the experiments, temperature was varied in steps ranging from 20 to 50 °C. The mixtures and the hydrogenated matrix were calibrated separately and corrected for background noise. The radii of gyration for a-PP and a-PEE are given in Table II. The coherent cross-sections were obtained using eq 6. Transmissions, densities (and hence the contrast factors), and the incoherent scattering are temperature dependent. Thus, the transmissions of all samples were measured at various temperatures. Due to inelastic processes the incoherent intensity rises slightly with temperature. Figures 2 and 3 show the experimental structure factors at three temperatures for a-PP (NIST and GKSS) (Figure 2) and a-PEE (GKSS) (Figure 3). The agreement between the NIST and GKSS results for a-PP is excellent.

In order to yield the qualitative behavior of $R_G(T)$ the data for a-PP (GKSS) are plotted in the Zimm format as

Table II
SANS-Based Radii of Gyration for Atactic Polypropylene and Poly(1-butene)

T, °C	R_{Gw}, Å 50%	 40%	 20%	R_{Gw}, Å
		a-PP (NIST)		
25			52.3	
27	51.4	51.3		51.7 ± 0.45[a]
50	51.1	51.0	50.9	51.0 ± 0.08
70	50.8	51.0		50.9 ± 0.10
95	50.8	51.0	50.8	50.9 ± 0.09
115	50.6	50.6		50.6
140			51.0	
160	50.1	50.6		50.4 ± 0.25
185	50.4	50.3	50.0	50.2 ± 0.17
230	50.4		50.5	50.5 ± 0.05
		a-PP (GKSS)		
20	50.2	49.5		49.9 ± 0.35
70	51.0	49.0		49.6 ± 0.55
115	50.1	48.8		49.5 ± 0.65
160	49.2	49.5		49.4 ± 0.15
220	49.9	47.7		48.8 ± 1.10
		a-PEE (GKSS)		
25	51.3	52.0	51.1	51.5 ± 0.3
54	52.5	51.8		52.2 ± 0.4
75	53.2	52.5	51.2	52.3 ± 0.6
123	52.9	52.6	52.6	52.7 ± 0.1
143	53.0	52.2		52.6 ± 0.4
168	52.9	53.6	53.8	53.4 ± 0.3
200	53.8	53.4	53.4	53.5 ± 0.1
223	53.4	52.2		52.8 ± 0.6

[a] Average of 25 and 27 °C values.

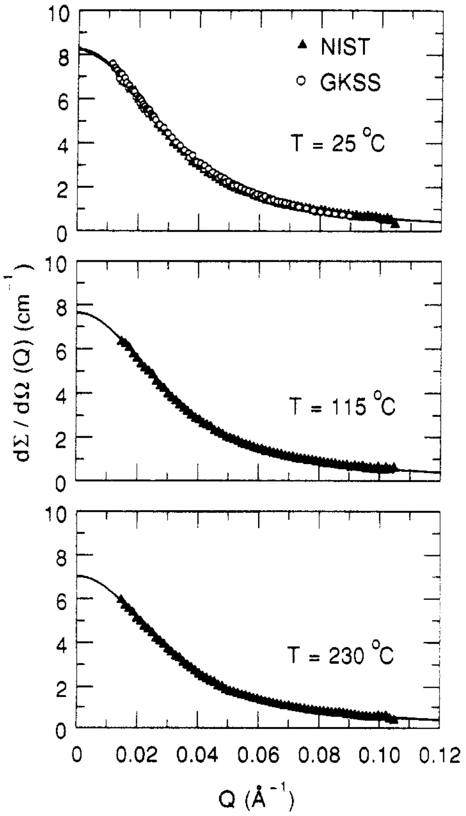

Figure 2. Structure factors as a function of temperature for a-PP. The solid line displays a fit with eq 3.

$S(Q)^{-1}$ vs Q^2. $S(Q)$ and $d\Sigma/d\Omega$ (Q) are simply related by $d\Sigma/d\Omega\,(Q)N_A/\Delta\rho^2 = S(Q)$. In Figure 4 the data are plotted as a function of temperature. The failure of the slopes to change as a function of temperature is a direct demonstration that for a-PP κ is virtually zero.

For a quantitative evaluation of the data one has to check for a possible non-zero χ parameter between the hydrogenated matrix and the partially deuterated chains since evidence is available[47-49] for a non-zero interaction

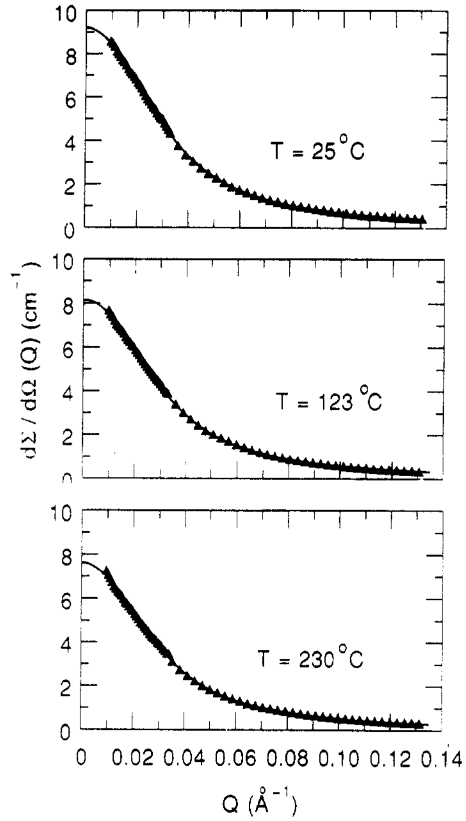

Figure 3. Structure factors as a function of temperature for a-PEE; (solid line) fit with eq 3.

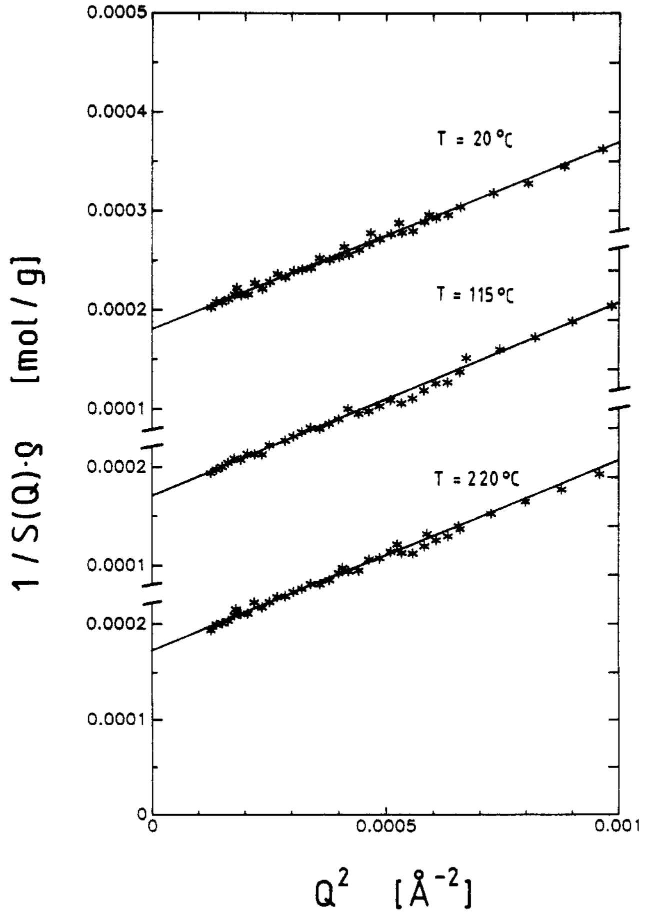

Figure 4. Zimm plots at different temperatures for a-PP (GKSS). $1/(S(Q)\rho)$ (ρ: density) is plotted in order to compensate for the influence of the chain volume, V_w, in eq 5.

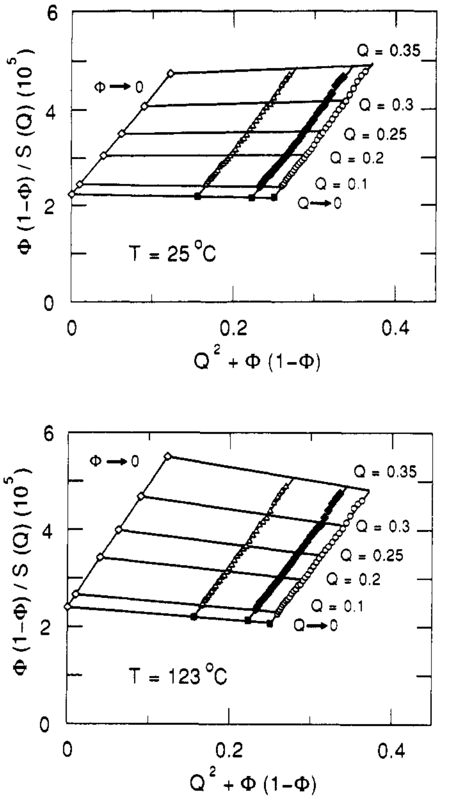

Figure 5. Concentration-dependent Zimm plots at two temperatures for a-PEE (GKSS).

parameter in isotope mixtures. For this case

$$S(Q)^{-1} = \frac{1 + Q^2 R_G^{\,2}/3}{\Phi(1-\Phi)V_w} - 2\chi \qquad (8)$$

where χ is measured in term of mol·cm^{-3} and V_w in cm^3·mol^{-1}. The data are plotted in a fashion analogous to that used for the determination of the second virial coefficient in light scattering.[27] The plots are shown in Figure 5 for a-PEE for two temperatures in the form of concentration-dependent Zimm plots. Clearly, the $Q \rightarrow 0$ slopes are very close to zero. Thus, when the small absolute values of χ are considered within the context of the corresponding experimental errors, the assignment of $\chi = 0$ is justified; a-PP showed the same behavior.

In order to determine $R_G(T)$ from the Zimm plot the condition $QR_G < 1$ is required. This criterium was met for the samples evaluated in this work but not for all Q values. Due to this R_G was obtained using the z-averaged Debye function in the form of eq 9.

$$\frac{d\Sigma}{d\Omega} = \Phi(1-\Phi)\Delta\rho^2 V_w g_z(\xi) = \frac{d\Sigma}{d\Omega}(0) g_z(\xi) \qquad (9)$$

The forward scattering $d\Sigma/d\Omega(0)$ and R_G were used as fitting parameters in the analysis. The values were then averaged at those temperatures where more than one concentration was measured. Those results are given in Table II and Figure 6. The absolute agreement between the NIST and GKSS R_G values for a-PP is excellent since the error across the common temperature range is not greater than 2%. The fact that the GKSS data are consistently below (by ca. 1 Å) the NIST results is likely caused by small systematic errors present in the two instruments.

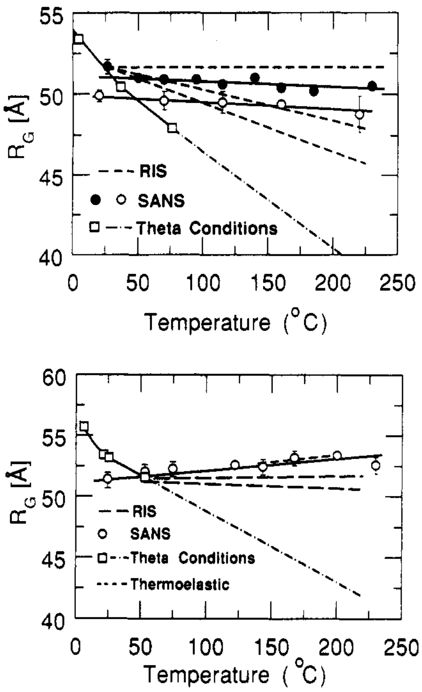

Figure 6. Radii of gyration for a-PP as a function of temperature. The dashed lines denote the RIS predictions of 0, −1.2, and −1.8 × 10^{-3} deg^{-1} (Table III). These RIS results are based on the 25 °C R_G value. The Θ-solvent-based results are those of ref 34 where the R_G values were calculated for the M_w of 2.3 × 10^4. Key: (●) NIST; (○) GKSS. Radii of gyration for a-PEE as a function of temperature. The dashed lines denote the RIS predictions (Table III). The RIS results are based on the 25 °C R_G value. The Θ-solvent-based results are those of ref 41 where the R_G values were calculated for the M_w of 3.6 × 10^4. The thermoelastic result is that of ref 56. Key: (○) SANS GKSS.

Table III
Polypropylene and Poly(1-butene) Chain Parameters from RIS Models

RIS model	i-PP C_∞	i-PP $10^{-3}\,d\ln\langle R^2\rangle_0/dT$, deg^{-1}	a-PP C_∞	a-PP $10^{-3}\,d\ln\langle R^2\rangle_0/dT$, deg^{-1}	temp, °C	ref
Abe	8.5	−1.9	5.0–6.3	~0		16
Heatley	5.6	−1.7			150	17
Boyd–Breitling	5.8	−1.0	5.0	−0.6	145	18
Biskup–Cantow	6.2	−3.8	5.3	−1.8	130	19
Mark	9.4	−4.0	6.7	−1.2	25	20
Allegra et al.	5.6	−3.5	6.5	−0.5	150[a], 100[b]	21
Suter–Flory	4.2	−1.7	5.5	−0.9	140	22
Wittwer–Suter	5.4	−2.5	4.5	−0.9	127	23
			a-PEE			
Abe			4.9	0–0.1		16
Wittwer–Suter			4.5	−0.1	127	23

[a] i-PP. [b] a-PP.

Discussion

A tacit assumption in the RIS models for tactic polyolefins is that the stereochemical constitution will exert a pronounced influence on the chain statistics and thus upon the magnitude of the chain dimensions and their variation with temperature. This is reflected in the survey of those findings for polypropylene given in Table III. A somewhat disquieting trend is the pronounced variation in the predicted characteristic ratios, C_∞, defined by $C_\infty = 6R_G^{\,2}/N_w n l^2$ and the chain dimension temperature coefficients. In the definition of C_∞, n denotes the (effective) number of bonds per monomer and N_w is the weight-average number of monomers. l = 1.53 Å is the mean distance between two backbone carbons. These intermodel disagreements indicate that problems remain in the formulation of the RIS models.

Table IV
Chain Parameters for Isotactic, Syndiotactic, and Atactic Polypropylene and Poly(1-butene)

polymer	method[a]	temp range, °C	$R_G/M^{0.50}$,[b] Å·mol$^{0.50}$·g$^{-0.50}$	C_∞	10^{-3}d ln $\langle R^2\rangle_o/dT$, deg^{-1}	ref
i-PP	SANS	23–220	0.34	6.2	~0	14
	IV	125–183	0.333–0.327	6.0–5.7	−4.2[c]	50
	IV	125–143	0.337[d]	5.9		51
	IV	145	0.349	6.5		52
s-PP	IV	30	0.357	6.8		53
a-PP	SANS:NIST	25–230	0.337–0.324	6.0–5.6	−0.12 ± 0.02	this work
	SANS:GKSS	20–220	0.324–0.316	5.7–5.4	−0.14 ± 0.10	this work
	IV	34–146	0.357–0.325	6.8–5.6	−1.8	51
	IV	74–153	0.362–0.322	7.0–5.5	−3.0	52
	IV	5–77	0.350–0.315	6.5–5.3	−2.9	34
	IV[e]	10–70			−2.4	34
	IV[e]	20–70			−1.0	54, 55
a-PEE	SANS:GKSS	25–223	0.271–0.278	5.1–5.5	0.4 ± 0.05	this work
	thermoelastic	140–220			0.5	56
	IV	−46 to +83	0.331–0.309	7.9–6.9	−1.2	57
	IV	23–141	0.313–0.304	7.0–6.6	−0.4	58
	IV	5–53	0.289–0.273	5.9–5.3	−2.3	41

[a] IV denotes Θ condition intrinsic viscosity unless otherwise noted. [b] From K_Θ using $\Phi = 2.5 \times 10^{21}$ with the exception of the SANS-based measurements. K_Θ values were evaluated, where feasible, via the Burchard–Stockmayer–Fixmann extrapolation procedure in order to correct for slight deviations from the Θ conditions: Burchard, W. *Makromol. Chem.* **1960**, *50*, 20. Stockmayer, W. H.; Fixmann, M. *J. Polym. Sci., Part C* **1963**, *1*, 173. [c] Moraglio et al.[51] reported that i-PP at 183 °C in dibenzyl ether (the solvent used in ref 50) underwent chain degradation. Thus, this value may be distorted by an artifically low K_Θ for this temperature. [d] Average value for this temperature range. [e] Athermal solvent approach.

Table V
Polyolefin Chain Parameters at 298 K

	$R_G/M^{0.5}$, Å·mol$^{0.50}$·g$^{-0.50}$		C_∞			10^{-3}d ln $\langle R^2\rangle_o/dT$, deg^{-1}				
polymer	Θ[a]	SANS[a]	Θ[a]	SANS[a]	RIS[a]	Θ	SANS	RIS	F–T[b]	ref
PE	0.473	0.482	8.0	8.3	7.8[c]	−1.2		−1.1	−1.2	7, 28–33, 63
PEB-2	0.452	0.473	7.6	8.3			−1.2			4, 24, 64
alt-PEP	0.381	0.397	6.7	7.3	6.8	−1.0	−1.2	−1.1	−1.2	20, 27, 34, 65
a-PP	0.333	0.336	6.0	6.1	4.5–6.7	−1.0 to −3.0	−0.1	0 to −1.8		16, 18–23, 34, 51, 52 54, 55, 66, this work
i-PP	0.340	0.340	6.2	6.2	4.2–8.5	−4.2	~0	−1.0 to −4.0		14, 16–23, 50–53
a-PEE	0.281	0.271	5.6	5.2	~4.5	−0.4 to −2.3	0.4	+0.1 to −0.1 and 0.5	0.5	16, 23, 34, 56–58, 66–68, this work

[a] The PE and PEB-2 values were calculated for 298 K via the use of the SANS-based κ for PEB-2. [b] From thermoelastic (force–temperature) measurements. [c] A recent Monte Carlo simulation also leads to this value. Baschnagel, J.; Qin, K.; Paul, W.; Binder, K. *Macromolecules* **1992**, *25*, 3117.

The method of choice and convenience, to date, for the experimental evaluation of chain size and its temperature dependence has been dilute solution viscometry augmented by the athermal solvent method. Table IV summarizes those results. Without exception, the dilute solution measurements for both i-PP and a-PP yield negative values for κ; findings which are in reasonable accord with some of the RIS-based values (Table III). Conversely, as mentioned, SANS measurements[14] for i-PP show that, in the melt, chain dimensions are essentially independent of temperature. A similar finding is available from this work on a-PP where a κ of −0.1 × 10^{-3} deg^{-1} is found from both the NIST and GKSS data (Table IV). Furthermore, the relation for a-PP (NIST) and a-PP (GKSS) at 220–230 °C of

$$R_G = 0.32_5 M^{0.50} \ (\text{Å}\cdot\text{mol}^{0.50}\cdot\text{g}^{-0.50}) \tag{10}$$

shows that both forms of polypropylene share, within experimental error, the same chain dimensions in the melt. A harbinger of this behavior is available[59] in the comparison of the melt newtonian viscosities at 190 °C for i-PP and a-PP where the two polypropylenes were found to be equivalent. A similar conclusion is obtainable from the intrinsic behavior of a-PP, i-PP, and syndiotactic polypropylene (s-PP) in decalin at 135 °C (Figure 7). The following Mark–Houwink relation is obtained:[53,60–62]

$$[\eta] = 1.066 \times 10^{-4} M^{0.804} \tag{11}$$

The foregoing universal behavior for polypropylene would not be found if substantial differences in R_G existed. Thus, these findings, coupled with those resulting from the SANS measurements, demonstrate that in good solvents and in the melt *the isotactic and atactic forms of polypropylene are identical.* This, of course, is not the scenario derivable nor expected from the current RIS treatments where substantial differences between these two forms of polypropylenes are predicted to exist (Table III).

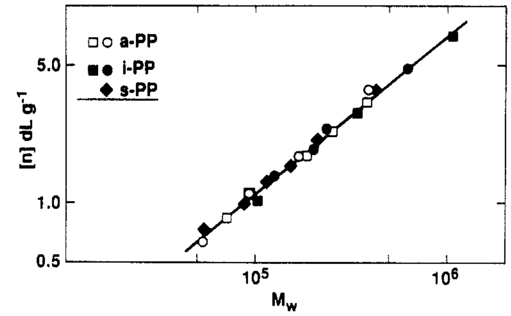

Figure 7. Intrinsic viscosities vs molecular weight for polypropylenes in decalin at 135 °C: (○, ●) ref 62; (□) ref 61; (■) ref 60; (◇) ref 53.

The case for polyethylene and PEP is markedly different, as can be seen from Table V. These two polyolefins share the common feature that their values of κ are essentially the same irrespective of source; Θ solvent, the melt, or RIS based. That type of agreement though is not reproduced for a-PP where a prominent discrepancy is the strikingly different behavior found between the Θ condition and melt-based (SANS) values of κ (Table V). That parameter exhibits large negative values according to the Θ results while showing little sensitivity of R_G on temperature in the melt. This finding is contrary to the notion that Θ-solution chain dimensions and their temperature dependencies are automatically transferable to the melt state. The state of play for a-PP involving the RIS predictions and the observables measured under Θ-solvent conditions and the melt are given in Figure 6.

A similar situation is encountered for a-PEE (Tables III and IV and Figure 6). The SANS measurements yield a κ of 0.4×10^{-3} deg^{-1}, while the Θ measurements yield prominent negative values. The recent RIS models predict that chain dimensions are effectively temperature independent. The SANS result is in excellent agreement with the thermoelastic-based value of 0.5×10^{-3} deg^{-1} and the rheological result of Carella et al.[43,69] $[0.4–0.6) \times 10^{-3}$ deg^{-1}].

At 25 °C the following R_G power laws emerge for a-PP and PEE in the melt:

$$R_G = 0.33_6 M^{0.50}\ (\text{Å}\cdot\text{mol}^{0.50}\cdot\text{g}^{-0.50}) \quad \text{a-PP} \tag{12}$$

$$R_G = 0.27_1 M^{0.50}\ (\text{Å}\cdot\text{mol}^{0.50}\cdot\text{g}^{-0.50}) \quad \text{PEE} \tag{13}$$

The Θ-solvent results[34,41] in turn are nearly identical:

$$R_G = 0.33_3 M^{0.50}\ (\text{Å}\cdot\text{mol}^{0.50}\cdot\text{g}^{-0.50}) \quad \text{a-PP} \tag{14}$$

$$R_G = 0.28_1 M^{0.50}\ (\text{Å}\cdot\text{mol}^{0.50}\cdot\text{g}^{-0.50}) \quad \text{PEE} \tag{15}$$

The statistical segment length, a (where $a^2 = 6R_G{}^2/N_w$) for a-PP at 25 °C is 5.3 Å in the melt state, while for PEE it is 4.9 Å, a value identical to that previously given by Bates et al.[67]

For temperatures above 25 °C, both a-PP and a-PEE Θ-condition-based results become progressively misleading insofar as they reflect melt behavior. A potential rationalization involves specific solvent effects,[70–74] which, for example, can influence[72,73] the "unperturbed" dimensions of polystyrene. Crescenzi and Flory have reported on a similar effect for polydimethylsiloxane.[74]

Rotational isomeric states are identified with the minima of the conformational energy maps, minima which apparently can be influenced by local-polymer solvent interactions—the so-called specific solvent effect. This event can be viewed as one that does not create new rotational isomeric states but instead modifies the potential energy of the existing states.[75] Thus, the location of the various minima remain unchanged while their magnitudes can be altered by the prevailing solvent–polymer interaction for any particular state. This scenario requires that the probabilities of occurrence of the most stable conformations—those isomeric states required by the short-range intramolecular interactions—can be modified by solvent interaction. Under Θ conditions such short-range interactions can be neglected *if solvent discrimination between conformations is absent*. This criterion is apparently met for polyethylene and *alt*-poly(ethylene–propylene) (Table V). Conversely, the state of play between the solution and melt behavior for a-PP and a-PEE seemingly demonstrates that their local conformational characteristics are considerably influenced by Θ-solvent interactions; interactions which lead to enhanced gauche populations with increasing temperature. It appears that the configuration of the skeletal bonds will lead, in some cases, to solvent discriminations regarding the attached side groups, with gauche sequences being more susceptible to such interactions than their trans counterparts.[75] Given the presence of such favorable interactions, the net effect is a decrease in the trans/gauche ratio with increasing temperature.

Similar behavior[34] is available for a-PP in either 2,4-dimethylheptane or 2,2,4-trimethylpentane where a κ of -2.4×10^{-3} deg^{-1} was found over the temperature range of 10–70 °C. The use of those alkanes was based on their apparent capacity to act as athermal solvents.[36] In a parallel fashion, IR work of Casal et al.[76] on n-tridecane-7,7-d_2 was interpreted as showing that the average gauch population increases from 35% to 60% when the solvent is changed from n-heptane to hexadecane.

Another potential complication involving Θ-solvent measurements is the likely failure of a chain to practice ideal chain statistics as a consequence of the third virial coefficient. This is due to the fact that although the second virial coefficient vanishes at the Θ point, the third virial coefficient does not. Thus, as Sanchez has noted,[77] ternary interactions cannot be ignored. According to Sanchez this could lead to different R_G probability distributions where the ideal distribution (the melt) differs from that found in solution $T = \Theta$. The consequence of this is that ideal chain statistics are unobtainable at Θ or at any other temperature; a conclusion reached previously by de Gennes[78] and Oono.[79,80] This, coupled with specific solvent effects, may serve to rationalize the observed differences seen between dilute Θ solutions and the melt for PP and PEE.

The gratifying success of the RIS method in correctly characterizing the polyethylene and PEP chain parameters is not replicated for a-PP and a-PEE where large deviations are encountered regarding the temperature influence on the chain dimensions of these two related polyolefins. The main feature of the RIS model is that the bond rotational angles are allowed to accept only discrete values which correspond to minima in the conformational energy maps. The simplest approach is based on the three-state model having the trans (t) and gauche± (g^+, g^-) states which are usually limited to rotations of 0, +120, and −120°, respectively. Polypropylene has been treated with models that use either three,[16,21] four,[66] or five states.[22] When the assumption is accepted that the rotational potential of C–C bond i depends only on the rotation of i and upon that of neighboring bonds (*thus neglecting longer range interactions*), the conformational energies can be rearranged so that the energy of bond i is a function characterizable by the indices ζ and ξ. ζ indicates the state of bond i − 1 while ξ that of bond i. The corresponding statistical weights $\exp(-E/RT)$ can be collected in a **n** × **n** matrix (**n**: number of states)

$$U_{\text{i}} = [U_{\zeta,\xi\text{i}}] = [\exp(E\zeta\xi;\text{i}/RT)] \tag{16}$$

Thus, knowledge of the statistical weight matrices for all bonds allows the calculation of the conformation-dependent properties of the chain. The RIS approach is a means to evaluate continuous integrals over the whole configuration space by transforming them into sums.

The RIS scheme can consider nonbonded interactions that arise from groups which are separated by three to five bonds where bonds pertaining to side groups are included in the counting. This may, at least, be a partial explanation for the RIS failure found for a-PP and i-PP and the (less pronounced) failure for a-PEE. In other words, the RIS model is incomplete as a consequence of the inability to correctly visualize the longer-range nonbonded interactions for polyolefins having aliphatic substituents on alternate carbons. The SANS results demonstrate that a-PP maintains a near-constant population of gauche$^{\pm}$ and trans conformers—if the simple three-state model is invoked—over the temperature range of interest. Replacement of the methyl unit by the articulated ethyl group leads to an increase in trans conformers with increasing temperature. Parenthetically, it should be mentioned that an early RIS treatment[66] by Flory, Mark, and Abe successfully predicted the behavior of κ for a-PP and a-PEE, a success, which latter RIS schemes have failed to duplicate.

Conclusions

The combined results, RIS, SANS, and Θ condition, for polyethylene and PEP are in good agreement (Table V), a situation not enjoyed for the two polyolefins having substituents on alternate backbone carbons. The SANS measurements for i-PP and a-PP have shown that both types of polypropylene are equivalent in the melt. Furthermore, the behavior of κ for i-PP and a-PP is at odds with both the majority of the RIS predictions *and* the findings from Θ-condition measurements where both methods yield large negative values for this parameter whereas the SANS measurements show that the chain dimensions are barely altered by variations in temperature. Thus, the RIS-based predictions of substantial differences for C_∞ and κ between i-PP and a-PP are incorrect. Thus, the current polypropylene RIS models are in need of refinement and revision since the single-body foundation of the RIS chain model is apparently inappropriate.

To a lesser degree a similar situation exists for a-PEE. The results for these two polyolefins indicate that the consideration of correlation effects in the melt may be a neglected aspect in the evaluation of these static chain parameters in the melt. Thus, the single body RIS approach would be replaced by a many body model. To this end simulations would be of value.

Acknowledgment. We wish to thank N. Balsara and R. Krishnamoorti for the DSC and density measurements and H. Eckerlebe for his valuable technical assistance at the GKSS instrument. Thanks are also in order for support of the NIST 8-m SANS instrument by Exxon Research and Engineering Co.

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$$b_T = \frac{G_N{}^\circ\{T\}}{G_N{}^\circ\{T_o\}} = \frac{\rho^d T C_\infty{}^{2d-3}}{[\rho^d T C_\infty{}^{2d-3}]_o}$$

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