Melt-State Polymer Chain Dimensions as a Function of Temperature

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ABSTRACT: The unperturbed chain dimensions ($\langle R^2\rangle_o/M$) of *cis/trans*-1,4-polyisoprene, a near-atactic poly(methyl methacrylate), and atactic polyolefins were measured as a function of temperature in the melt state via small-angle neutron scattering (SANS). The polyolefinic materials were derived from polydienes or polystyrene via hydrogenation or deuteration and represent structures not encountered commercially. The parent polymers were prepared via lithium-based anionic polymerizations in cyclohexane with, in some cases, a polymer microstructure modifier present. The polyolefins retained the near-monodisperse molecular weight distributions exhibited by the precursor materials. The melt SANS-based chain dimension data allowed the evaluation of the temperature coefficients [$d\ln \langle R^2\rangle_o/dT(\kappa)$] for these polymers. The evaluated polymers obeyed the packing length (p)-based expressions of the plateau modulus, $G_N^o = kT/n_t^2p^3$ (MPa), and the entanglement molecular weight, $M_e = \rho N_a n_t^2 p^3$ (g mol^{-1}), where n_t denotes the number ($\sim$21) of entanglement strands in a cube with the dimensions of the reptation tube diameter (d_t) and ρ is the chain density. The product $n_t^2p^3$ is the displaced volume (V_e) of an entanglement that is also expressible as pd_t^2 or kT/G_N^o. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 40: 1768–1776, 2002

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INTRODUCTION

A primary pursuit of polymer science has been to relate the chain structure and macroscopic properties, that is, to relate the sizes of polymer coils to the degree to which they entangle and, therefore, to their rheological behavior in the melt. This notion has been realized[1–7] with the packing model. Central to this model is the concept of the packing length (p), which is defined[8] as the occupied volume of a chain (V_c) divided by its root-mean-square unperturbed end-to-end distance ($\langle R^2\rangle_o$):

$$p = M/[\langle R^2\rangle_o \rho N_a] = V_c/\langle R^2\rangle_o \quad (\AA) \qquad (1)$$

where V_c is equal to $M/\rho N_a$ where M denotes molecular weight, Na the Avogadro number, and

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ρ is the chain density. The concept of packing length unites the volume filling and conformational characteristics of a polymer into a chain-length-independent parameter. The magnitude of p can be viewed as representing the relative thickness of a polymer chain.[6]

The notion of packing length has facilitated the development[5–7] of correlations between $\langle R^2\rangle_o$, ρ, the entanglement molecular weight (M_e), and the plateau modulus (G_N^o). The interplay of these parameters leads[5–7] to a species-independent relation

$$G_N^o = kT/[n_t^2 p^3] \quad (\text{MPa}) \qquad (2)$$

and, therefore,

$$M_e = \rho N_a n_t^2 P^3 = [pn_t]^2[M/\langle R^2\rangle_o] \quad (\text{g mol}^{-1}) \qquad (3)$$

where n_t denotes[2] the number (~21) of entanglement strands in a cube with the dimensions of the tube diameter. Equation 3 leads to

$$M_e = m_b N_e = \rho N_a n_t^2 p^3 \qquad (4)$$

where N_e denotes the number of chain backbone atoms per entanglement strand and m_b is the average molecular weight per backbone bond. We then obtain

$$N_e = \frac{\rho N_a n_t^2}{m_b}\left[\frac{M}{\langle R^2\rangle_o \rho N_a}\right]^3 = \left[\frac{n_t p}{B}\right]^2 = \frac{V_e}{V_b} \qquad (5)$$

where B is defined as the statistical segment length or the effective bond length[9] and is expressed as $B = [m_b\langle R^2\rangle_o/M]^{0.5}$. N_e is simply the ratio of the displaced volumes associated with the entanglement event (V_e) and the backbone bond (V_b).

These relations seem to be universal for Gaussian chains in the melt state. They can be extended[7] to include the critical molecular weight (M_c), which marks the observable onset, from a viscosity standpoint, of entanglement effects and the reptation molecular weight (M_{rep}). This denotes the crossover from the experimental slope of 3.4 to the pure reptation-driven gradient of 3.0. Knowledge of p allows evaluations[5–7] of G_N^o, M_e, M_c, M_{rep} (the molecular weight at the crossover to a reptation gradient of 3), and the tube diameter (d_t; i.e., the entanglement length).

Therefore, the melt-state chain dimensions and their temperature coefficients have taken on renewed importance in view of their pivotal role in polymer melt rheological behavior. In this article, we report small-angle neutron scattering (SANS)-based melt-state chain dimensions and their temperature dependence for 1,4-polyisoprene (1,4-PI), atactic poly(methyl methacrylate) (PMMA), and a range of atactic polyolefins. With the exception of poly(cyclohexyl ethylene) (PCHE), the polyolefins are, to date, not available via olefin-based polymerizations.

EXPERIMENTAL

The monomers used for the preparation of the polyolefin precursors were 2-methyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and styrene. The samples were prepared according to procedures given elsewhere.[10] The lithium-based anionic polymerizations (298 K) in cyclohexane used either triethylamine or tetrahydrofuran (THF) as the modifier of the diene microstructure. Toluene was used for the methyl methacrylate polymerization (~200 K). The polyolefins were derived from the parent polydienes via saturation with either hydrogen or deuterium. This led to the preparation of isotopic matched pairs for the polyolefins. The 1,4-PI and PMMA data were derived from the use of isotopic pairs of the hydrogenated and deuterated polymers. These pairs had nearly identical degrees of polymerization. Head-to-head polypropylene is the alternating copolymer of ethylene and 2-butene. This poly(co-olefin) can only be synthesized via the use of the monomer 2,3-dimethyl-1,3-butadiene followed by the hydrogenation step.

The hydrogenation of polystyrene followed the procedure given by Gehlsen et al.[11] The molecular weights were analyzed via low-angle laser light scattering and size exclusion chromatography. ^{1}H NMR and ^{13}C NMR were used for both polydiene microstructure evaluations and saturation levels. Tables 1 and 2 contain the nomenclature, molecular parameters, and chain dimensions. The residual double-bond content in the polyolefins was less than 0.11%. The SANS measurements were performed at the National Institute of Science and Technology (Gaithersburg, MD) with the 8-m (NG-5) and 30-m (NG-7) instruments. The SANS-based data handling procedures were those previously used and reported.[12–14] The acronyms

Table 1. Polymer Nomenclature And Molecular Characteristics

Polymer	$M_w \times 10^4$ (g mol^{-1})	Nomenclature
PCHE	5.95 (1.04)[a]	[—$CH_2CH(C_6H_{11})$—] Atactic poly(cyclohexyl ethylene)
PEP/PIPE	10.4 (1.05)	—$[CH_2CH_2CH_2CH(CH_3)]_{50}$–$[CH_2CH(CH(CH_3)_2)]_{50}$— Poly(ethylene propylene)–poly(isopropyl ethylene)
PEB/PsBE	8.4 (1.03)	—$[CH_2CH_2CH_2CH(CH_2CH_3)]_{50}$–$[CH_2CH(CH(CH_3)CH_2CH_3)]_{50}$— Poly(ethylene 1-butene)–poly(*s*-butyl ethylene)
PIPE/PMEE	7.08 (1.05)	—$[CH_2CH(CH(CH_3)_2]_{75}$–$[CH_2C(CH_3)(CH_2CH_3)]_{25}$— Poly(isopropyl ethylene)–poly(methyl ethyl ethylene)
alt-PEB	4.67 (1.06)	—$[CH_2CH_2CH_2CH(CH_2CH_3)]$— *alt*-Poly(ethylene-1-butene)
hhPP	2.75/7.64/17.2 (1.02/1.05/1.08)	—$[CH_2CH_2CH(CH_3)CH(CH_3)]$— *alt*-Poly(ethylene 2-butene) (head-to-head polypropylene)
1,4-PI[b]	8.89 (1.03)	—$[CH_2CH = C(CH_3)CH_2]$— 1,4-Polyisoprene[b]
PMMA	16.0 (1.10)	—$[CH_2CH(COOCH_3)]$— Atactic poly(methyl methacrylate)

[a] Numbers within parentheses are M_w/M_n ratio, obtained via size exclusion chromatography; M_z/M_w ratios were identical to or less than M_w/M_n.

[b] *trans*, ~23%; *cis*, ~70%; 3,4, ~7%.

used to identify the polymers in Figures 5 and 6 (shown later) are defined in refs. 5 and 6.

RESULTS AND DISCUSSION

The chain dimension data of Table 2 (shown in Figs. 1 and 2) lead directly to $10^{-3}\, d\ln \langle R^2\rangle_o/dT(\kappa)$ and the characteristic ratio (C_∞; Table 3 and Figs. 1 and 2). For 1,4-PI, these values are 0.4 and 4.8 (at 298 K), respectively. Both values are in agreement with their calculated counterparts.[15,16] The three *alt*-poly(ethylene 2-butene) (hhPP) polymers (Fig. 2) show that $\kappa = 0$. This value is virtually identical to that of atactic polypropylene. The PCHE material virtually retains the κ value possessed by the parent polystyrene. However, the chain dimension is markedly decreased, and this accounts for the differences in the plateau moduli: polystyrene, $C_\infty = 9.6$ and $G_N^o = 0.20$ (MPa), and

Table 2. Melt-Phase Polymer Chain Dimensions

Temperature (K)	$[\langle R_g^2\rangle_o]^{0.5}$ (Å)							
	PCHE	PEP/PIPE	PEB/PsBE	PIPE/PMEE	*alt*-PEB	hhPP	1,4-PI	PMMA
298	—	103.6	102.1	—	—	—	—	—
300	—	—	—	73.0	74.8	55.5/94.2/139.7	92.6	—
324	—	—	—	73.3	73.4	56.1/94.4/139.7	93.2	—
353	—	101.6	100.7	—	—	—	—	—
356	—	—	—	74.9	73.3	56.2/94.1/139.2	93.8	—
381	—	—	—	—	—	—	94.1	105.1
394	—	—	—	76.4	73.3	56.2/94.1/139.4	94.5	—
400	—	—	—	—	—	—	—	105.3
403	—	100.7	99.9	—	—	—	—	—
411	—	—	—	—	—	—	94.9	—
420	—	—	—	—	—	—	—	105.0
433	58.3	—	—	—	—	—	—	—
440	—	—	—	79.2	73.3	56.4/94.4/140.2	95.8	105.6
453	—	99.7	98.3	—	—	—	—	—
460	—	—	—	—	—	—	—	105.9
483	56.9	—	—	—	—	—	—	—
513	—	99.3	99.1	—	—	—	—	—
533	57.0	—	—	—	—	—	—	—

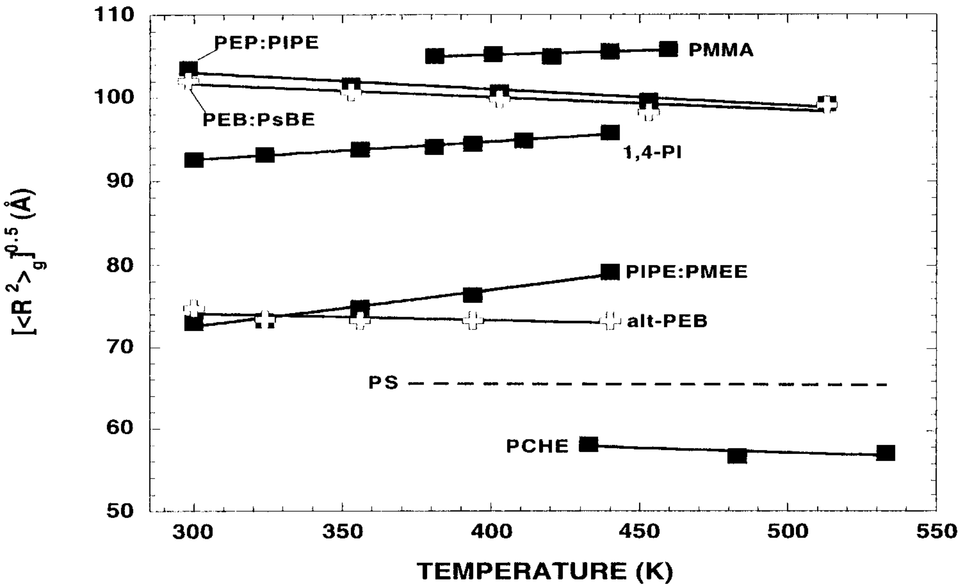

Figure 1. Chain dimension data as a function of temperature.

PCHE, C_∞ = 7.6 and G_N^o = ~0.07 (MPa).[7] The smaller C_∞ value for PCHE is attributable to the flexibility present in the cyclohexyl unit, which allows the formation of the chair and boat forms. The dashed line in Figure 1 illustrates the characteristics of the parent polystyrene relative to those of its hydrogenated offspring with the same number of backbone bonds. The poly(isopropyl ethylene) (PIPE)/poly(methyl ethyl ethylene) (PMEE) chain is, to date, unique among polyolefins in that it possesses a large positive κ. The results of this are addressed later.

The melt-based results[17–19] for both C_∞ and κ for PMMA generally disagree with the θ-condi-

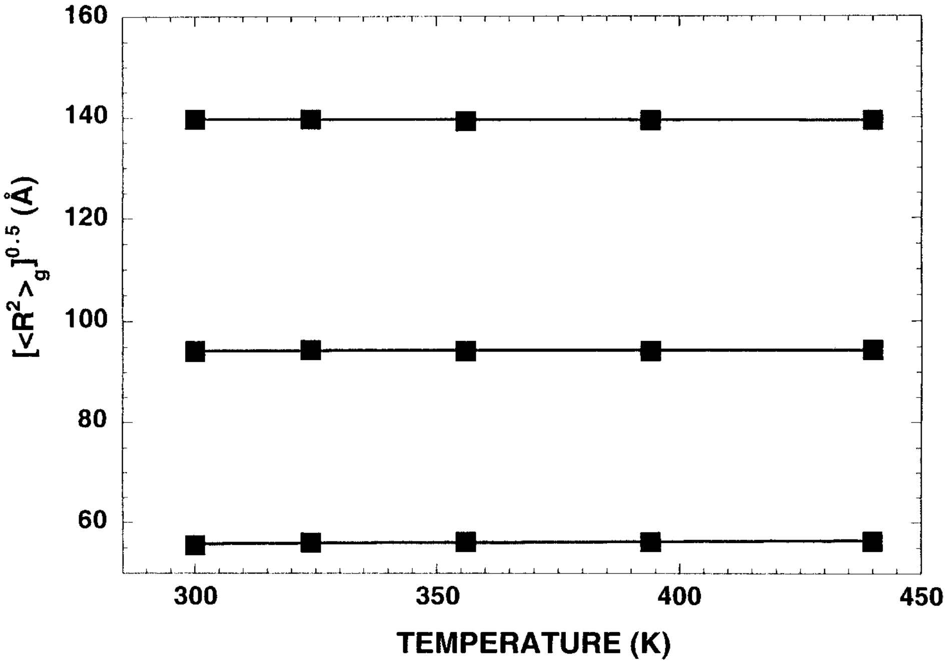

Figure 2. hhPP chain dimension data as a function of temperature.

Table 3. Melt-Phase Sans-Based Chain Parameters

Polymer	m_b (g mol^{-1})	$\kappa \times 10^3$ (deg^{-1})	$[\langle R_g^2\rangle_o/M]^{0.5}$ (Å mol$^{0.5}$ g$^{0.5}$)	Temperature (K)	C_∞[a]
PE[b]	14	−1.1	0.456	413	7.5
hhPP	21	0	0.339	298/413	6.2
alt-PEB	22.1	≈0	0.346	298	6.8
PEP/PIPE	23.3	−0.2	0.321	298	6.2
PEB/PsBE	28	−0.2	0.352	298	8.9
PIPE/PMEE	35	1.2	0.274	300	6.8
PIPE/PMEE	35	1.2	0.294	413	7.8
a PCHE	55	~0	0.234	453	7.8
1,4-PI	17.5	0.4	0.317 (0.321)[c]	298	4.8
1,4-PI	17.5	0.4	0.324	413	5.0
a PMMA	50	≈0.1	0.265	413	9.0

[a] $C_\infty = [m_b \langle R^2\rangle_o/M] l^{-2}{}_o$, where l_o^2 is the mean square bond length.

[b] Polyethylene. This data set is presented as the polyolefin benchmark.

[c] This value is from light and SANS scattering measurements in dioxane at the θ temperature (307 K).

tion-based values.[19,20] A similar state of play exists for polypropylene[21–23] and poly(ethyl ethylene)[24–29] [i.e., poly(1-butene)]. This behavior is displayed in Figures 3 and 4. These figures show that vivid differences can exist with respect to θ-based chain dimension behavior relative to what is found in the melt state. This behavior is unexpected because of the generally good agreement that exists between the θ-condition and melt-state data previously obtained for polyethylene and alternating poly(ethylene propylene) (PEP).[30–35] The behavior shown in Figures 3 and 4 is seemingly caused by the capacity of some θ solvents to induce a conformer population different from what is favored in the melt state. In the simplest scenario, this notion requires gauche and trans populations in solution different from those in the melt state. The potential for such nonuniform trends was shown by Ciferri[20] and Bianchi[36] in 1964 for PMMA.

Nonetheless, many[34,35,37] θ-condition-based chain dimensions illustrate that useful rheological approximations are feasible. It was shown previously[5] that M_e could be expressed as follows:

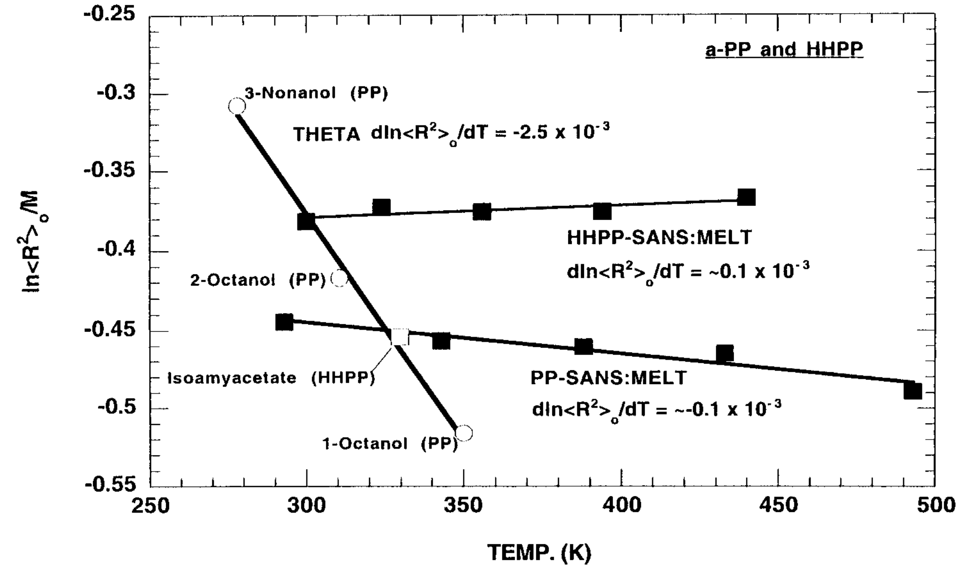

Figure 3. θ-condition and melt-based chain dimension data as a function of temperature for atactic polypropylene (a-PP).

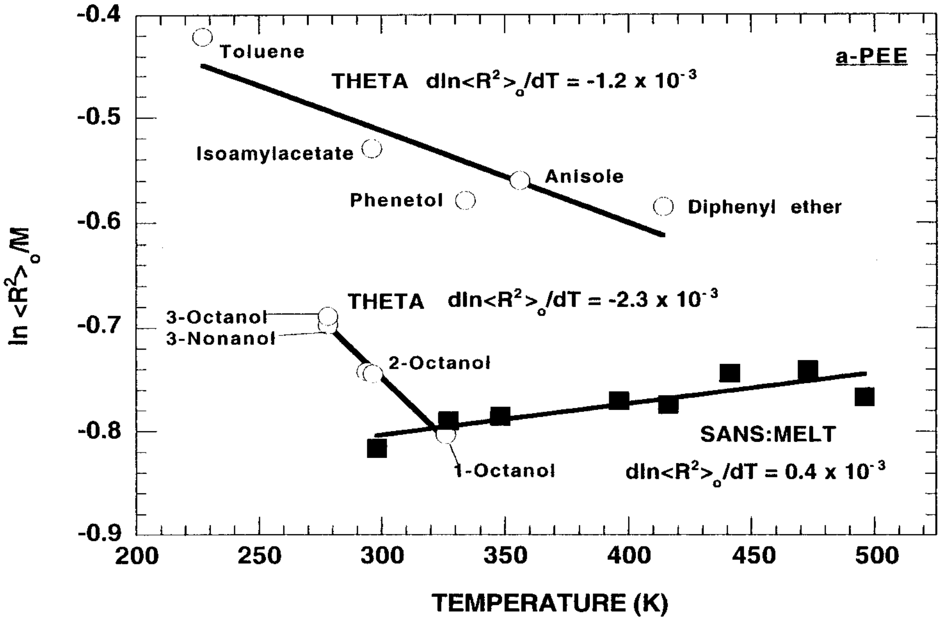

Figure 4. θ-condition and melt-based chain dimension data as a function of temperature for atactic poly(ethylethylene) (a-PEE).

$$M_e = [\Phi n_t/\rho N_a K_\theta]^2 \tag{6}$$

where

$$K_\theta = [\eta]_\theta M^{-1/2} = \Phi[\langle R^2\rangle_o/M]^{3/2} \tag{7}$$

The merit in this use of K_θ as the chain dimension source is shown in Figure 5, where we find an acceptable correlation when M_e is plotted against $[\rho K_\theta]^{-2}$. The practical outcome is the qualification of the use of size exclusion chromatography, on-

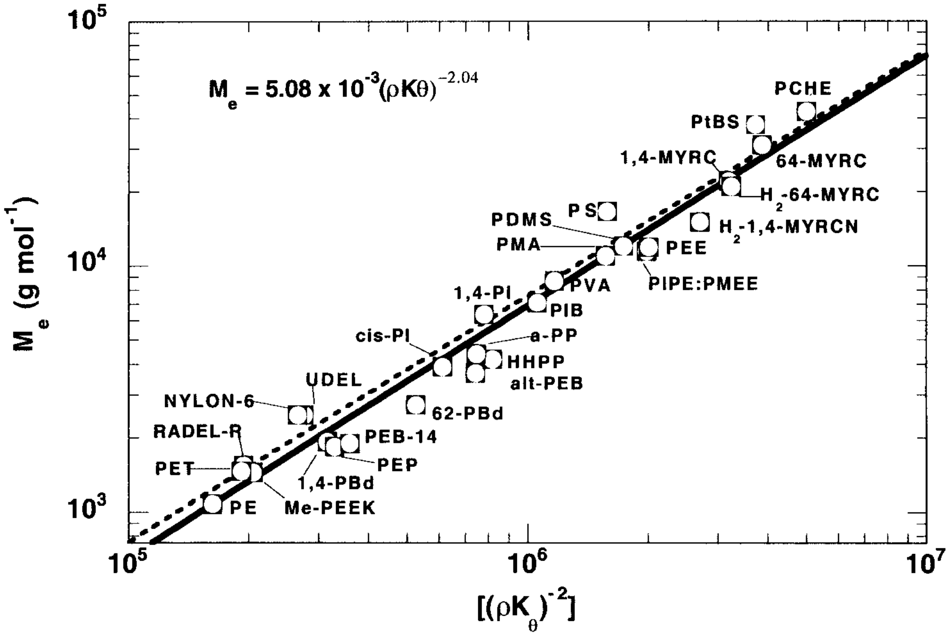

Figure 5. M_e versus $(\rho K_\theta)^{-2}$. The dashed line has been drawn according to eq 6. The solid line is data-driven and yields $M_e = 0.00508(\rho K_\theta)^{-2.04}$.

Table 4. Dilute Solution Properties of a-PCHE (298 K)

10^{-4} Mw (g mol^{-1})	$[\eta]$ (dL g^{-1}) $\{k_H\}$				
	Cyclohexane	Toluene	THF	Benzene	θ^{a}
4.50	0.191 {0.48}	0.141 {0.53}	0.137 {0.59}	0.136 {0.50}	0.104
5.95	0.228 {0.50}	0.169 {0.50}	0.165 {0.57}	0.163 {0.46}	0.120
34.2	0.827 {0.39}	0.550 {0.41}	0.516 {0.48}	0.501 {0.44}	0.287
56.0	1.18 {0.36}	—	0.714 {0.47}	—	0.367
$[\eta]$ (dL g^{-1})	$0.78 \times 10^{-4}\ M\text{w}^{0.727}$	$1.02 \times 10^{-4}\ M\text{w}^{0.675}$	$1.24 \times 10^{-4}\ M\text{w}^{0.654}$	$1.40 \times 10^{-4}\ M\text{w}^{0.642}$	—
(10^4) K_θ [dL (g mol)$^{-0.5}$]	4.92	4.70	4.99	5.06	4.92 (±0.16)
$[\langle R_g^2\rangle_o/M]^{0.5}$ (Å^2 mol g^{-1})	0.237	0.234	0.238	0.240	0.237 (±0.003)
Characteristic ratio	7.9	7.7	8.0	8.1	7.9 (±0.2)

[a] Values are from the calculated equation $[\eta]_\theta = 4.92 \times 10^{-4}\ \mathrm{M}^{0.5}$ dL g^{-1}.

line viscometry, and light scattering as instrumentation to preview rheological properties of new or unstudied polymers. The parameter K_θ can be evaluated by the use of an extrapolation approach such as that of Burchard[38] and Stockmayer and Fixman[39] or that of Tanaka.[40] Both procedures eliminate the influence of excluded volume effects on the good solvent chain dimension and, therefore, allow reasonable evaluations of K_θ. In a speculative sense, the combined use of good solvent data combined with an extrapolation procedure would seemingly eliminate the potential for specific solvent influences on K_θ obtained via the conventional θ-condition approach. This maneuver also eliminates the need to identify a θ solvent.

A trend is seen in Table 3 for poly(α-olefins) in which the parameter κ assumes a value of zero or greater when tertiary carbons occur in an alternating fashion. This reverses the behavior of the unadorned polyethylene chain (see Table 3). Along this line, the addition of a methyl group to every fourth carbon (see PEP in Table 3) leaves κ untouched relative to its polyethylene parent. However, the presence of the methyl group on alternate carbons (polypropylene) yields $\kappa = \sim 0$. The substitution of the propyl group by ethyl yields a positive value of κ. The exception to this is PCHE, for which the side chain is the cyclohexyl ring. PCHE and polystyrene share a κ value of virtually zero (Fig. 1). However, the C_∞ value decreases (Table 3) when the rigid aromatic ring of polystyrene is converted into the flexible cyclohexyl group, which then allows $\langle R^2\rangle_o/M$ to decrease relative to the polystyrene parent. This is shown in Figure 1, where the parent polystyrene chain dimension/temperature[17] behavior is displayed along with that of the offspring PCHE. Recall that unlike the rigid aromatic ring, the cyclohexyl unit can adopt either the boat or chair conformers; this permits, relative to polystyrene, an increase in the gauche$^{\pm}$ conformer population.

We attempted to measure the θ-condition chain dimensions of PCHE. However, we were thwarted by our failure to find a θ solvent for this polymer. Data were, therefore, collected in four nonideal solvents, and the Tanaka[40] extrapolation procedure was used to evaluate K_θ. These results are given in Table 4. The combined K_θ values lead to $C_\infty = 7.9$ (298 K), which is in good agreement with that from melt-state (433–533 K) measurements, $C_\infty = 7.8$. This commonality of C_∞ over the temperature range of 298–533 K supports the conclusion that κ is virtually zero for PCHE. The dilute solution work also shows that the solvent quality for PCHE increases in the order of benzene, THF, toluene, and cyclohexane (see Table 4). These data negate a long standing report[42] that THF is a θ solvent for PCHE at 298 K.

The chain dimension data of Table 2 can be used to calculate the packing lengths and, therefore, the rheological parameters via eqs 2, 3, and 5. These results are given in Table 5, where they are compared with their measured counterparts. Figure 6 shows a plot of $M_e\rho^{-1}$ versus p for the samples listed in Table 3. The line is drawn according to eq 3. As can be seen, the agreement is quite satisfactory. These findings support the validity of the packing model and the packing length concept. A generic trend observed[5–7,43] for M_e shows that its value generally increases with increasing temperature.

Table 5. Measured and Calculated Values of Rheological Parameters

Polymer	Temperature (K)	ρ (g cm^{-3})	p (Å)	G_N^o (MPa) Measured	G_N^o (MPa) Calculated[a]	(10^{-3} M_e (g mol^{-1})) Measured	(10^{-3} M_e (g mol^{-1})) Calculated[b]	N_e Measured	N_e Calculated[c]
hhPP	298	0.878	2.71	0.52	0.48	4.18	4.56	199	224
alt-PEB	298	0.861	2.69	0.58	0.48	3.70	4.45	168	201
PEP/PIPE	298	0.861	3.14	0.35	0.31	6.09	6.96	261	301
PEB/PsBE	298	0.860	2.59	0.50	0.55	4.26	3.90	152	142
PIPE/PMEE	298	0.858	4.28	0.12	0.12	17.7	17.9	506	510
PIPE/PMEE	413	0.810	3.91	0.22	0.22	12.6	12.9	367	368
PCHE	453	0.900	5.62	0.07	0.08	44.7	42.4	813	772
1,4-PI	298	0.900	3.06	0.35	0.33	6.37	6.85	364	391
1,4-PI	413	0.830	3.18	0.42	0.40	6.79	7.67	388	404
PMMA	413	1.13	3.45	0.31	0.32	12.5	12.1	250	249

[a] Equation 2.
[b] Equation 3.
[c] Equation 5.

This behavior is reversed for PIPE/PMEE (Table 5), for which a decrease in M_e occurs with increasing temperature. This is due to the magnitude and positive sign of κ for this copolyolefin. A similar state of play holds for polyisoprene and poly(ethyl ethylene)[5], where κ is about one-third that of PIPE/PMEE. This serves to render M_e for these two polymers nearly temperature-independent (see ref. 5 and Table 5). These examples serve to reinforce the importance of the chain dimension influence on polymer rheological behavior.

CONCLUSIONS

We conclude that a wide range of rheological behaviors can be found in olefin polymeric systems and that the melt-state chain dimension controls these behaviors. Recall that polyolefin densities

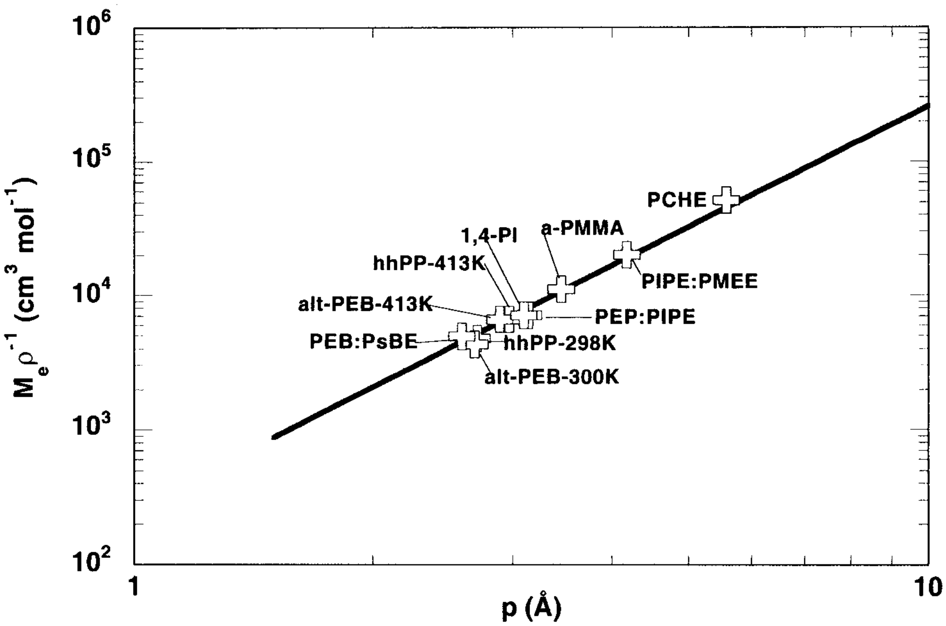

Figure 6. $M_e\rho^{-1}$ versus p for the polyolefins studied in this work. The line has been drawn according to eq 3.

are, with the exception of polyisobutylene and PCHE, virtually identical at a given temperature. An understanding of how the chain dimensions depend on the polymer architecture gives us a way to predict much of polyolefin rheology for both homopolymeric and copolymeric materials.

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