10096 *Macromolecules* **2002,** *35,* 10096−10101

Prediction of Melt State Poly(α-olefin) Rheological Properties: The Unsuspected Role of the Average Molecular Weight per Backbone Bond

Lewis J. Fetters[†] **and David J. Lohse***

Corporate Strategic Research Laboratories, ExxonMobil Research and Engineering Co., Annandale, New Jersey 08801

César A. García-Franco and Patrick Brant

Baytown Polymers Center, ExxonMobil Chemical Co., Baytown, Texas 77522

Dieter Richter

Research Center, Jülich Institute for Solid State Research, Jülich, Germany 52425

Received September 9, 2002; Revised Manuscript Received November 1, 2002

ABSTRACT: It has previously been shown that the entanglement molecular weight (M_e) and the plateau modulus (G_N^0) of flexible polymers can be correlated to the unperturbed chain dimension, $\langle R^2\rangle_0/M$, chain density (ρ) via the use of the packing length (p), which is defined as the volume of a chain divided by its mean square end to end distance. For polyolefins and co-polyolefins where $\langle R^2\rangle_0/M$ remains unmeasured a method is presented herein where knowledge of the average molecular weight per backbone bond (m_b) allows G_N^0 and thus M_e to be estimated. This is particularly valuable for the case of polyolefin copolymers where the melt chain dimensions (and thus the packing length) are unknown.

Introduction

In 1952 Bueche[1] proposed that the melt viscosity of short polymer chains (pre-entanglement regime) could be expressed as follows (here and below, "BR" stands for "Bueche−Rouse")

$$\eta^{BR} = f_o N[\rho N_a\langle R^2\rangle_0/36M] \tag{1}$$

Here, the observable parameters are the chain density (ρ), Avogadro's number (N_a), the chain molecular weight (M), the unperturbed chain dimension $\langle R^2\rangle_0$ expressed in terms of the root-mean-square end to end distance, the number of backbone bonds (N), and the segmental friction factor (f_o). Fox and Allen[2] demonstrated the validity of eq 1 in 1964.

Bueche[1] also showed that the combination of the melt viscosity and the diffusion constant led to the now well-known relations

$$[\eta D]^{BR} = kT[\rho N_a\langle R^2\rangle_0/36M] \tag{2}$$

$$D^{BR} = [kT/f_o N] \tag{3}$$

where k is Boltzmann's constant. Thus, Bueche's work was the first to show that densities and the unperturbed chain dimensions were directly connected to polymer melt rheological properties.

In 1969 Flory[3] offered the following observation; "Comprehension of the configurational statistics of chain molecules is indispensable for a rational interpretation and understanding of their properties". The verity of his statement has become more apparent in the intervening years with the realization that chain dimensions were relatable to the melt state plateau modulus G_N^0. The initial rigorous attempt to relate Gaussian chain dimensions to G_N^0 is the binary contact model of Graessley and Edwards.[5] Shortly thereafter, Ronca[6] derived the basics of what is now referred to as the packing model. In a sense, the packing model is a special case of the Graessley−Edwards model. Later contributions to the packing model were made by Lin[7] and Noolandi and Kavassalis.[8,9] At the same time Witten, Milner, and Wang[10] introduced the concept of a material-independent parameter, called the packing length (p), which is defined as the chain volume ($V_c = M/\rho N_a$) divided by the unperturbed mean square chain end-to-end distance. The average displaced volume of an entanglement strand, V_e, is the volume displaced by a chain section having the entanglement molecular weight, M_e, while the volume per bond, V_b, is given as $m_b/\rho N_a$, where m_b denotes the average molecular weight per backbone bond:

$$p = [M/\langle R^2\rangle_0\rho N_a] = [V_c/\langle R^2\rangle_0] = [V_e M/\langle R^2\rangle_0 M_e] = [V_b M/\langle R^2\rangle_0 m_b] \tag{4}$$

The packing length unites the volume filling and conformational characteristics of a polymer into an N-independent parameter that can be taken to denote the relative thickness of a chain.[12]

It is obvious that the Bueche equations, (1) and (2), can be recast in terms of the packing length in the regime of Bueche−Rouse behavior:

$$\eta^{BR} = [f_o N/36p] \tag{5}$$

$$[\eta D]^{BR} = [kT/36p] \tag{6}$$

In our previous work,[12,13] we have shown that p can be connected to the rheology of entangled chains. The plateau modulus, G_N^0, is proportional to p^{-3}, and so can

---

[†] Current address: School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY, 14853

10.1021/ma025659z CCC: $22.00

Table 1. PEB-2 and alt-PEP Characteristics

parameter	analytical method	
	Bueche−Rouse	measurement
$[D\eta]^{BR}$ (PEB-2) at 448 K[11]	100	
p (Å)	1.72	1.80
G_N^0 (MPa)	2.7	2.5
M_e (kg/mol)	1.1	1.15
$[D\eta]^{BR}$ (PEP) at 373 K[11]	62	
p (Å)	2.31	2.36
G_N^0 (MPa)	0.95	1.0
M_e (kg/mol)	2.7	2.45

be related to the Bueche−Rouse expressions:

$$G_N^0 = \lfloor kT/n_t^{\,2}p^3 \rfloor = \lfloor 36[\eta D]^{BR}/n_t^{\,2}p^2 \rfloor \qquad (7)$$

As M_e in inversely proportional to G_N^0, it can also be related to these quantities:

$$M_e = \lfloor \rho RT/G_N^0 \rfloor = n_t^{\,2}p^3N_a\rho = \lfloor RTn_t^{\,2}p^2/36[\eta D]^{BR} \rfloor \qquad (8)$$

Here n_t is the Ronca−Lin parameter,[6,7] which is defined as the number of entanglement strands in a cube with sides equal to d_t, the tube diameter. From our survey of all polymers, we find that $n_t = 20.8 \pm 0.8$; for just the polyolefins discussed herein, we find $n_t = 21.2 \pm 0.1$. This has operationally been taken[6,7,12,13] as independent of temperature and species. As Lin noted[7] this would be the case “if only the topological constraint effect is important”. This parameter is defined as

$$n_t = d_t/p = [M_e\langle R^2\rangle_0/M]^{1/2}p^{-1} = [kT/p^3G_N^0]^{1/2} \qquad (9)$$

Hence, the packing length is shown to exert control over η^{BR}, $[D\eta]^{BR}$, G_N^0, and hence M_e.

Equations 5−8 may seem initially surprising since they rely on the value of the constant product of the D and η parameters in the Bueche−Rouse region, and so do not represent a property of an entangled polymer system (for that matter the same can be said of p). The three parameters, p, G_N^0, and M_e can, though, be evaluated via available D and η data for model polyethylene (PEB-2) and poly(ethylene−propylene[11]) (alt-PEP). The resultant values are compared with their counterparts in Table 1. Good agreement is found between the $[D\eta]^{BR}$ based values and those determined by the conventional approach.

Experimental Section

The values of G_N^0 and the unperturbed chain dimensions for most of the polymers described herein are taken from refs 4, 12, and 13; the acronyms used to identify the polymers are identified in the Appendix. The chain dimension data are mostly derived from melt-state SANS measurements or from dilute solution Θ condition measurements.[14] When such data are missing, the chain dimensions are estimated from the rheological results. The rheological[15] and chain dimensions[16] data for syndiotactic polypropylene (*s*-PP) are from more recent work. The rheological data on the ethylene−hexene and ethylene−propylene copolymers (EHR*x* and EPR*x*) are from a recent paper by Miyata et al.[17]

For syndiotactic-poly(1-pentene) (*s*-PPEN), isotactic and syndiotactic poly(1-hexene) (*i*- or *s*-PHEX), syndiotactic poly(1-octene) (*s*-POCT), and poly(ethylene-co-octadecene) (PE-ODEC) the values of G_N^0 are not available in the open literature and are presented here for the first time. These syndiotactic polymers were prepared using the metallocene μ-[(diphenylcarbon)fluorenylcyclopentadienyl]hafnium dimethyl. The PE-ODEC was made using $Me_2Si(C_5Me_4)(NC_{12}H_{23})TiCl_2$ as catalyst and contained 79 wt % of the long chain α-olefin. The rheological characterization of these polyolefins relied on the measurement and analysis of the linear viscoelastic functions. The rheological behavior was studied using small amplitude oscillatory shear tests in an ARES mechanical spectrometer with parallel plates of 25 mm diameter. The angular frequency, ω, varied from 10^{-2} to approximately 390 rad/s at the following temperatures: 0, 10, 20, 30, and 40 °C. All the tests were conducted under an atmosphere of nitrogen. The isotherms were shifted to obtain master curves at a reference temperature (T_o = 0 °C) using the IRIS program. The values of G_N^0 were obtained by the methods outlined in ref 4. It is interesting to note that *s*-PPEN, *i*-PHEX, *s*-PHEX, and *s*-POCT showed no evidence of crystallinity over the range of measurement temperatures.

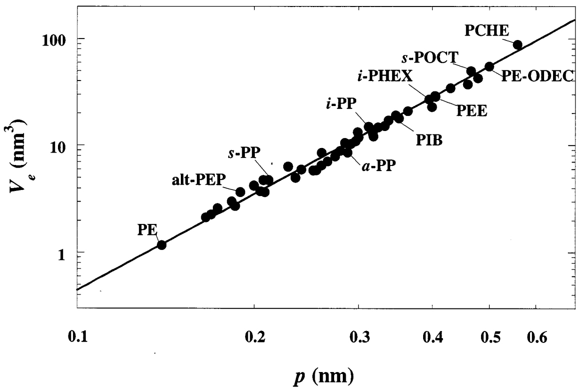

Figure 1. Entanglement volume of polyolefins as a function of packing length. Solid line is eq 11. The points for a representative set of the polyolefins are marked.

Results and Discussion

Equation 9 allows the plateau modulus to be expressed in terms of n_t and p:

$$G_N^0 = \rho RT/M_e = \lfloor kT/n_t^{\,2}p^3 \rfloor \cong 0.032Tp^{-3} \qquad (10)$$

The chain dimension and rheological parameters for a wide range of polyolefins are shown in Table 2, which also contains the characteristic ratio. This is a dimensionless parameter defined by $C_\infty = m_b\langle R^2\rangle_0/Ml_o^2$ where l_o is the polyolefin backbone bond of length of 1.53 Å.

Equation 8 shows[4] that M_e is related by a power law to the packing length of the polymer species. The entanglement volume can be expressed in terms of p and n_t via the following

$$V_e = M_e/\rho N_a = kT/G_N^0 = n_t^{\,2}p^3 \qquad (11)$$

These values are presented in Table 2 and Figure 1 where the solid line is based on eq 11. The entanglement volume notion offers a more physical perspective to the entanglement event than does the entanglement molecular weight alone since the density parameter is neutralized. Table 3 contains some useful packing-length-based expressions.

The absence of measured unperturbed chain dimensions in the melt-state for most polymers, including polyolefins, dictates the need to uncover a method by which such dimensions can be predicted simply from a knowledge of the chemical architecture of the chains. A quick glance at the data in Table 2 shows that qualitatively the chain dimensions decrease as branching frequency and side group size increases (i.e., $\langle R^2\rangle_0/M$ decreases as m_b increases). The simplest model to

Table 2. Characteristics of Olefinic Polymers and Copolymers

polymer	m_b (g/mol)	G_N^0 (MPa)	$\langle R^2\rangle_0/M$[a] (Å^2 mol g^{-1})	ρ (g/cm^3)	p[a] (Å)	M_e (kg/mol)	M_e[d] (kg/mol)	V_e (nm^3)	C_∞[a]	n_t[e]	T[f] (K)
PE	14.0	3.5	1.40	0.851	1.39	0.60	0.61	1.18	8.5	21.4	298
PE	14.0	2.5	1.25	0.785	1.69	1.1	1.0	2.28	7.5	21.3	413
PEB-2	14.6	2.5	1.25	0.802	1.66	1.0	0.97	2.15	7.8	21.7	389
PEB-2	14.6	2.2	1.22	0.785	1.73	1.2	1.1	2.59	7.6	22.3	413
PEB-5	15.3	1.9	1.15	0.788	1.83	1.4	1.3	3.00	7.6	22.1	413
PEB-7	16.0	1.6	1.11	0.789	1.90	1.8	1.4	3.68	7.6	23.2	413
EPR37	16.6	1.1		0.861		2.0		3.86			296
PEB-10	16.7	1.4	1.05	0.791	2.00	2.0	1.7	4.22	7.6	23.0	413
PEB-12	17.3	1.5	1.04	0.860	1.86	1.4	1.5	2.74	7.8	20.8	298
PEB-12	17.3	1.2	1.01	0.793	2.07	2.3	1.9	4.75	7.6	23.1	413
alt-PEP	17.5	1.1	0.946	0.856	2.05	1.9	2.0	3.74	7.5	20.8	298
alt-PEP	17.5	1.0	0.871	0.812	2.35	2.4	2.8	5.00	6.9	19.6	373
alt-PEP	17.5	0.97	0.834	0.782	2.55	2.8	3.4	5.88	6.6	18.8	413
PEB-18	18.9	1.1	0.926	0.860	2.08	1.9	2.1	3.67	7.5	20.1	298
PEB-18	18.9	0.90	0.913	0.797	2.28	3.0	2.5	6.34	7.4	23.1	413
PEP:PIPE-16	19.0	0.88	0.813[b]	0.812	2.52	2.9	3.4	5.85	6.6[b]	19.1	373
PEP:PIPE-20	19.4	0.79	0.788[b]	0.812	2.59	3.2	3.8	6.52	6.5[b]	19.4	373
PEP:PIPE-29	20.5	0.58	0.732[b]	0.812	2.79	4.3	4.7	8.88	6.4[b]	20.2	373
PEB-25	20.9	0.69	0.800	0.864	2.40	3.1	3.2	5.96	7.0	20.8	298
PEB-25	20.9	0.67	0.799	0.799	2.60	4.1	3.8	8.51	7.2	22.0	413
a-PP	21.0	0.48	0.678	0.852	2.87	4.4	5.4	8.57	6.1	18.6	298
a-PP	21.0	0.47	0.660	0.791	3.18	5.8	6.8	12.1	5.9	19.9	413
a-PP	21.0	0.42	0.653	0.765	3.32	7.0	7.5	15.2	6.0	21.1	463
i-PP	21.0	0.43	0.694	0.766	3.12	6.9	6.2	14.9	6.2	22.1	463
s-PP	21.0	1.35	1.03	0.762	2.22	2.2	1.9	4.74	9.2	22.6	463
hh-PP	21.0	0.52	0.691	0.878	2.74	4.2	4.8	7.91	6.2	19.6	298
hh-PP	21.0	0.52	0.691	0.810	2.97	5.4	5.6	11.0	6.2	20.5	413
EHR25	21.1	0.60		0.853		3.5		6.81			296
PEP:PIPE−34	21.1	0.50	0.703[b]	0.812	2.91[b]	5.0	5.3	10.3	6.3[b]	20.4	373
alt-PEB	21.5	0.58	0.725	0.861	2.66	3.7	4.3	7.09	6.8	19.4	298
alt-PEB	21.5	0.48	0.692	0.800	3.00	5.7	5.8	11.9	6.5	21.0	413
PEB-32	23.0	0.39	0.676	0.863	2.85	5.5	5.3	10.6	6.6	19.8	298
PEB-32	23.0	0.43	0.692	0.802	2.99	6.4	5.7	13.3	6.8	22.3	413
PEP:PIPE-50	23.3	0.35	0.632	0.812	3.24	7.2	7.3	14.7	6.3	20.0	373
EHR33	23.4	0.42		0.853		5.0		9.73			296
PEB-40	25.0	0.24	0.570	0.864	3.37	8.9	8.8	17.1	5.9	21.2	298
PEB-40	25.0	0.30	0.595	0.805	3.47	9.2	8.9	19.0	6.4	21.3	413
EHR40	25.1	0.44		0.858		4.8		9.29			296
PIB	28.0	0.32	0.570	0.918	3.08	7.1	7.8	12.9	6.8	21.0	298
PIB	28.0	0.32	0.557	0.849	3.51	9.1	9.8	17.8	6.7	20.3	413
a-PEE	28.0	0.18	0.480	0.866	3.99	11.9	14.7	22.9	5.6	19.0	298
a-PEE	28.0	0.20	0.508	0.807	4.02	13.9	14.3	28.5	6.1	20.9	413
EHR51	28.1	0.31		0.857		6.8		13.2			296
a-PPEN	35.0		0.535[b]	0.846	3.67		11.1		8.0		306
i-PPEN	35.0		0.556[b]	0.828	3.60		10.4		8.3		337
s-PPEN	35.0	0.20	0.558[c]	0.871	3.42	10.7	10.9	20.9	8.3	21.7	273
PIPE:PMEE	35.0	0.12	0.452[b]	0.855	4.30	17.7	18.1	34.3	6.8	20.8	298
PHMYRC-1,4	36.8	0.12	0.434[b]	0.832	4.60[b]	18.7	21.6	37.3	6.8[b]	19.9	324
a-PHEX	42.0		0.527[b]	0.830	3.80		12.1		9.5		334
i-PHEX	42.0	0.14	0.556[b]	0.871	3.43	14.1	14.3	26.9	8.6	21.0	273
s-PHEX	42.0	0.13	0.470[c]	0.871	4.04	15.2	15.4	29.0	8.4	21.2	273
$H_2$64-PMYRC	42.7	0.10	0.409[b]	0.849	4.78	21.7	24.8	42.5	7.5	19.7	308
PE-ODEC	49.9	0.075	0.390[c]	0.851	5.00	28.2	28.3	54.9	8.3	20.9	298
a-PCHE	55.0	0.068	0.323	0.920	5.59	48.7	42.8	87.9	7.5	22.4	433
a-POCT	56.0		0.409[b]	0.836	4.85		25.5		12.2		323
s-POCT	56.0	0.076	0.393[c]	0.872	4.66	26.2	23.5	49.8	9.8	22.2	273
a-PDEC	70.0		0.381[b]	0.850	5.13		30.5		11.4		303
a/*i*-PHDEC	112.0		0.213[b]	0.796	9.79		199		10.2		418

[a] As measured by SANS in the melt unless otherwise indicated. [b] As measured in dilute solution at the Θ condition. [c] As calculated from eq 10. [d] As calculated from eq 8. [e] As calculated by eq 9. [f] Measurement temperature of G_N^0 or, in its absence, the chain dimension.

Table 3. Packing-Length-Based Expressions

$$p = [M/\langle R^2\rangle_0 \rho N_a] = [V_c/\langle R^2\rangle_0] = [V_e M/\langle R^2\rangle_0 M_e] = [V_b M/\langle R^2\rangle_0 m_b]$$
$$n_t = d_t/p = [M_e\langle R^2\rangle_0/M]^{1/2}\ p^{-1} = [kT/p^3 G_N^0]^{1/2} = 20.8\ (\pm 0.8)$$
$$d_t = p n_t = [kT/pG_N^0]^{1/2} = [M_e/\rho p N_a]^{1/2}$$
$$G_N^0 = \rho RT/M_e = [kT/n_t^2 p^3] = kT/V_e$$
$$M_e = [\rho RT/G_N^0] = n_t^2 p^3 N_a \rho$$
$$V_e = M_e/\rho N_a = kT/G_N^0 = n_t^2 p^3$$
$$\langle R^2\rangle_0/M = n_t^{2/3}[G_N^0/kT]^{1/3}[\rho N_a]^{-1}$$

explain this is that the chain dimensions only depend on the length or molecular weight of the backbone for a polyolefin. Another way to describe this "backbone equivalence" (BE) model is to say that a polyolefin chain has the same dimension in the melt as does the "mother" polyethylene chain that has a molecular weight equal to that of the backbone of the polyolefin in question. This leads to the following simple prediction (ignoring steric effects) for all polyolefins in terms of m_b:

$$\frac{\langle R^2\rangle_0}{M} = \frac{14}{m_b}\left(\frac{\langle R^2\rangle_0}{M}\right)_{PE} \qquad (12)$$

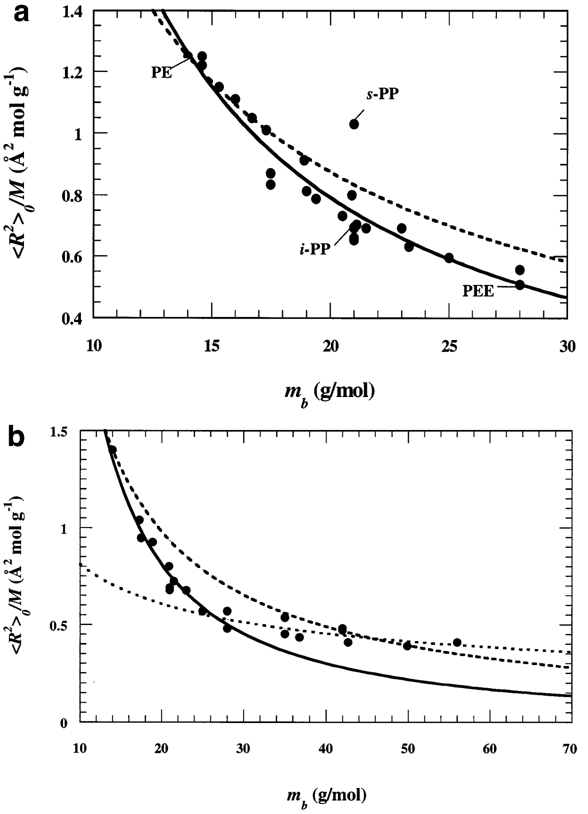

Figure 2. Polyolefin chain dimensions as a function of m_b: (a) for $T = 363-413$ K, dashed line is eq 12 and solid line is eq 15; (b) for $T = 298$ K, dashed line is eq 12, solid line is eq 14, and dotted line is eq 16.

Combining eq 12 with the expressions of Table 3 the following simple predictions can be made, taking density as independent of chemical structure:

$$p = \left(\frac{m_b}{14}\right) p_{PE} \tag{13a}$$

$$d_t = \left(\frac{m_b}{14}\right)(d_t)_{PE} \tag{13b}$$

$$G_N^0 = \left(\frac{14}{m_b}\right)^3 (G_N^0)_{PE} \tag{13c}$$

$$M_e = \left(\frac{m_b}{14}\right)^3 (M_e)_{PE} \tag{13d}$$

How well does the backbone equivalence model work? This can be seen in Figure 2, which shows $\langle R^2\rangle_0/M$ *vs* m_b for two temperature ranges. Figure 2a shows the fit for polyolefins with m_b from 14 to 28 at 373 to 463 K, while Figure 2b presents the state of play at temperatures near ambient where m_b ranges from 14 to 70. The backbone equivalence expression, eq 12, is given by the dotted line and can be seen to be a poor predictor of the dimensions in both temperature ranges. The results indicate that the backbone equivalence model is only an approximation of the experimental state of play. It does, though, correctly point out that $\langle R^2\rangle_0/M$ does scale with m_b.

For some reason, the chain dimensions of these polyolefins are even smaller than what the backbone equivalence model would predict. Fitting the data for $14 < m_b < 28$, where we have the best values of dimensions from neutron scattering, results in the following expressions:

$$\langle R^2\rangle_0/M = 59.4 m_b^{-1.43} \quad (298\text{ K}; m_b \text{ of } 14-28) \tag{14}$$

$$\langle R^2\rangle_0/M = 39.5 m_b^{-1.30} \quad (373/463\text{ K}; m_b \text{ of } 14-28) \tag{15}$$

We have found no explanation for these expressions and present them here simply as a means to estimate chain size for other polyolefin structures. In Figure 2a there is one conspicuous outlier from the expression of eq 15. This is *s*-PP, which we discuss in depth in the next section. As can be seen in Figure 2b, the data at higher values of m_b do not obey eq 14. Here there are no data from neutron scattering (PCHE excepted), and we rely on dimensions from Θ solutions. If we fit these data separately, we obtain

$$\langle R^2\rangle_0/M = 2.12 m_b^{-0.42} \quad (\sim 298\text{ K}; m_b \text{ of } 35-70) \tag{16}$$

So why does the backbone equivalence model fail to predict the chain dimensions? The interplay between polyolefin chain dimensions and m_b must be a reflection of the influence of m_b upon the trans−gauche$^\pm$ conformer populations present in the carbon−carbon backbone. This must mean that, for $14 < m_b < 28$, the presence of the branches increases the population of gauche$^\pm$ conformers over that found in polyethylene. For $m_b > 28$, that is for *n*-propyl branches and larger, there is an enhancement of the backbone trans conformer population (relative to what is seen for PEE) at the expense of the more compact gauche$^\pm$. The change in the identity of the secondary interactions for polyolefins is reflected by the change in the corresponding characteristic ratios: see Table 2. Therein, it is seen that that at $m_b > 28$ the characteristic ratios increase as m_b becomes progressively larger. Saturation seems to occur when C_∞ reaches the range 11−12.

The behavior shown in parts a and b of Figure 2 is foreshadowed by the observation[18] that the unperturbed chain dimensions of ethylene−butene copolymers (PEB) scaled with the ethyl branch content (α). For example, the following expressions are representative of this behavior:

$$\langle R^2\rangle_0/M = 1.34\mathrm{e}^{-0.0214\alpha} \quad (300\text{K}) \tag{17}$$

$$\langle R^2\rangle_0/M = 1.21 e^{-0.0172\alpha} \quad (440\text{K}) \tag{18}$$

These expressions show that as one moves from polyethylene to poly(ethyl ethylene) (PEE) the chain dimensions undergo a monotonic decrease. Inspection of Table 2 shows that in concert with this chain dimension change the values of G_N^0 also decrease.

The relation of G_N^0 to m_b can be examined in a similar fashion. Figure 3 shows that the backbone equivalence model (eq 13c) is again a poor predictor. Although G_N^0 is a function of temperature, this is generally quite weak due to the compensating effects of density and chain dimensions. Thus, for the kind of fitting we are doing here, we feel justified in using all of the G_N^0 data in a given m_b range. Fitting the G_N^0 data

Table 4. Rheological Parameters for Selected Polyolefins

	G_N^0 (MPa)			$\langle R^2\rangle_0/M$ (Å^2 mol g^{-1})		M_e (kg/mol)		
sample	measd	calcd[a]	calcd[b]	measd	calcd[c]	measd	calcd[d]	*T* (K)
PE	2.5	2.7	2.5	1.25	1.28	1.08	1.01	413
PEB-5	1.9	2.1	1.8	1.15	1.14	1.42	1.29	413
PEP	1.1	1.1	1.1	0.946	0.991	1.93	1.97	298
PEP	0.97	0.78	1.1	0.834	0.956	2.77	3.44	413
a-PP	0.48	0.39	0.60	0.678	0.764	4.40	5.39	298
a-PP	0.47	0.40	0.60	0.660	0.755	5.78	6.78	413
hh-PP	0.52	0.45	0.60	0.691	0.764	4.18	4.80	298
hh-PP	0.52	0.49	0.60	0.691	0.755	5.35	5.64	413
PEB-25	0.69	0.67	0.61	0.800	0.769	3.10	3.19	298
PEB-25	0.67	0.73	0.61	0.799	0.759	4.09	3.75	413
PEB-40	0.24	0.24	0.33	0.570	0.595	8.92	8.83	298
PEB-40	0.3	0.31	0.33	0.595	0.602	9.21	8.94	413
a-PEE	0.18	0.15	0.22	0.480	0.506	11.9	14.7	298
a-PEE	0.2	0.19	0.22	0.508	0.519	13.9	14.3	413
s-PPEN	0.2	0.20	0.15	0.558[e]	0.476	10.7	10.9	273
i-PHEX	0.14	0.14	0.11	0.556	0.441	14.1	14.3	273
s-PHEX	0.13	0.13	0.11	0.471[e]	0.441	15.2	15.4	273
s-POCT	0.076	0.08	0.07	0.393[e]	0.391	26.2	23.5	273
PE-ODEC	0.075	0.07	0.09	0.390[e]	0.410	28.2	28.3	273
PCHE	0.068	0.08	0.07	0.323	0.394	48.7	42.8	433

[a] Via eq 10. [b] Via eq 19 or 20. [c] Via eq 14, 15, or 16. [d] Via eq 8. [e] Table 2; see expression for $\langle R^2\rangle_0/M$.

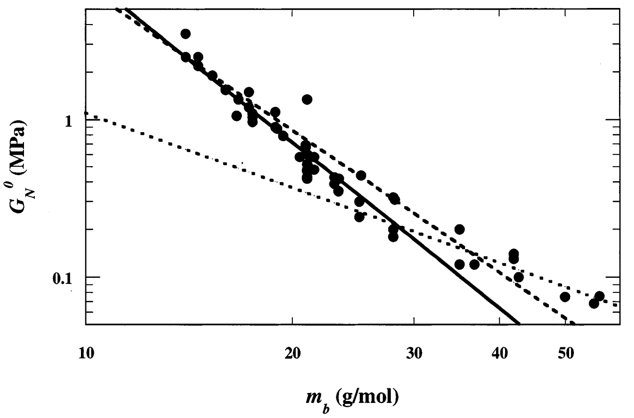

Figure 3. Polyolefin plateau moduli as a function of m_b. Dashed line is eq 13c, solid line is eq 19, and dotted line is eq 20.

from Table 2 in the same manner as was done for the $\langle R^2\rangle_0/M$ results yields

$$G_N^0 = 24\,820 m_b^{-3.49} \quad (m_b = 14-28) \tag{19}$$

$$G_N^0 = 41.84 m_b^{-1.58} \quad (m_b = 35-56) \tag{20}$$

These expressions are valuable since they permit direct estimates of G_N^0, and thus M_e via eq 8, for polyolefin copolymers without direct knowledge of the chain dimensions. Again, we have no justification for these expressions, except as fits to the data. Miyata et al.[17] tried to fit their data on the ethylene copolymers with an expression containing m_b to the 2.3 power. (There are several mathematical errors in ref 17; when we apply the model they discuss, we find that the model of Miyata et al. does not fit the data at all.) Their argument was akin to what we have called here the backbone equivalence model (eq 12), except that they contend that the variation in chain dimensions from one polymer to another is not significant. We have clearly shown here that this variation is critical. The complete set of polyolefin data can only be fit by an expression like eqs 19 and 20.

Table 4 compares the measured and calculated rheological values for selected polyolefins. The agreement is satisfactory. Our experience, to date, has shown that for $m_b \geq 28$ the plateau moduli are essentially temperature independent. This state of play is traceable to the fact that these poly(α-olefins) apparently exhibit positive temperature coefficients (PCHE excepted[19]) for their chain dimensions. These latter expressions would clearly benefit from additional data from poly(α-olefins) where $m_b > 56$. The merit of eqs 19 and 20 lies in the convenience of eliminating the need for direct knowledge of the unperturbed chain dimension of the subject polyolefin homo- or copolymer.

These simple states of play seemingly hold as long as heterotactic, isotactic, and most syndiotactic polyolefins are under consideration. This commonality of behavior is based upon the observation that these tactic formats seemingly share identical chain dimensions. The single exception to this is *s*-PP,[15] which is reported to exhibit a substantially larger plateau modulus than *i*-PP and *a*-PP (1.35 vs 0.42 MPa; see Table 2). This must mean that the *s*-PP chains are substantially larger than *i*-PP (and *a*-PP) chains in the melt. Recent[16] melt-state SANS chain dimension measurements on *s*-PP yields $\langle R^2\rangle_0/M = 1.03$ Å^2 mol g^{-1}, in good agreement with the value of 0.98 Å^2 mol g^{-1} calculated[12] from the measured[15] G_N^0. Molecular dynamics based calculations[20] predict *s*-PP to have unperturbed chain dimensions about 50% greater than *a*-PP or *i*-PP. The polypropylene data of Table 2 yield this ratio.

This can be explained by a greater number of trans conformers for *s*-PP than *i*-PP or *a*-PP and in fact even more than for PE. The characteristic ratio for *s*-PP is 9.2 while at the same temperature the corresponding value of PE is 7.1. A fuller understanding of this will require better calculations of bond rotation potentials for propylene conformers. These calculations must be done with the recognition that the syndiotactic format does not seemingly lead to large chain dimension differences for poly(1-pentene) and larger poly(α-olefins) (see Table 2). Currently G_N^0 and $\langle R^2\rangle_0/M$ for *s*-PEE remain unmeasured; data on this polymer would thus be quite valuable. Along this line the chain dimensions of hetero-, iso-, and syndiotactic polystyrene are, within experimental error, identical.[21-23]

Finally, it should be pointed out that there are several conflicting reports of values of the plateau modulus of *s*-PP in the literature. Yamaguchi and Miyata[24] report a value of G_N^0 about half that reported in Table 2. Moreover, the G' and G'' data of Eckstein et al.[15] may indicate that some branched polymer was present in the *s*-PP sample (see Figures 3−5 in ref 15). We therefore recommend further measurements of the *s*-PP G_N^0. This would best be done on material prepared using the single site polymerization system described by Tian, Hustad, and Coates.[25] Their *s*-PP polymers exhibited a *rr*-diad content of 0.99% along with narrow molecular weight distributions. Unlike the organometallocene family of catalysts, their system does not generate double bonds at the chain ends. This feature effectively eliminates the potential for the formation of long chain branched structures.

Conclusions

We conclude that a wide range of rheological behavior can be found in olefin polymeric systems. Practical polyolefins can be prepared where the plateau moduli differ by about ∼50-fold. No other polymer family exhibits such a wide G_N^0 range. This explains why copolymers of various compositions can find utility in so many different areas. An understanding of how the chain dimensions depend on polymer composition thus gives a way to predict much of the rheology of polyolefins. We show here an empirical relation that explains most, but not all, of the currently known polyolefin data. The power of expressions such as eqs 14−16 and 19−20 lies in the ability to make good estimates of the rheological performance of polymers that have not yet been synthesized. This shows the need to find predictive schemes to calculate chain dimensions from polymer architecture.

Appendix: Abbreviations Used for Polymer Identification

PE	polyethylene
PEB-*x*	poly(ethylene-*co*-butene); the integer (*x*) denotes the number of ethyl branches per 100 backbone carbons. These have been made by the hydrogenation of polybutadienes of varying vinyl content.
EPR*x*	ethylene−propylene copolymer with *x* mole percent propylene incorporation.
EHR*x*	ethylene-hexene copolymer with *x* mole percent hexene incorporation.
a-PEE	poly(ethyl ethylene); hydrogenated poly(vinyl ethylene) or 1,2-polybutadiene; equivalent to atactic poly(butene-1) or PEB-50
alt-PEP	essentially alternating poly(ethylene-*co*-propylene); hydrogenated 1,4-polyisoprene
PEP:PIPE-x	poly[(ethylene propylene)$_{100-x}$-*ran*-(isopropyl ethylene)$_x$]; hydrogenated polyisoprene (100-x/x 1,4/3,4)
PIPE:PMEE	poly(isopropyl ethylene)-*ran*-(methyl ethyl ethylene); hydrogenated polyisoprene (75/25 3,4/1,2)
alt-PEB	essentially alternating poly(ethylene-*co*-1-butene); hydrogenated 1,4-poly(ethyl butadiene).
PHMYRC-1,4	hydrogenated 1,4 polymyrcene (97/3 1,4/3,4)
H_2 64-MYRC	hydrogenated version of 1,4−3,4 polymyrcene (64/36 1,4/3,4)
a-PCHE	poly(cyclohexyl ethylene) from the hydrogenation of polystyrene
hh-PP	head-to-head polypropylene; hydrogenated poly(2,3-dimethyl butadiene).
a-PP	atactic polypropylene; hydrogenated 1,4-poly(2-methyl-1,3-pentadiene)
i-PP	isotactic polypropylene
s-PP	syndiotactic polypropylene
a-PPEN	atactic poly(pentene-1)
i-PPEN	isotactic poly(pentene-1)
s-PPEN	syndiotactic poly(pentene-1)
a-PHEX	atactic poly(hexene-1)
i-PHEX	isotactic poly(hexene-1)
s-PHEX	syndiotactic poly(hexene-1)
a-POCT	atactic poly(octene-1)
s-POCT	syndiotactic poly(octene-1)
a-PDEC	atactic poly(decene-1)
a-PHDEC	atactic poly(hexadecene-1)
i-PHDEC	isotactic poly(hexadecene-1)
PE-ODEC	poly(ethylene co-octadecene); 79 wt % octadecene
PIB	polyisobutylene

References and Notes

(1) Bueche, F. *J. Chem. Phys.* **1952**, *20*, 1959.
(2) Fox, T. G.; Allen, V. R. *J. Chem. Phys.* **1964**, *41*, 344.
(3) Flory, P. J. *Statistical Mechanics of Chain Polymers*; Interscience: New York, 1969
(4) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
(5) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.
(6) Ronca, G. *J. Chem. Phys.* **1983**, *79*, 1031.
(7) Lin, T. *Macromolecules* **1987**, *20*, 3080.
(8) Kavassalis, T. A.; Noolandi, J. *Macromolecules* **1988**, *21*, 2869.
(9) Kavassalis, T. A.; Noolandi, J. *Phys. Rev. Lett.* **1988**, *59*, 2674.
(10) Witten, T. A.; Milner, S. T.; Wang, Z.-G. In *Multiphase Macromolecular Systems*; Culbertson, B. M., Ed.; Plenum: New York, 1989.
(11) Pearson, D. S.; Fetters, L. J.; Graessley, W. W.; ver Strate, G.; von Meerwall, E. *Macromolecules* **1994**, *27*, 711.
(12) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1999**, *37*, 1023.
(13) Fetters, L. J.; Lohse, D. J.; Milner, S. T.; Graessley, W. W. *Macromolecules* **1999**, *32*, 6847.
(14) Sundararajan, P. R. in *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; American Institute of Physics, Woodbury, NY, 1996, Chapter 15..
(15) Eckstein, A.; Suhm, J.; Friedrich, C.; Maier, R.-D.; Sassmannhausen, J.; Bochmann, M.; Mülhaupt, R. *Macromolecules* **1998**, *31*, 1335.
(16) Jones, T. D.; Chaffin, K. A.; Bates, F. S.; Annis, B. K.; Hagaman, E. W.; Kim, M.-H.; Wignall, G. D.; Fan, W.; Waymouth, R. *Macromolecules* **2002**, *35*, 5061.
(17) Miyata, H.; Yamaguchi, M.; Akashi, M. *Polymer* **2001**, *42*, 5763.
(18) Fetters, L. J.; Graessley, W. W.; Krishnamoorti, R.; Lohse, D. J.; *Macromolecules* **1997**, *30*, 4973.
(19) Krishnamoorti, R.; Graessley, W. W.; Zirkel, A.; Richter, D.; Hadjichristidis, N.; Fetters, L. J.; Lohse, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **2002**, *40*, 1768.
(20) Pütz, M.; Curro, J. G.; Grest, G. S. *J. Chem. Phys.* **2000**, *114*, 2847.
(21) Boothroyd, A. T.; Rennie, A. R.; Wignall, G. D. *J. Chem. Phys.* **1993**, *99*, 9135.
(22) Stolken, S.; Ewen, B.; Kobayaski, M.; Nakaoki, T. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32*, 881.
(23) Guenet, J. M.; Picot, C.; Benoît, H. *Macromolecules* **1979**, *12*, 86.
(24) Yamaguchi, M.; Miyata, H. *Macromolecules* **1999**, *32*, 5911.
(25) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134.

MA025659Z