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Reviews

Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties

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ABSTRACT: One of the main goals of polymer science has been to relate the structure of macromolecular chains to their macroscopic properties. In particular, it has been hoped that one could relate the sizes of polymer coils to the degree to which they entangle with one another and thus to their viscoelasticity in the melt. In recent years, the availability of model polymers with nearly monodisperse molecular weight distributions and precisely controlled chemical structures has allowed for improved data both on rheology and on the dimensions of the chains. This has now allowed us to determine the correlations between such properties as chain dimensions, density, and plateau modulus and to show that some quite simple relations exist between them. The main body of these data is on polymers that can be considered to be models for polyolefins. These have been made by the hydrogenation of polydienes synthesized by anionic polymerization techniques. In this way the molecular weight distribution can be made to be nearly monodisperse (M_w/M_n < 1.1) and the chemical structure is well controlled. For example, models of a wide range of ethylene–butene copolymers have been made by the saturation of polybutadienes with a range of vinyl content. Such polymers can be made at many molecular weights as well. The viscoelastic properties of these polymers have been measured very precisely, and their chain dimensions have been determined by small-angle neutron scattering. To a high degree of correlation, we find that the mean-square unperturbed end-to-end distance, $\langle R^2\rangle_0$, the density, ρ, and molecular weight, M, are related to the plateau modulus, G_N^0, $G_N^0 \propto \{\langle R^2\rangle_0\rho/M\}^3$ a finding in accord with that of Ronca. This simple relationship gives us a deep understanding of what controls the rheology of these polyolefins and of how we might be able to predict the properties of as yet unsynthesized polymers.

Introduction

The interplay between the physical properties of a polymer chain and its unperturbed dimension was enunciated by Flory[1] in 1969; "Comprehension of the conformational statistics of chain molecules is indispensable for a rational interpretation and understanding of their properties". This recognition that chain dimensions (as given, for example, by $\langle R^2\rangle_0$, the unperturbed mean-square end-to-end distance) lie at the heart of polymer physics is of vital importance. In turn, this led to developments which attempt to correlate such viscoelastic properties as the plateau modulus, G_N^0, with the chain dimensions.[2–16] These enterprises have had as their aim the establishment of the essential physical laws of melt polymer behavior without reference to the structural details of any particular polymer.

The measurement of unperturbed chain dimensions has historically been done via dilute solution measurements. Rotational isomeric state (RIS) calculations have also been carried out. For the case of polyethylene[1,17] good agree-

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ment with regard to the chain dimension and its temperature coefficient were obtained between measurements in Θ solutions and the melt, as well as calculations by RIS. However, recent results[18,19] from small-angle neutron scattering (SANS) of melt systems have revealed prominent discrepancies between those findings and those from Θ conditions and RIS calculations. The polymers involved were polypropylene, poly(1-butene), polystyrene, and poly(methyl methacrylate). Those findings indicate that the melt-state-based chain dimensions are free of ambiguity and are thus preferred.

Chain dimensions are often expressed[1] in terms of the characteristic ratio, C_∞, which is defined by:

$$\langle R^2\rangle_0 = C_\infty M m_0^{-1} l_0^2 \tag{1}$$

or, since $\langle R^2\rangle_0 = 6\langle R_g^2\rangle_0$:

$$\langle R_g^2\rangle_0 = C_\infty M m_0^{-1} l_0^2 6^{-1} \tag{2}$$

where m_0 is the average molecular weight per backbone bond of length l_0. The SANS-based values of $\langle R^2\rangle_0/M$ in the melt were used for the evaluation of the connection between unperturbed chain dimensions and viscoelastic properties. As will be shown the following relations hold:

$$G_N^0 \propto [\rho\langle R^2\rangle_0/M]^3 \tag{3}$$

$$M_e \propto \rho^{-2}[\langle R^2\rangle_0/M]^{-3} \tag{4}$$

$$d_t \propto [\rho\langle R^2\rangle_0/M]^{-1} \tag{5}$$

where ρ is the polymer density, M_e the molecular weight between entanglements, and d_t the reptation tube diameter. Thus, in effect, the unperturbed radius of gyration, R_g, and polymer density combine to control those viscoelastic parameters.

Results and Discussion

The Model. The following model is predicated on the idea that there is a relation between the sizes of the polymer coils and the degree to which they are entangled with each other. Basically, the idea is that the larger the dimensions of a chain, the greater the volume it sweeps out, so the greater the number of other chains it will encounter and with which it might entangle. This requires a knowledge of the volume the chain occupies (just given by M/ρ) and also the volume "pervaded" by the chain, that is, the volume spanned by the chain, which is quite difficult to calculate. Here we will approximate this volume by V_{sp}, the volume of the smallest sphere which completely contains the chain. We assume this is proportional to the cube of the radius of gyration:

$$V_{sp} = A\langle R_g^2\rangle_0^{3/2} \tag{6}$$

where A is a constant of order unity. From eq 2

$$V_{sp} = A C_\infty^{3/2} M^{3/2} m_0^{-3/2} 6^{-3/2} \tag{7}$$

Let N be the number of chains of length M that would completely fill a volume V_{sp}. Then we have

$$N = V_{sp}\rho N_A/M \tag{8}$$

where N_A is Avogadro's number and so

$$N = A C_\infty^{3/2} M^{1/2} m_0^{-3/2} l_0^3 \rho N_A 6^{-3/2} \tag{9}$$

Now $N - 1$ can also be considered as the number of chains with which a particular chain is entangled, since that is the number of other chains that are in the volume it pervades. In a highly entangled melt, N will be a large number. For shorter chains, there is less entanglement and N becomes smaller. We may now ask, what is the number of chains N in V_{sp} when $M = M_e$? Let us define M_e as the molecular weight of a chain at which $N = 2$, that is, when there is just one other chain in the spanned volume. For $M < M_e$, there is thus no full chain in that volume, so there is no entanglement. This leads to the following expression for M_e:

$$M_e = B^{-2} C_\infty^{-3} m_0^3 l_0^{-6} \rho^{-2} N_A^{-2} \tag{10}$$

where $B = A/6^{3/2}/2$. The corresponding expression for C_∞ is

$$C_\infty = B^{-2/3} M_e^{-1/3} m_0 l_0^{-2} \rho^{-2/3} N_A^{-2/3} \tag{11}$$

Using eq 1 we can rewrite eq 10 in terms of $\langle R^2\rangle_0/M$ and ρ, thus leading to the following expression:

$$M_e = B^{-2}(\langle R^2\rangle_0/M)^{-3}\rho^{-2}N_A^{-2} \tag{12}$$

Witten, Milner, and Wang[20] have defined a quantity called the packing length p, which is used to denote the number of individual chains present in a given small volume of the melt. This parameter is given by

$$p = M/\langle R^2\rangle_0 \rho N_A \tag{13}$$

and so is intrinsically related to the size of the polymer coil and the volume that it takes up. From the work of Witten et al.,[20] which considered the effect of stretching on tethered chains, the packing length is found to be a characteristic parameter that controls many of the fundamental physical properties of polymers. It is also germane to note that p is essentially (within a numerical coefficient) the inverse of the statistical segment length parameter β^2, introduced by Helfand and Sapse.[21] It arose naturally as a parameter in their description of the interfacial tension and profile between two immiscible polymers. One can see from eq 12 that it is also a natural parameter to describe the properties considered here, so we can recast these expressions in terms of it. Combining eqs 12 and 13, we have

$$M_e = B^{-2}p^3\rho N_A \tag{14}$$

Using the following standard relation[22] for the plateau modulus and M_e,

$$G_N^0 = \frac{4}{5}\frac{\rho k T N_A}{M_e} \tag{15}$$

where k is Boltzmann's constant, we get

$$G_N^0 = (4/5)B^2 kTp^{-3} \tag{16}$$

Since the reptation tube diameter, d_t, is related to M_e and the chain dimensions by

$$\frac{d_t^2}{M_e} = \frac{\langle R^2\rangle_0}{M} \tag{17}$$

we have the simple relation

$$d_t = p/B \tag{18}$$

Comparison with the Data. We have chosen to compare these relations proposed in eqs 10–18 with experimental data at 413 (Table 1) and 298 K (Table 2). The plateau moduli listed there were either taken from Ferry,[23] Carrella,[24] Roovers,[25,26] Colby,[27] or Fetters[28] or from the references listed in Appendix I. The majority of the values given were obtained from the area under the terminal loss peak[23]

$$G_N^0 = \frac{2}{\pi}\int_{-\infty}^{\infty} G''(\omega)\, \mathrm{d}\ln\omega \tag{19}$$

The high molecular weights coupled with the near-monodisperse nature of the molecular weight distributions to facilitate this integration method. The dynamic and storage shear moduli were determined with a Rheometrics System IV rheometer using the dynamic head and 25-mm-diameter parallel plates. Generally measurements commenced at a frequency of 400 s^{-1} which was then decreased to 0.001 s^{-1} or until the torque amplitude became too small to be reliably measured. Virtually all the samples in Tables 1 and 2 were prepared by anionic polymerization, the exceptions being PE, PIB, PVA, *cis*-PBd, *cis*-PI, PPOX, and PMA. The polyolefins were prepared by hydrogenating or deuterating polydienes. The SANS-based values of $\langle R^2\rangle_0/M$ either are taken from the literature[18,19,29–40] or are based on unpublished results from our laboratories.

These two temperatures were picked for our comparison of the model with the data since those are the ones for which the most and best data exist for many polymer types. In Table 1 we show the measured values of chain dimensions, density, and plateau modulus for a wide range of polymers at 413 K. We first limit ourselves to those polymers for which the chain dimensions have been measured by SANS, since these are the ones in which we have the most confidence. To estimate A, we perform a least-squares linear regression (forced through the origin) of G_N^0 *vs* p^{-3} (eq 16) and use the following equation:

$$A = [5(6^3 G_N^0 p^3)/kT]^{1/2} \tag{20}$$

Taking the 26 polymers with SANS-measured chain dimensions at 413 K gives a value of $A = 1.518$ with an r^2 of 0.979. Placing this value of A into eqs 11, 14, 16, and 18 gives at 413 K:

$$C_\infty = [10.11\ \mathrm{mol}^{2/3}] M_e^{-1/3} m_0 l_0^{-2} \rho^{-2/3} \tag{21}$$

$$G_N^0 = [12.16\ \mathrm{MPa}\ \text{Å}^3] p^{-3} \tag{22}$$

$$M_e = [225.8\ \mathrm{cm}^3\ \text{Å}^{-3}\ \mathrm{mol}^{-1}] p^3 \rho \tag{23}$$

$$d_t = 19.36 p \tag{24}$$

Table 2 shows similar data for 298 K. Using the 17 polymers with SANS-measured chain dimensions, we find $A = 1.662$ ($r^2 = 0.988$). Placing this value into eqs 11, 14, 16, and 18 gives the following expressions at 298 K:

$$C_\infty = [9.518\ \mathrm{mol}^{2/3}] M_e^{-1/3} m_0 l_0^{-2} \rho^{-2/3} \tag{25}$$

$$G_N^0 = [10.52\ \mathrm{MPa}\ \text{Å}^3] p^{-3} \tag{26}$$

$$M_e = [188.3\ \mathrm{cm}^3\ \text{Å}^{-3}\ \mathrm{mol}^{-1}] p^3 \rho \tag{27}$$

$$d_t = 17.68 p \tag{28}$$

Note that the fact that neither A nor the coefficients of the quantities above are independent of temperature is strictly speaking against the spirit of this model. The presence of this temperature dependence indicates a contribution from dynamical events, whose identity, or identities, is not yet understood. A similar conclusion was reached previously from neutron spin-echo studies[41] on PEP and PEB-2. However, it is gratifying that this dependence is not very large, so such contributions are probably not large. Moreover, the fact that A does work out to be very close to 1 supports this model, since this means that the radius of the sphere that spans a chain is closely related to its radius of gyration.

Also shown in Tables 1 and 2 are the values for G_N^0 and M_e calculated by means of eqs 22, 23, 26, and 27. These are in good agreement with their measured counterparts. Since the parameters in these equations were derived from the same data via eq 20, this should be expected in general; however, note that the fit is good for all of the polymers listed. This is remarkable, considering the wide range of polymer types in this list. Figure 1 shows a log–log plot of the data contained in Table 1. The gradient in question is drawn to the predicted value of −3. As can be seen, good agreement is also found for the linear plot (Figure 2) over a range of G_N^0 from 2.6 MPa for polyethylene to 0.06_8 MPa for poly(vinylcyclohexane). The calculated values of the tube diameter, d_t, are also shown in these tables. Directly measured values, via neutron spin-echo[38,41,42] are available only for PEB-2, alt-PEP, and 1,4-polyisoprene (Table 1). For those three cases good agreement is obtained between the measured and calculated values.

Another source of data on chain dimensions is the measurement of dilute solution viscosity. The intrinsic viscosity equation at the Θ condition is expressed as:

$$[\eta]_\Theta = K_\Theta M^{1/2} \tag{29}$$

where

$$K_\Theta = \Phi[\langle R^2\rangle_0/M]^{3/2} \tag{30}$$

and Φ denotes the universal hydrodynamic constant which is equal to 2.5×10^{21} dL cm^{-3} mol^{-1}. Hence, the parameter K_Θ scales directly with the unperturbed chain dimensions. By eqs 12, 16, and 17 we can relate K_Θ to G_N^0, M_e, and d_t:

$$M_e = (\Phi/BK_\Theta\rho N_A)^2 \tag{31}$$

$$G_N^0 = \frac{4}{5}B^2 kT\rho^3 N_A^{\,3}\left(\frac{K_\Theta}{\Phi}\right)^2 \tag{32}$$

$$d_t = \left(\frac{\Phi}{K_\Theta}\right)^{2/3}\frac{1}{\rho B N_A} \tag{33}$$

If we plot G_N^0 *vs* $K_\Theta^2\rho^3$, we find that we get a remarkably good correlation, as can be seen in Figure 3, where the K_Θ values are from refs 43–46. Using the value of B we have derived above from the melt data (eq 20) and the slope of the line in Figure 3, we get a value of $\Phi = 2.40 \times 10^{21}$ dL cm^{-3} mol^{-1}, which is quite close to the accepted value. This result also lends credence to the ideas used here. The 298 K G_N^0 data (Table 2) yield

$$G_N^0 = [3.68 \times 10^5\ \mathrm{MPa\ cm^9\ mol^{-1}\ dL^{-2}}]\, K_\Theta^{\,2}\rho^3 \tag{34a}$$

Table 1. Molecular and Rheological Characteristics for Polymers at 413 K

polymer[a]	$\langle R^2\rangle_0/M$ (Å^2 mol g^{-1})	ρ (g cm^{-3})	p (Å)	G_N^0(meas) (MPa)	G_N^0(calc) (MPa)	M_e(meas)	M_e(calc)	d_t(calc) (Å)
PE	1.25	0.784	1.6942	2.60	2.50	828	861	32.8
PEB-2	1.21	0.785	1.7480	2.21	2.28	976	947	33.9[b]
PEB-4.6	1.15	0.788	1.8322	1.90	1.98	1139	1095	35.5
PEO	0.805	1.064	1.9384	1.80[c]	1.67	1624	1751	37.5
PEB-7.1	1.05	0.789	2.0041	1.55	1.51	1398	1435	38.8
PEB-9.5	1.05	0.791	1.9990	1.40	1.52	1552	1427	38.7
PEB-10.6	1.06	0.792	1.9777	1.30	1.57	1674	1384	38.3
1,4-PBd	0.876	0.826	2.2946	1.25	1.01	1815	2254	44.4
PEB-11.7	0.952	0.793	2.1993	1.20	1.14	1815	1905	42.6
alt-PEP	0.834	0.790	2.5200	0.95	0.76	2284	2856	48.8[b]
PEB-17.6	0.913	0.797	2.2817	0.90	1.02	2433	2139	44.2
PEB-24.6	0.799	0.799	2.6007	0.67	0.69	3276	3175	50.4
alt-PEB	0.692	0.800	2.9991	0.52	0.45	4226	4875	58.1
HHPP	0.691	0.810	2.9664	0.52	0.47	4279	4776	57.4
a-PP	0.670	0.791	3.1328	0.47	0.40	4623	5494	60.7
PEB-32	0.690	0.802	3.0003	0.43	0.45	5124	4893	58.1
1,4-PI	0.625	0.830	3.2006	0.42	0.37	5429	6147	62.0[d]
PIB	0.570	0.849	3.4309	0.32	0.30	7288	7745	66.4
PMMA	0.425	1.13	3.4572	0.31[e]	0.29	10013	10547	67.0
PEB-39.3	0.645	0.805	3.1977	0.30	0.37	7371	5945	61.9
PEB-40.9	0.604	0.805	3.4147	0.29	0.31	7652	7240	66.1
H_2-3,4-PI	0.529	0.810	3.8748	0.22	0.21	10114	10644	75.0
PS	0.434	0.969	3.9480	0.20	0.20	13309	13469	76.5
PDMS	0.457	0.895	4.0593	0.20	0.18	12293	13522	78.6
PEE	0.507	0.807	4.0579	0.20	0.18	11084	12181	78.6
PVCH	0.323	0.920	5.5872	0.06_8[f]	0.07_0	38966	36246	108.2

[a] See Appendix I for identification of polymer nomenclature and references. R_g was measured by SANS. [b] Neutron spin-echo values: PEB-2, 38.5 Å; *alt*-PEP, 40.0 Å.[38,41] [c] Reference 11. [d] Neutron spin-echo value at 473 K: 1,4-PI, 52.0 Å.[38] [e] Colby, R. H., unpublished data. [f] Measurement temperature of 433 K.

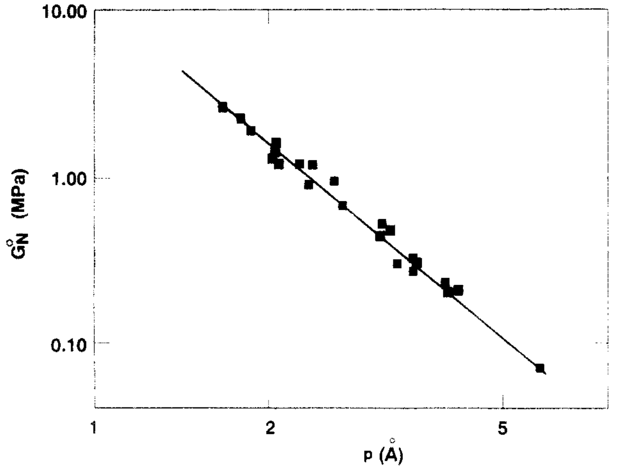

Figure 1. log–log plot of plateau modulus *vs* packing length at 413 K. The gradient is drawn with a slope of −3. The data-driven gradient is −2.89 (cc: 0.9924).

$$M_e = [5.39 \times 10^{-3}\ \mathrm{dL^2\ cm^{-6}}]K_\Theta^{-2}\rho^{-2} = 53.9K_\Theta^{-2}\rho^{-2} \tag{34b}$$

$$d_t = [0.537\ \text{Å}\ \mathrm{dL^{2/3}\ cm^{-3}\ mol^{1/3}}]K_\Theta^{-2}\rho^{-1} \tag{34c}$$

Within the confines of experimental error and the uncertainty of the influence of specific solvent effects, the approach utilized in eqs 34a through 34c nonetheless offers a convenient route for the estimation of G_N^0, M_e, and d_t from Θ condition measurements.

Polymers containing backbone phenylene units (many of which are engineering plastics) tethered to one another by, for example, C–O–C and/or C–SO_2–C bonds are characterized by their excellent physical properties both above and below their glass transition temperatures. Unlike polymers with a polyolefin backbone, these materials may be considered to consist of rigid subunits connected one to the other by the freely, or nearly freely, rotating bonds mentioned. This means that all rotational angles should be nearly statistically distributed in the melt. It is thus of interest to compare their known properties with those calculated via the expressions developed herein which have as their basis the polyolefin and polydiene families where free, or nearly free, rotation is absent. The success of these relations would offer a strong indication that they are independent of the influences of a polymer's structural details.

Generally good agreement is obtained between the calculated and measured values for G_N^0 and M_e of the engineering plastics shown in Table 3. The calculated values (numbers in brackets) were obtained using prefactors[47] adjusted to the measurement temperature of G_N^0. It should be noted that $\langle R^2\rangle_0/M$ would be expected to be virtually independent of temperature for polymers with such nearly freely rotating subunits. That *ansatz* has been verified via experimentation[48–51] and theory.[52–55] Thus, the virtual temperature independence of chain dimensions resulted in no adjustments of $\langle R^2\rangle_0/M$. Table 3 carries entries for PEEK and PI-2 (a polyimide), materials for which no measured G_N^0 values exist. The calculated values of G_N^0 are, though, comparable with materials of the same general type.

The case for polycarbonate is unsettled (Table 3) as a consequence of the spread in the reported $\langle R^2\rangle_0/M$ values. Good agreement between the calculated G_N^0 values and its measured counterpart is found for the smaller values[48,56] of $\langle R^2\rangle_0/M$, with the discrepancy increasing for the larger chain dimension values. Recent RIS calculations[52–54,56] yield $\langle R^2\rangle_0/M$ of ca. 1.1 Å^2 mol g^{-1}, which in turn yields G_N^0 of 5.7 MPa. Resolution of this inconsistency must await further results. A similar state of play exists for poly(alkyl methacrylates) other than PMMA.

Another interesting case involves a side-chain liquid crystalline polymer, having a mesogenic group pendant from a polymethacrylate backbone (PAPHM). Kirste and Ohm[57] have measured the chain dimensions of these polymers at 120 °C by SANS and saw that a chain with

Table 2. Molecular and Rheological Characteristics for Polymers at 298 K

polymer[a]	$\langle R^2\rangle_0/M$ (Å^2 mol g^{-1})	$K_\Theta \times 10^3$ (dL g$^{-3/2}$ mol$^{1/2}$)	ρ (g cm^{-3})	p (Å)	G_N^0(meas) (MPa)	G_N^0(calc) (MPa)	M_e(meas)	M_e(calc)	d_t(calc) (Å)
SANS									
1,4-PBd	0.876	1.99	0.895	2.1177	1.15	1.11	1543	1601	37.5
alt-PEP	0.924	2.03	0.856	2.0991	1.15	1.14	1475	1491	37.1
PEB-17.6	0.926		0.860	2.0849	1.12	1.16	1522	1468	36.9
PEB-14	0.925	1.94	0.860	2.0871	1.12	1.16	1522	1473	36.9
PEB-24.6	0.800		0.864	2.4021	0.69	0.76	2482	2256	42.5
alt-PEB	0.725	1.35	0.861	2.6598	0.58	0.56	2942	3052	47.0
HHPP	0.691	1.26	0.878	2.7366	0.52	0.51	3347	3389	48.4
a-PP	0.664	1.36	0.852	2.9348	0.48	0.42	3518	4057	51.9
PEB-32	0.641		0.863	3.0014	0.44	0.39	3888	4395	53.1
PEB-39.3	0.623		0.864	3.0845	0.38	0.36	4507	4776	54.5
H_2-50-PI	0.633	0.980	0.861	3.0464	0.35	0.37	4876	4585	53.9
1,4-PI	0.596	1.26	0.900	3.0953	0.35	0.35	5097	5027	54.7
PIB	0.570	1.06	0.918	3.1730	0.32	0.33	5686	5524	56.1
PEB-40.9	0.547	0.892	0.864	3.5131	0.30	0.24	5709	7056	62.1
PDMS	0.422	0.783	0.970	4.0561	0.20	0.16	9613	12192	71.7
H_2-3,4-PI	0.464	0.810	0.878	4.0754	0.19	0.16	9160	11194	72.1
PEE	0.485	0.815	0.866	3.9530	0.18	0.17	9536	10076	69.9
Non-SANS									
1,4–1,2-PBd	0.797	1.78	0.884	2.3566	0.87; 0.93	0.80	1880; 2014	2179	41.7
62-PBd	0.727	1.55	0.890	2.5660	0.81	0.62	2178	2832	45.4
cis-PBd	0.758	1.65	0.900	2.4338	0.76	0.73	2347	2444	43.0
PPOX	0.599	1.16	1.00	2.7718	0.70	0.49	2832	4011	49.0
cis-PI	0.679	1.40	0.913	2.6782	0.58	0.55	3120	3304	47.4
PVE	0.664	1.25	0.889	2.8127	0.57	0.47	3091	3726	49.7
P2MP	0.585	1.12	0.850	3.3390	0.42[b]	0.30	4685	6492	61.4
50-PI	0.546	1.01	0.893	3.4052	0.41	0.27	4317	6641	60.2
3,4-PI	0.563	1.06	0.890	3.3135	0.37[c]	0.30	5168	6365	59.8
PVA	0.490	0.858	1.080	3.1374	0.36[b]	0.36	6944	6843	57.7
55-DMBD	0.640	1.26	0.861	3.0130	0.33[b]	0.41	6257	4832	55.4
PαMS	0.442	0.735	1.04	3.6119	0.32[e]	0.28	10225	12450	73.3
1,4-PEB	0.543	1.00	0.891	3.4317	0.29	0.26	6090	6782	60.7
PMA	0.436	0.720	1.11	3.4307	0.25	0.26	8801	8442	60.7
$H_2$55-DMBD	0.431	0.708	0.838	4.5969	0.16[d]	0.12	13691	18037	87.6
H_2-1,4-MYRC	0.434	0.714	0.853	4.4848	0.14	0.12	12077	14494	79.3
PtBS	0.361	0.542	0.957	4.8058	0.10[e]	0.12	30108	26987	97.5
1,4-MYRC	0.398	0.628	0.892	4.6767	0.10	0.10	17681	17186	82.7
$H_2$64-MYRC	0.409	0.655	0.849	4.7814	0.10	0.10	16828	17481	84.6
64-MYRC	0.374	0.571	0.891	4.9824	0.07_1	0.08_5	24874	20757	88.1

[a] See Appendix I for identification of polymer nomenclature and references. "SANS" refers to polymers where R_g was measured in the melt by that technique. "Non-SANS" refers to Θ-condition-based R_g values. Those measurements were made between 15.7 and 62.0 °C.
[b] Measurement temperatures of 348 K. Density corrected to the noted temperature.
[c] Measurement temperatures of 323 K. Density corrected to the noted temperature.
[d] Measurement temperatures of 393 K. Density corrected to the noted temperature.
[e] Measurement temperatures of 473 K. Density corrected to the noted temperature.

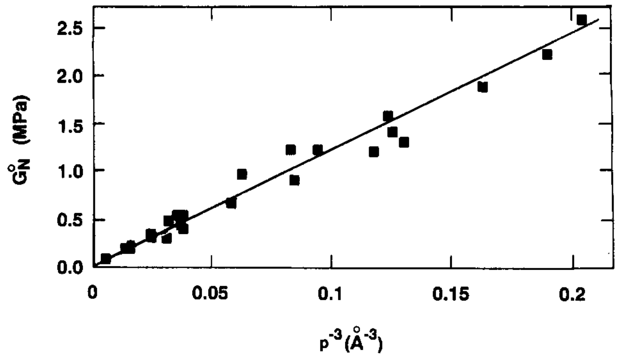

Figure 2. Linear plot of plateau modulus *vs* inverse cube of the packing length at 413 K.

M_w = 500 000 had $\langle R_g^2\rangle^{1/2}$ = 11.8 nm. The plateau modulus of these liquid crystalline polymers was measured by Rubin and Kornfield[58] to be 0.015 MPa, which yields an M_e of 201 000 if one uses a value of ρ = 1.1 g/cm^3 (typical of poly(methacrylate)s). Applying the value of A found from the other polymers and eq 22, we predict a value of G_N^0 of 0.016 MPa, which is in excellent agreement. Because the chains are so compact, there is relatively little overlap between neighboring chains and so a low value of the plateau modulus. This example extends the range of the validity of eq 22 over more than 2 orders of magnitude in G_N^0, from 0.015 MPa for PAPHM to 2.6 MPa for PE.

It appears that the relationships given herein apply to quite a broad class of linear polymers. As such, these relations should be useful to develop a deeper understanding of the molecular origins of the rheological and perhaps other physical properties of polymers. Moreover, this should also provide us with a means to estimate the behavior of other polymers, including those which have not yet been made. An example of this is to consider the plateau modulus that would correspond to an amorphous polyethylene at 298 K. Equation 26 yields the value of 3.8 MPa for the plateau modulus for such an amorphous PE. This agrees well with the value of 3.5 MPa used by Kardos and Raisoni for the shear modulus of the amorphous fraction in a composite model of semicrystalline PE.[59] Thus, the relations described here should prove very useful.

Comparison with Other Models. Wu[11,15] has offered an expression for the calculation of the plateau modulus which is

$$G_N^0 = 0.333\rho kTN_A m_0^{-1}C_\infty^{-2} \qquad (35)$$

The premise upon which this expression is based, namely, that $M_e \propto C_\infty^2$ is incorrect since contour length density is ignored and the experimental observations that C_∞ can

Table 3. Molecular and Rheological Parameters of Engineering Plastics (Calculated Values in Parentheses)

polymer[a]	temp[b] (K)	G_N^0 (MPa)	m_0	l_0 (Å)	ρ (g cm^{-3})	$\langle R^2\rangle_0/M$ (Å^2 mol g^{-1})	p (Å)	$M_e \times 10^3$	d_t (Å)
RADEL-R	555	3.6 (3.2)	133	7.39	1.22	0.821	1.6576	1.24 (1.57)	(35.9)
Me-PEEK	463	3.3 (2.6)	100.8	5.58	1.16	0.834[d]	1.7162	1.16 (1.43)	(34.6)
PET	548	3.1 (1.8–2.6)	32.0	2.68	0.989	0.844–0.949	1.7690 –1.9891	1.17 (1.53–2.18)	(38.1–42.8)
PC	473	2.7 (2.7–11.2)	127	7.00	1.14	0.864–1.384	1.0523 –1.6857	1.33 (0.33–1.36)	(21.4–34.2)
m-AEK	473	2.2 (2.3)	85	4.94	1.20	0.775[c]	1.7853	1.72 (1.70)	(36.2)
PSF	523	2.1 (1.6–2.0)	110	5.76	1.15	0.699–0.756	1.9097 –2.0654	1.90 (2.15–2.72)	(40.3–43.6)
UDEL	513	2.0 (1.6–2.0)	110	5.76	1.16	0.699–0.756	1.8932 –2.0476	1.98 (2.08–2.63)	(39.7–42.9)
N6[e]	543	1.8 (1.9)	16.1	1.49	0.985	0.853	1.9761	1.98 (2.11)	(42.4)
POM	473	1.7 (1.9)	15.0	1.43	1.142	0.763	1.9054	2.11 (1.96)	(38.7)
PPO	493	0.95–1.2 (1.2)	120	5.40	1.00	0.741	2.2406	2.68–3.62 (2.88)	(46.2)
PEEK	623	*d* (4.0)	96	5.58	1.20	0.876[c]	1.5794	*d* (1.49)	(36.1)
PI-2	598	*d* (1.8)	114	3.43	~1.22	0.663	2.0526	*d* (3.19)	(46.0)

[a] See Appendix I for identification of polymer nomenclature and references. [b] Measurement temperature of G_N^0. [c] From nearly free rotating chain. [d] G_N^0, and thus M_e, not measured.

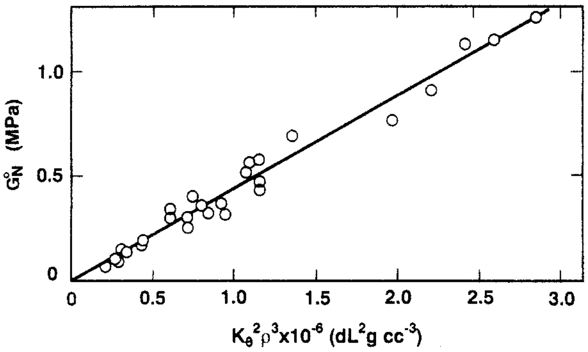

Figure 3. G_N^0 (298 K) as a function of $K_\theta^2\rho^3$ from the data of Table 2.

Table 4. Comparison of Calculated and Measured Values of the Plateau Modulus at 413 K

polymer[a]	G_N^0 (MPa) Wu[b]	G_N^0 (MPa) this work[c]	G_N^0 (MPa) measured	M_e	C_∞
PE	1.20	2.50	2.60	828	7.3
PEO	2.73	1.67	1.80	1624	5.5
1,4-PBd	2.15	1.01	1.25	1810	5.6
alt-PEP	1.20	0.76	0.95	2284	6.4
PEB-24.6	0.87	0.69	0.67	3276	7.1
alt-PEB	0.97	0.45	0.52	4226	6.6
a-PP	1.19	0.40	0.47	4623	6.0
1,4-PI	2.13	0.37	0.42	5429	5.0
PIB	0.75	0.30	0.32	7288	6.8
PMMA	0.31	0.29	0.31	10013	9.1
PEE	0.94	0.18	0.20	11084	5.9
PDMS	0.70	0.18	0.20	12293	6.3
PS	0.23	0.20	0.20	13309	9.6
PVCH	0.33	0.07_0	0.06_8	38966	7.6

[a] See Appendix I for identification of polymer nomenclature and references. [b] Equation 35. [c] Equation 22.

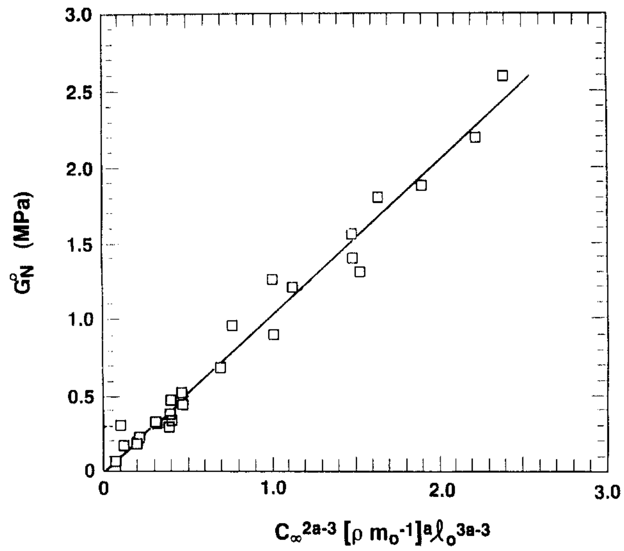

Figure 4. Graessley–Edwards format at 413 K for polyolefins. C_∞ based on SANS. For an a of 3, the x axis units are g^6 cm^{-6} mol^{-3} Å^6.

increase, remains constant or decreases with increasing temperature, while M_e only becomes larger with an increase in temperature. Table 4 compares measured G_N^0 values with those calculated via eqs 22 and 35. The inadequacy of the Wu proposal is further highlighted in Table 4 wherein it is seen that M_e fails to scale with C_∞. Similar proposals from Aharoni[5] and Wool[16] are likewise incorrect.

Graessley and Edwards[4] assumed that large-scale interactions in dense polymer systems should relate only to the chainlike structure of the molecules, the essential effect being the topological interaction arising from the mutual uncrossability of chains. Thus, the important quantity is the chain contour length per unit volume. In polymer networks the modulus reflects the cross-link density. In terms of this rubber analogy, the plateau modulus G_N^0 should relate to the interaction density and be largely determined by the contour length density. More bulky chains like polystyrene correspond to a lower contour length density, exhibiting a smaller G_N^0, while slim chains like polyethylene have a high contour length density and consequently a high plateau modulus. To construct scaling relations, dimensionless quantities are required. They may be obtained by considering the length characteristic for the polymer conformation, the Kuhn length $l_K = C_\infty l_0$. Letting ϕ = polymer volume fraction, $\nu = N_A\rho\phi/M$, and $L = Ml_0/m_0$, the scaling relation between the plateau modulus and the contour length density then reads

$$G_N^0 l_K^{\,3}/kT = F(\nu L l_K^{\,2}) \tag{36}$$

Considering further $\nu L l_K^2 \propto \phi$ and the experimental relation $G_N^0 \propto \phi^a$ (with a between 2 and 2.3), eq 36 assumes the form of a power law:

$$G_N^0 l_K^{\,3}/kT \propto (\nu L l_K^{\,2})^a \tag{37}$$

Using the relation of ν, l_K, and L to molecular quantities (see above), they arrive at:

$$G_N^0 \propto kTC_\infty^{2a-3}\left(\frac{\rho\phi}{m_0}\right)^a l_0^{3a-3} \tag{38}$$

An evaluation of the data in Tables 1 and 2 in terms of the Graessley–Edwards format[4] reveals that the best fit for eq 38 yields the value (for both temperatures) of 2.9 ± 0.1 for the scaling factor (a) which is outside the predicted range of 2.0–2.3. This is shown in Figure 4 where the 413 K polyolefin results are given. These data yield a value for $\sum\chi^2$ (a measure of the success of the data fit) of 0.332 for $a = 2.9$, while fixing the value of a at 3 gives $\sum\chi^2$ of 0.338. This demonstrates that within experimental error the packing length exponent of 3 is appropriate. Acceptance of this exponent reduces the x-axis legend in Figure 4 to $\{\langle R^2\rangle_0\rho/M\}^3$.

Considering packing effects as the determining factor for entanglement formation (an assumption made on geometrical grounds), it should be of no significance whether a certain packing density of chain contour is achieved by slim chains diluted with an oligomer or by more bulky chains. In contrast to this reasoning, rheological[25,27,60–64] and neutron spin-echo[41] experiments on concentrated polymer solutions result in a scaling exponent of $a \cong 2.3$. That value agrees with the theoretical one given by Colby and Rubinstein[13] but is significantly different from the packing premise of $a = 3$ and that of 2.9 found in the melt via the Graessley–Edwards approach (Figure 4). The origin of this discrepancy remains unresolved.

The development described above has used either parameters determined at the respective temperatures or interpolated values. This is a necessary step since both $\langle R^2\rangle_0/M$ and G_N^0 can show temperature dependencies. Previous efforts[4–16] have not considered this potential problem in their presentations. It is also germane to point out that Ronca[6] and Kavassalis and Noolandi[9] predicted that $G_N^0 \propto \rho^3$ and $M_e \propto \rho^{-2}$. Those exponents were also obtained in this development.

This development is equivalent to that of Lin[7] and Ronca.[6] Lin defines a constant, n_t, which is the number of entanglement strands in a cube with side d_t. This is given by (eq 4 of ref 7)

$$n_t = \frac{\rho N_A}{M_e}\left(C_\infty \frac{M_e}{m_0} l_0^2\right)^{3/2} \tag{39}$$

Using eq 1 this can be reordered as:

$$n_t = \rho N_A \left(\frac{\langle R^2\rangle_0}{M}\right)^{3/2} M_e^{1/2} \tag{40}$$

and using eq 12 we have

$$n_t = B^{-1} \tag{41}$$

So at 413 K we have $n_t = 19.36$ from the data in Table 1, and using that in Table 2 we have $n_t = 17.68$ at 298 K. This is in good agreement with Lin's values, and even the temperature dependence of n_t is suggested by the values in Table 1 of ref 7.

Conclusion

The foregoing development has shown that direct and simple connections exist between the various viscoelastic parameters and chain packing length; therefore:

$$G_N^0 \propto p^{-3} \tag{42}$$

$$M_e \propto p^3\rho \tag{43}$$

$$d_t \propto p \tag{44}$$

findings which support Ronca's proposals.[6] The packing length is under the combined control of $\langle R^2\rangle_0/M$ and ρ, both of which are identifiable characteristics of a polymer chain. Thus, control of viscoelastic properties is possible by the manipulation of the above parameters. These procedures would also appear to be useful in defining the performance limits of specific polymer structures and, potentially, miscible polymer blends as well as predicting the properties of not yet synthesized polymers. Furthermore, these approaches may serve, for example, to elucidate the entanglement contribution to the elastic modulus in cross-linked networks, the moduli of the amorphous regions of semicrystalline polymers, and adhesive properties in view of the fact that these parameters are coupled with the plateau modulus.

Appendix I. Abbreviations Used for Polymer Identification (References for Physical Properties of Each Polymer Listed in Parentheses; Additional References Given in Text and Tables)

PE	polyethylene (the PE G_N^0 is from an extrapolation involving values for the PEB-x samples (see below) where x ranged from 2 to 19.7)[24,29,30]
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; these copolymers have a minimum of two ethylene units between two 1-butene units as a consequence of the 1,4-units in the parent polybutadienes; thus, PEB-2 is equivalent to an 8 wt % EB and PEB-50 to polybutene)[1,17,24,32]
PEO	poly(ethylene oxide)[11,32]
62-PBd	1,2–1,4-polybutadiene ~ 62/30/8 vinyl/trans/cis[65,66]
cis-PBd	1,4-polybutadiene ~ 96% cis content[23,45]
1,4-PBd	1,4-polybutadiene ~ 50/40/10 trans/cis/vinyl[24,25,67–73]
1,4–1,2-PBd	copolymer of 1,4-polybutadiene and 1,2-polybutadiene 60/40; parent material of PEB-14[24,32,44]
cis-PI	1,4-polyisoprene ~ 100% cis content; natural rubber[45,74,75]
1,4-PI	1,4-polyisoprene ~ 75/20/5 cis/trans/3,4[32,76–78]
alt-PEP	essentially alternating poly(ethylene-*co*-propylene); hydrogenated 1,4-PI[31,38,76]
1,4-PEB	1,4-poly(ethylbutadiene) ~ 75/20/5 cis/trans/3,4[44,79]
alt-PEB	essentially alternating poly(ethylene-*co*-1-butene); hydrogenated 1,4-PEB[32,44,79]
HHPP	head-to-head polypropylene; hydrogenated poly(2,3-dimethylbutadiene)[32,44,79]
P2MP	1,4-poly(2-methyl-1,3-pentadiene) ~ 100% 1,4[46,80]
a-PP	atactic (in the Bernoullian sense) polypropylene; hydrogenated P2MP[18,43,46,80]
PIB	polyisobutylene[28,32,33,81]
PMA	poly(methyl acrylate)[11,45,82]
PMMA	poly(methyl methacrylate) (~75% syndiotactic)[11,19,32,83]
3,4-PI	polyisoprene copolymer containing 75% 3,4 units and 25% 1,2 units[79,84]
H_2-3,4-PI	copolymer of poly(isopropylethylene) and poly(1-methyl-1-ethylethylene) 75/25; hydrogenated 3,4-PI[32,79,84]

PS	polystyrene[19,61,85–87]
PαMS	poly(α-methylstyrene)[88,89]
PtBS	poly(*tert*-butylstyrene)[79,90]
PVCH	poly(vinylcyclohexane) from the hydrogenation of polystyrene[32,84]
PDMS	poly(dimethylsiloxane)[11,91–96]
PVA	poly(vinyl acetate)[11,45,97]
PVE	poly(vinylethylene) or 1,2-polybutadiene[26,44]
PEE	poly(ethylethylene); hydrogenated PVE[18,32]
55-DMBD	poly(dimethylbutadiene) copolymer containing 55% 1,4 units and 45% 3,4 units[44,81]
$H_2$55-DMBD	hydrogenated version of 55-DMBD[44,81]
50-PI	polyisoprene copolymer containing 50%-1,4 units and 50%-3,4 units[79,84]
$H_2$50-PI	hydrogenated version of 50-PI[79,84]
1,4-MYRC	1,4 polymyrcene 97/3 1,4/3,4[44,84]
H_2-1,4-MYRC	hydrogenated 1,4-MYRC[44,84]
64-MYRC	1,4-3,4 polymyrcene 64/36 1,4/3,4; parent of $H_2$64-MYRC[44,84]
$H_2$64-MYRC	hydrogenated version of 64-MYRC[44,84]
PAPHM	poly[6-[4-[(4-anisyloxy)carbonyl]phenoxy]hexyl methacrylate][57,58]
RADEL-R	alternating copolymer of 4,4′-biphenol and dichlorodiphenyl sulfone[98,99]
UDEL (PSF)	alternating copolymer of Bisphenol A and dichlorodiphenyl sulfone[11,99]
PC	polycarbonate[54,99,100]
PPO	poly(phenylene oxide)[99,100]
PPOX	poly(propylene oxide)[45,101]
m-AEK	poly(*m*-arylene ether ketone)[99]
PEEK	poly(aryl ether ether ketone)[99]
Me-PEEK	methylpoly(aryl ether ether ketone); prepared from methylhydroquinone and 4,4′-difluorobenzophenone[102,103]
PET	poly(ethylene terephthalate)[11,40,104–106]
N6	poly(caprolactam), nylon 6[11,107,108]
POM	poly(oxymethylene)[11,109]
PI-2	poplyimide from 3,3′,4,4′-benzophenonetetracarboxylic acid and 2,2-dimethyl-1,3-bis(4-aminophenoxy)propane[110,111]

Appendix II

Partially epoxidized 1,4-PI (50 mol %) and 1,4-PBd (58 mol %) exhibit G_N^0 values of 0.53 and 1.60 MPa, respectively, at 303 K. Taking the appropriate parameters in refs 112 and 113, the use of eq 25 leads to a C_∞ of 5.2 for the partially modified 1,4-PI and 6.4 for the 1,4-PBd counterpart. (For the polybutadiene case the parent and modified material exhibit virtually the same value of $\langle R^2 \rangle_0/M$ (Table 3), while for polyisoprene there is a decrease in $\langle R^2 \rangle_0/M$ from 0.596 Å^2 mol g^{-1} for the parent material to 0.540 Å^2 mol g^{-1} for the epoxidized one.) These C_∞ values are in qualitative accord with the parent values (1,4-PI, 4.8; 1,4-PBd, 5.6) coupled with the incorporation of the modified polyolefin structure with the less flexible epoxidized carbon–carbon single bond. Thus, we view as unlikely the suggestion that epoxidation leads to an attenuation of C_∞ relative to those of the parent polydienes.

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