Entanglement interactions in polymers and the chain contour concentration

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The plateau region in viscoelastic response is one of several characteristics of concentrated polymer liquids which have been attributed to chain entanglement interactions. The plateau modulus G_N^0 is insensitive to temperature and independent of chain length for long chains. It varies with polymer species in the undiluted state: it also varies with polymer concentration in a manner which is essentially independent of species. We propose here that the species dependence and the concentration dependence are related, and that to a first approximation both are manifestations of a universal law relating a mechanical interaction density, measured by G_N^0/kT to the length of uncrossable chain contour per unit volume. Data on many species and concentrations support this proposition and conform reasonably well to a universal power law:

$$\frac{G_N^0}{kt}=K(\nu L l^2)^a$$

in which ν is the number of chains per unit volume, L is the chain contour length, and l is the Kuhn step length of the species.

INTRODUCTION

The relaxation spectrum of an undiluted polymer liquid or concentrated solution extends over many orders of magnitude in relaxation time[1]. For systems of long linear chains with narrow distribution, the relaxations are grouped into two rather well-defined dispersions: the transition region at short times and the terminal region at long times. The transition spectrum is insensitive to chain length and associated with local chain motions. The terminal spectrum is associated with large scale rearrangements of chain conformation. Its location relative to the transition region is a strong function of chain length. The two dispersions are well-separated for sufficiently long chains, resulting in a rubber-like plateau response at intermediate times or frequencies. For these conditions (long linear chains, narrow distributions, high concentrations) the terminal spectrum, expressed in reduced form, appears to be universal, i.e. independent of polymer species, chain length, diluent species, temperature and concentration[1-3]. As a result, certain characteristics are common to many species.

The plateau modulus G_N° is the instantaneous modulus associated with the terminal spectrum[1]. Being independent of chain length and insensitive to temperature, G_N° is virtually a characteristic constant for the undiluted species. It decreases with dilution, but within the limits of experimental precision the concentration dependence is independent of diluent species and insensitive to polymer species. Thus:

$$G_N^0=(G_N^0)_0\varphi^a \tag{1}$$

where $(G_N^0)_0$ is the value for the undiluted species and φ is the volume fraction of polymer. The exponent a lies in the range 2.0 ~ 2.3 and may vary slightly with polymer species. The steady state recoverable shear compliance, J_e^0, becomes independent of chain length for sufficiently long chains. The limiting value $(J_e^0)_\infty$ varies with polymer concentration inversely to the plateau modulus:

$$(J_e^0)_\infty \propto \varphi^{-a} \tag{2}$$

such that the product $(J_e^0)_\infty G_N^0$ is constant. Moreover, $(J_e^0)_\infty G_N^0$, a measure of the width of the terminal spectrum[2], lies in the range 2.5 ~ 3.5 for different polymer species. The characteristic molecular weight, M_c, governing the behaviour of zero-shear viscosity η_0 has similar properties. It separates the short chain dependence ($\eta_0 \propto M$) and long chain dependence ($\eta_0 \propto M^{3.4}$), and:

$$M_c=(M_c)_0\,\varphi^b \tag{3}$$

Within experimental precision M_c is independent of temperature, and $b=1-a$. The product $\varphi M_c G_N^0$, like $(J_e^0)_\infty G_N^0$, is practically a universal constant.

This set of features provides the basis for ideas about chain entanglement effects in concentrated polymer liquids. The insensitivity of G_N^0, $(J_e^0)_\infty$ and M_c to temperature and the diluent species and the nearly universal character of their concentration dependences suggest that the large scale chain dynamics in concentrated media are strongly influenced by interactions which derive only from the chain-like structure of the molecules and which are essentially geometrical or topological in nature. A variety of theories start from the picture of a medium densely filled with long

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featureless chains whose contours are mutually uncrossable[4-7].

A question naturally arises about what determines the values of G_N^0, $(J_e^0)_\infty$ and M_c for each species in its undiluted state. A pattern clearly exists, and several empirical correlations of M_c with various chain properties have already been proposed[8-11]. However, the undiluted state should play no special role, from any viewpoint, in interactions which arise merely from mutual uncrossability of chain contours. The undiluted state, of course, represents the practical upper limit on the concentration of chain contour (length/volume) which can be achieved by any particular species. However, it is at least conceivable that the laws governing concentration dependence (equations 1–4) would continue smoothly if one could somehow get past this volume occupation limit. Similarly, the differences in G_N^0 among various undiluted species might in large measure simply reflect differences in their respective limiting chain contour concentrations.

Consider the example of undiluted polyethylene and polystyrene. These differ by about an order of magnitude in plateau modulus, $G_N^0 = 2.06$ and 0.20 MPa, respectively. Polyethylene has a greater length of chain contour per unit volume because its diameter is smaller. In fact, a simple calculation shows that the number of main chain bonds per unit volume is higher by about a factor of three in polyethylene. If polyethylene were diluted to $\varphi \sim 0.3$, the contour length concentration would be about the same as for undiluted polystyrene, and from equation (1) the values of G_N^0 would then be roughly the same. This and similar examples suggest the possibility that the concentration dependence and the species dependence are merely different manifestations of the same universal law. Some simple consequences of this idea are discussed below.

THEORETICAL

Suppose the interactions which govern G_N^0 derive from the uncrossability of chains alone. Real chains could then just as well be represented by volumeless uncrossable contours, suitably matched in number density and length, and with conformations appropriate to the species. We will express the interaction density as G_N^0/kT where k is the Boltzmann constant and T the temperature. If G_N^0 were the equilibrium modulus of a network, G_N^0/kT would be proportional to the concentration of network junctions. However, the choice of G_N^0/kT as a measure of interaction density implies nothing specific about the mechanism other than that it has an entropic or topological origin.

At high concentrations the chain dimensions appear to be virtually independent of concentration and the diluent species[12,13]. In that case the only variables which can influence the concentration dependence of G_N^0 for a given species are L, the chain length, and ν, the number of chains per unit volume. Since G_N^0 is independent of chain length G_N^0/kT must be a function only of the product νL, the total length of chain contour per unit volume. Indeed, we could just as well consider the polymer to be a single infinitely long chain with νL length of contour per unit volume.

The variation of G_N^0 with species may reflect changes in the conformational characteristics as well. We assume that the large scale conformations are of primary importance, i.e. that to a first approximation the variations with species do not depend in any more direct way on local details of the chain structure. The Kuhn step length, l, is a natural species variable to use in this case because L and l alone determine the distribution of large scale conformations of random walks. The interaction density G_N^0/kT for long uncrossable random coils should thus be a function of νL and l alone*.

If the law is universal it should relate dimensionless variables. The fundamental units of G_N^0/kT and νL are $(\text{length})^{-3}$ and $(\text{length})^{-2}$, respectively. Each can be made dimensionless using appropriate powers of l, so the hypothesis is:

$$\frac{G_N^0 l^3}{kT} = F(\nu L l^2) \tag{4}$$

where F is a universal function.

As noted earlier, G_N^0 varies with concentration as φ^a, where a for many species is in the range $2.0 \sim 2.3$. Both L and l are independent of φ so $\nu L l^2 \propto \varphi$. To accommodate these observations the function $F(\ )$ must have the form of a power law over a significant range of $\nu L l^2$ values:

$$\frac{G_N^0 l^3}{kT} \propto (\nu L l^2)^a \tag{5}$$

where a and the constant of proportionality are universal constants if the same power law applies everywhere. Similar arguments lead to corresponding expression for M_c and J_e^0, with the results:

$$G_N^0 = K_1 (\nu L)^a \, l^{2a-3} kT \tag{6}$$

$$\frac{1}{M_c} = K_2 \frac{(\nu L)^a l^{2a-3}}{\rho \varphi N_a} \tag{7}$$

$$\frac{1}{(J_e^0)_\infty} = K_3 (\nu L)^a \, l^{2a-3} \, kT \tag{8}$$

where N_a is Avogadro's number, ρ is the density of the undiluted polymer and K_1, K_2 and K_3 are universal constants.

The variables ν, L and l can be expressed in terms of measurable quantities:

$$\nu = \frac{N_a \rho \varphi}{M} \tag{9}$$

$$L = \frac{M}{m_0} l_0 . \tag{10}$$

$$l = C_\infty l_0 \tag{11}$$

in which l_0 is the average length of the main chain bonds, m_0 is the average molecular weight per main chain bond, and $C_\infty = \langle R^2 \rangle_\theta / n l_0^2$ is the characteristic ratio for the species[14]. The constants K_1, K_2 and K_3 for particular choices of the exponent a can thus be calculated from G_N^0, M_c and $(J_e^0)_\infty$ and compared for different species.

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* It is interesting to consider the possibility that there is no additional length scale as l in the problem. In that case, the variables G_N^0/kT (dimensions of $(\text{length})^{-3}$) and νL (dimensions of $(\text{length})^{-2}$) would need to be related in a dimensionally consistent way, i.e. $G_N^0/kT \propto (\nu L)^{3/2}$. However, this would require G_N^0 for each polymer species to vary with the polymer concentration as $\varphi^{3/2}$, which is clearly inconsistent with the experimental results

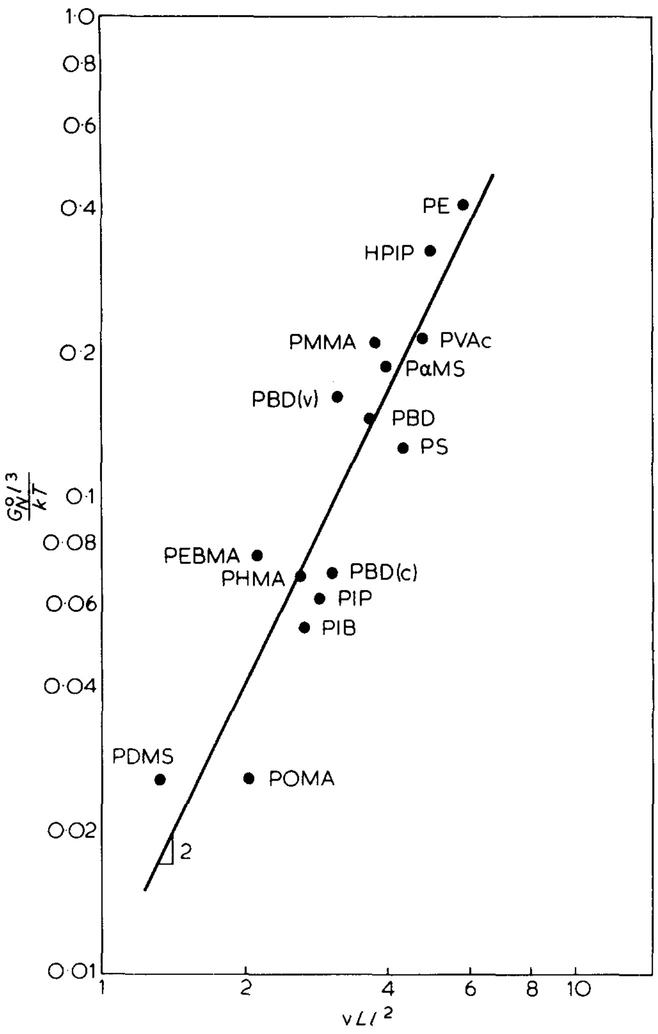

Figure 1 Dimensionless interaction density vs. dimensionless contour length concentration for various undiluted polymer species. Species designations are given in *Table A1*

RESULTS AND DISCUSSION

Figure 1 shows $G_N^0 l^3/kT$ vs. $\nu L l^2$ for 15 species in their undiluted states. The scatter is considerable, but the overall trend is consistent with power law behaviour (equation 5) and an exponent a of approximately 2.

Values of K_1, K_2 and K_3 were calculated from experimental data (see Appendix) for $a=2$ and $a=2.3$, the limits of observed exponents in the concentration dependence of G_N^0. Average values and standard deviations are given in *Table 1*. There seems to be no trend with the magnitudes of G_N^0 for the various undiluted species, and the exponents $a=2$ and $a=2.3$ give similar deviations. However, the departures of particular species from the average K values seem larger than can be accounted for by the various experimental uncertainties. Polyisoprene (high-*cis*) gives consistently low values for example, while poly(dimethyl siloxane) gives high values (see Appendix *Table 2*). Thus there appears to be some individuality of response superimposed on the differences among species in contour length concentration and large scale conformation. Similar variations have been noted in earlier correlations. It is nonetheless gratifying to find that the major differences among species can be accounted for by such a simple picture.

Universal relationships among viscoelastic parameters can be obtained from the average K values. Thus from equations (6)–(8):

$$(J_e^0)_\infty G_N^0 = K_1/K_3 \tag{12}$$

$$\frac{M_c}{M_e} = K_1/K_2 \tag{13}$$

where $M_e \equiv \rho\varphi RT/G_N^0$ is the characteristic molecular weight associated with G_N^0[1]. From *Table 1*:

$$\left.\begin{aligned}(J_e^0)_\infty G_N^0 &= 3.09 \quad (14)\\ \frac{M_c}{M_e} &= 2.20 \quad (15)\end{aligned}\right\} a=2$$

$$\left.\begin{aligned}(J_0^e) G_N^0 &= 2.66 \quad (16)\\ \frac{M_c}{M_e} &= 2.14 \quad (17)\end{aligned}\right\} a=2.3$$

These values lie within the ranges reported for individual species and at various concentrations[2,3].

How realistic is it to consider a universal value for the exponent a, i.e. a single power law over all the accessible ranges of data? The most complete information on concentration dependence is that for polystyrene and polybutadiene. *Figure 2* shows G_N^0/RT and $1/(J_e^0)_\infty RT$ vs. $c=\rho\varphi$ for polystyrene solutions and *Figure 3* for polybutadiene solutions. The exponents obtained for the two species are slightly different (2.10 for polystyrene and 2.25 for polybutadiene), and these differences seem to lie outside the experimental error. However, G_N^0/RT for the undiluted species is higher in polybutadiene by about an order of magnitude, so the dilution studies centre around somewhat different ranges of the interaction density. It is therefore possible that the fundamental law is more complicated, perhaps changing from quadratic dependence ($a=2$) at low interaction densities to a stronger dependence at higher values. However, effects associated with residual variations in chain dimensions with diluent and concentrations might also be involved[15].

There is an interesting consequence of these relationships in regard to time–temperature superposition. According to equation (6), with $a=2$:

$$G_N^0 \propto T\nu^2 L^2 l \propto T\rho^2\varphi^2 \frac{\langle R^2\rangle_\theta}{M}\frac{l_0}{m_0} \tag{18}$$

In forming master curves from linear viscoelastic data on polymer liquids it is common to apply a temperature dependent shift along the modulus axis in addition to the usual time axis shift. From molecular considerations

Table 1 Average values and standard deviations of K_1, K_2, K_3

	$a=2$	$a=2.3$
K_1 (av., 15 species)	0.0108	0.0077
standard deviation/average	0.33	0.37
K_2 (av., 14 species)	0.0049	0.0036
standard deviation/average	0.25	0.33
K_3 (av., 5 species)	0.0035	0.0029
standard deviation/average	0.41	0.27

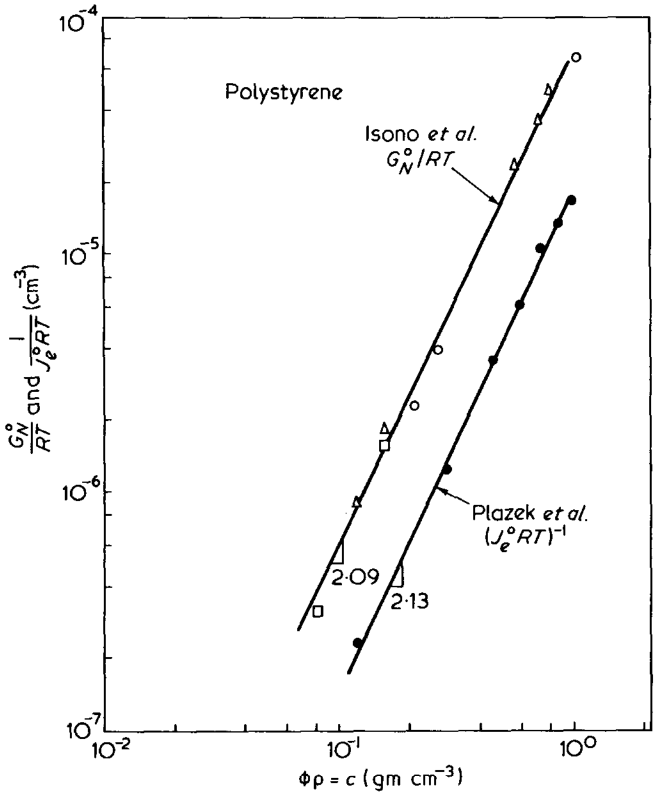

Figure 2 Reduced interaction densities based on plateau modulus and recoverable compliance for polystyrene solutions. The G_N^0 data are taken from Ref. 27 (numerical values provided through the courtesy of Professor M. Nagasawa). J_e^0 data are given in Ref 27. Concentrations were calculated from pure component densities at each temperature of measurement assuming additivity of volumes. The various symbols indicate samples of different molecular weight

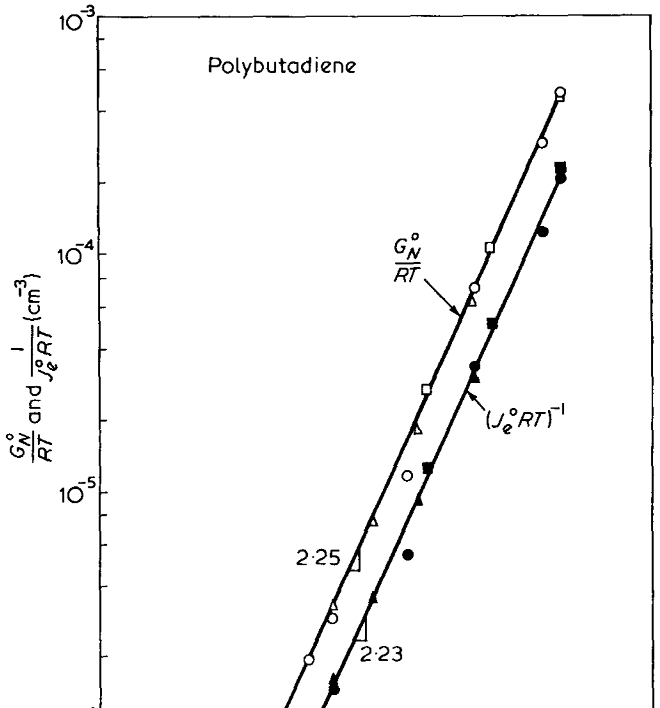

Figure 3 Reduced interaction densities based on plateau modulus and recoverable compliance for 1,4-polybutadiene solutions at 25°C. The data are taken from Ref 20. Symbols indicate samples of different molecular weight

based on the Rouse model, the modulus shift factor is taken to be $b(T)=(\rho T)_0/\rho T$ (T_0 = reference temperature)[1]. Equation (18) suggests that in the terminal plateau regions the modulus shift factor should instead be

$$b(T)=(\rho^2 T\langle R_\theta^2\rangle)_0/\rho^2 T\langle R^2\rangle_\theta \qquad (19)$$

However, the modulus shift is relatively small in any case, so the differences may be unobservable except in the most careful of studies.

Finally, we point out that equation (7) with $a=2$ reduces to a form which is virtually indistinguishable from the Fox–Allen correlation for M_c[18]. They found:

$$\left(\frac{\langle R^2\rangle_\theta}{M}\right)\frac{M_c\rho\varphi}{m_0}=2.4\times10^{-14}\pm20\%\ \mathrm{cm}^{-1} \qquad (20)$$

for a wide range of species. For $a=2$, equation (7) reduces to:

$$\left(\frac{\langle R^2\rangle_\theta}{M}\right)\frac{M_c\rho\varphi}{m_0}=\frac{1}{N_aK_2l_0} \qquad (21)$$

The length of a main chain bond does not vary much among the species, and if a typical value, $l_0=1.5\times10^{-8}$ cm, is used the right side of equation (21) is equal to 2.3 $\times 10^{-14}$ cm^{-1}.

CONCLUSIONS

The viscoelastic parameters G_N^0, M_c and $(J_e^0)_\infty$ characterize the terminal response region for high concentration systems of long linear chains with narrow molecular weight distributions. These parameters depend on both polymer species and on the polymer concentration. We have shown that the two dependences are closely related. The interaction density, expressed as G_N^0/kT, for instance, is primarily a function of the length of chain contour per unit volume. When the Kuhn step length is used to express this relationship in dimensionless form the separate variations with species and concentration fall along the same curve. Although the residual scatter indicates that some individual variations remain, the major trends seem to be well accounted for.

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Table A1 Selected values of G_N^0, M_c and other properties for undiluted polymers

Polymer	G_N^0 (dyne cm^{-2})	M_c	T (K)	ρ (g cm^{-3})	C_∞	l_0 (cm)	K_1 (a = 2)	K_1 (a = 2.3)	K_2 (a = 2)	K_2 (a = 2.3)
Polyethylene, PE	2.06×10^7	3800	463	0.76	7.0	1.54×10^{-8}	1.18×10^{-2}	0.69×10^{-2}	0.44×10^{-2}	0.26×10^{-2}
Polybutadiene (ctv = 50/40/10), PBD	1.20	4500	298	0.895	(5.4)	1.47	1.07	0.73	0.44	0.30
Hydrogenated polyisoprene, HPIP	1.15	—	298	0.854	(6.8)	1.54	1.31	0.81	—	—
Polybutadiene (high *cis*), PBD(c)	0.76	—	298	0.90	4.9	1.47	0.73	0.52	—	—
Polybutadiene (high vinyl), PBD(v)	0.62	—	298	0.885	(6.6)	1.54	1.61	1.14	—	—
Polyisoprene (high *cis*), PIP	0.44–0.52	10 000	298–243	0.90	(5.3)	1.47	0.63	0.46	0.32	0.23
Poly(methyl methacrylate), PMMA	0.48–0.62	31 000	473–423	1.14	8.7	1.54	1.49	1.00	0.37	0.25
Poly(vinyl acetate), PVAc	0.36	24 500	330	1.14	(9.0)	1.54	0.93	0.59	0.33	0.21
Poly(α-methylstyrene), PαMS	0.32	28 000	473	1.04	10.1	1.54	1.18	0.78	0.54	0.36
Polyisobutylene, PIB	0.25	15 200	298	0.89	6.2	1.54	0.74	0.55	0.43	0.32
Poly(dimethyl siloxane), PDMS	0.24	24 500	298	0.97	5.2	1.46	1.45	1.33	0.60	0.55
Polystyrene, PS	0.20	35 000	463	0.97	10.3	1.54	0.66	0.42	0.35	0.23
Poly(2-ethyl butyl methacrylate), PEBMA	0.14	—	373	0.995	9.1	1.54	1.64	1.31	—	—
Poly(n-hexyl methacrylate), PHMA	0.087	—	373	0.95	10.3	1.54	0.99	0.74	—	—
Poly(n-octyl methacrylate), POMA	0.033	—	373	0.927	10.0	1.54	0.55	0.44	—	—
Poly(ethylene oxide), PEO	—	3600	298	1.08	3.8	1.49	—	—	0.78	0.58
Poly(propylene oxide), PPO	—	5800	298	1.00	5.1	1.49	—	—	0.64	0.48
Polypropylene, PP	—	7000	463	0.75	5.8	1.54	—	—	0.66	0.50

Table A2 Selected values of $(J_e^0)_\infty$ for undiluted polymers and concentrated solutions

Polymer	$(J_e^0)_\infty$ (cm^2 dyne^{-1})	T (K)	ϕ	ρ (g cm^{-3})	K_3 (a = 2)	K_3 (a = 2.3)
PBD	2.0×10^{-7}	298	1.0	0.895	0.41×10^{-2}	0.32×10^{-2}
	8.9	298	0.48	0.895		
HPIP	1.8	298	1.0	0.854	0.63	0.39
PIP	6.1	298	1.0	0.90	0.21	0.19
	50	298	0.36	0.90		
	150	298	0.22	0.90		
PVAc	240	298	0.224	1.18	0.26	0.27
	460	298	0.147	1.18		
PαMS	180	323	0.273	1.07	0.35	0.38
	630	323	0.161	1.07		
PS	14.0	453	1.0	0.97	0.24	0.17
	56	323	0.57	1.05		

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APPENDIX

Table 1A contains values of G_N^0 and M_c for a selection of undiluted polymers. The quantities needed to calculate νL and l are also included. Values of G_N^0 were taken from Ferry (Ref 1, *Table 13-I*) except HPIP[16], PIP[16], PαMS[17] and PDMS[18]. Values of M_c were taken from Ferry (Ref 1, *Table 13-II*) except PBD[19], PIP[20], PEO[21], PPO[21], PP[21]. Values of ρ and C_∞ were obtained or estimated from data in Polymer Handbook[22]. Estimated values are in paraentheses. Values of l_0 were averages calculated from the main chain bond lengths.

Table A2 contains $(J_e^\circ)_\infty$ for undiluted polymers and some selected values in concentrated solutions (PBD[19], HPIP[16], PIP[16,23], PVAc[24], PαMS[17,25], and PS[26]). All samples have narrow distribution ($\bar{M}_w/M_n < 1.1$).

The listings are fairly representative but by no means comprehensive. Although beyond the scope of the present work, a critical survey of literature values would be quite useful.