Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power

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The effects of polymer concentration on chain dimensions in good solvents is discussed in order to define the boundary between the semi-dilute and concentrated regimes. Based upon the screening principle of Edwards and de Gennes, it appears that chain dimensions should approach their unperturbed values for many systems at polymer volume fractions in the range of 0.05–0.20, independent of molecular weight. From these results we propose a method for correlating viscoelastic properties in the semi-dilute region which takes into account the contraction of dimensions with concentration. We also suggest the use of a concentration–molecular weight diagram to distinguish the several regions of viscoelastic behaviour.

INTRODUCTION

The dimensions of random coil polymers in solution depend on both the choice of solvent and the polymer concentration. In θ-solvent systems the coil dimensions retain their unperturbed values at all concentrations[1–3]. For dilute solutions in good solvents the coils are expanded by the excluded volume effect[4]. Dimensions vary from one solvent to another depending on the thermodynamics of mixing: they contract with increasing concentration as the excluded volume repulsions betwen segments in the same chain become screened by segments of neighbouring chains. At high concentrations the dimensions approach their unperturbed values[5–7].

The effects of solvent and concentration on chain dimensions are reflected in viscoelastic behaviour. The corresponddence is clear in dilute solutions where the intrinsic viscosity $[\eta]$ depends directly on chain dimensions[4]. At moderate concentrations, the viscosity is controlled primarily by the extent of coil overlap as characterized by the product $c[\eta]$ [8,9]. However, the relationship is different in θ solvents and good solvents which may be due, at least in part, to changes in chain dimensions with concentration in good solvents. At high concentrations the effects of chain entanglements become important. Viscosities differ from one solvent to another due to differences in the segmental friction coefficient[10,11]. The viscosity appears to vary with molecular weight, M, in the same way for all solvents at high concentration, and the characteristic molecular weight for entanglement, M_c [$(M_c)_{\mathrm{soln}}$ in solutions], also appears to be the same simple function of polymer concentration in different solvents[9,12]. These observations are consistent with the expected universal approach to unperturbed dimensions at high concentrations, but they do raise a question as to the range of concentrations over which the dimensions may be regarded as remaining essentially constant.

In this paper we discuss the distinction between the moderate (semi-dilute) and concentrated régimes with respect to chain dimensions. We also consider how the concentration dependence of chain dimensions might influence the correlations of viscoelastic properties with molecular structure and concentration. For convenience of discussion we will treat the boundaries between the various régimes as though they were well defined, although the transition, like that between the dilute and semi-dilute regimes, is likely to be a rather gradual one.

CHAIN DIMENSIONS

De Gennes and coworkers have considered the relationship between chain dimensions and concentration in the limit of long chains and large excluded volume[6]. For this case:

$$R^2(0) = KM^{6/5} \tag{1}$$

in which $R^2(0)$ is the mean-square end-to-end distance at zero concentration. For the semi-dilute region, i.e. above the overlap concentration, c^*, but still at small volume fractions of polymer, they use scaling arguments to deduce:

$$R^2(c) = R^2(0)\left(\frac{c^*}{c}\right)^{1/4} \tag{2}$$

in which $R^2(c)$ is the mean-square end-to-end distance at concentration c. The overlap concentration c^* is not precisely defined, but it should correspond roughly to the concentration at which the average chain spacing is $2S(0)$, where $S(0)$ is the radius of gyration at zero concentration.

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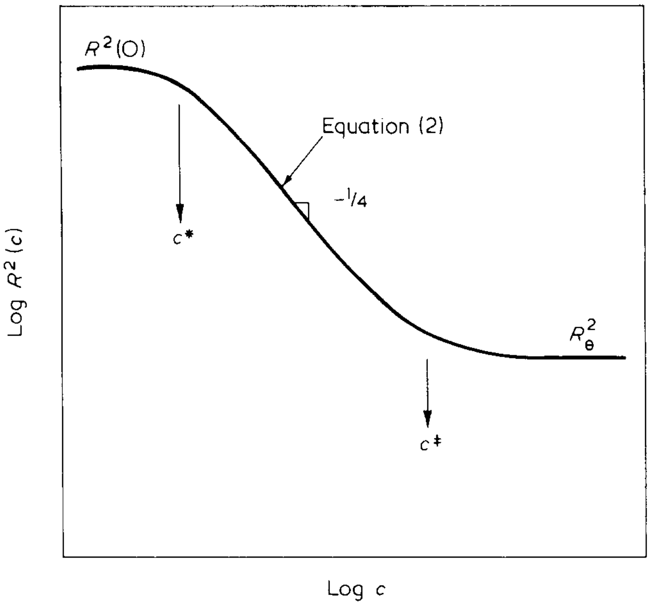

Figure 1 Chain dimensions vs. concentration according to the theory of de Gennes

With $S^2 = R^2/6$ for random coils:

$$c^* = \frac{6^{3/2} M}{8 N_a R^3(0)} \tag{3}$$

in which N_a is Avogadro's number. Other overlap criteria[1,9,12] yield values of c^* within a factor of two of those from equation (3).

Eventually the contraction must bring the chains to their unperturbed dimensions R^2_θ. The behaviour expected is sketched in *Figure 1*. The concentration $c‡$ separates the semi-dilute region from the concentrated region, the latter being defined as the region where chain dimensions become independent of concentration. An estimate of $c‡$ is obtained by equating the expression for $R^2(c)$ in equation (2) to R^2_θ, the unperturbed dimensions. Thus:

$$c‡ = c^* \left(\frac{R^2(0)}{R^2_\theta}\right)^4 \tag{4}$$

or, since $R^2(0)/R^2_\theta$ is $\alpha^2(0)$ where $\alpha(0)$ is the expansion ratio of the chains at infinite dilution:

$$c‡ = c^* [\alpha(0)]^8 \tag{5}$$

Also,

$$R^2_\theta = K_\theta M \tag{6}$$

so equations (1), (3), (4) and (6) combine to give:

$$c‡ = \frac{6^{3/2}}{8 N_a} \frac{K^{5/2}}{K^4_\theta} \tag{7}$$

showing that $c‡$ is expected to be independent of molecular weight.

The limiting law given as equation (1) is frequently not attained in molecular weight ranges of practical interest. Nevertheless, the approach used to deal with concentration effects, and particularly the idea of a screening distance for excluded volume interactions[6,13] may still be valid. The following discussion parallels closely that given recently by Berry, Fox and Nakayasu[12].

For $c > c^*$, the interactions between units separated beyond some distance along any chain are assumed to be screened out by the other chains. For shorter distances the interactions are assumed to remain fully in effect. Let M_s be the molecular weight corresponding to this screening distance and R^2_s the mean-square end-to-end distance for chains of molecular weight M_s at zero concentration in the same solvent. For a given solvent both M_s and R^2_s are assumed to be functions of concentration alone, i.e. independent of M, the molecular weight of the chains. For $M \gg M_s$ the mean chain dimensions $R^2(c)$ are then the same as for an unrestricted random walk of M/M_s steps, each of mean-square step length R^2_s:

$$R^2(c) = \frac{M}{M_s} R^2_s \tag{8}$$

Thus:

$$\frac{R^2(c)}{R^2_\theta} = \frac{M}{M_s} \frac{R^2_s}{R^2_\theta} = \left(\frac{R^2_s}{M_s}\right) \Big/ \left(\frac{R^2_\theta}{M}\right) \tag{9}$$

or, since R^2_θ/M is independent of M:

$$\alpha^2(c) = \frac{R^2(c)}{R^2_\theta} = \frac{R^2(M_s)}{R^2_\theta(M_s)} \tag{10}$$

Thus, the expansion ratio $\alpha(c)$ depends only on the dimensions of chains with molecular weight M_s in the solvent compared to those in a θ-solvent.

Data on intrinsic viscosities are more generally available than data on chain dimensions. With the Fox–Flory equation:

$$[\eta] = \Phi \frac{R^3(0)}{M} \tag{11}$$

results can be expressed in terms of $[\eta]$ and $[\eta]_\theta$. To a first approximation the Flory constant Φ is independent of the polymer–solvent system for linear chains, $\Phi \approx 2.5 \times 10^{23}$ (c.g.s. units)[4]. Thus, equation (3) can be written:

$$c^* = \frac{6^{3/2}\Phi}{8 N_a} \frac{1}{[\eta]} = \frac{0.77}{[\eta]} \tag{12}$$

and equation (10) becomes:

$$\alpha^2(c) = \left(\frac{[\eta]}{[\eta]_\theta}\right)^{2/3}_{M_s} \tag{13}$$

The concentration corresponding to a screening length of M_s is the overlap concentration for chains with molecular weight M_s, which, from equation (12), is given by:

$$c = 0.77/([\eta]_{M_s}) \tag{14}$$

Thus, if $[\eta]$ and $[\eta]_\theta$ are given as functions of molecular weight, equations (13) and (14) can be used to construct a plot of $\alpha^2(c)$ vs. c. The results obtained with data on two

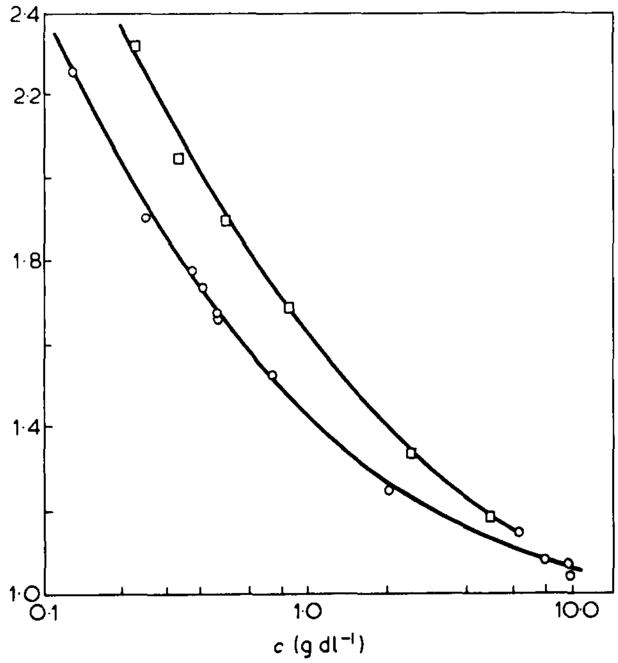

Figure 2 Expansion factor vs. concentration calculated from dilute solution intrinsic viscosities. Values of $[\eta]$ for polystyrene in toluene were taken from ref 15. Values for polybutadiene in tetrahydrofuran are unpublished data from this laboratory (see *Figure 3*). □, Polystyrene–toluene; ○, polybutadiene–tetrahydrofuran

good solvent systems, polystyrene–toluene and polybutadiene–tetrahydrofuran, are shown in *Figure 2*. In both cases $\alpha^2(c)$ is predicted to fall to values near unity for concentrations of the order of 10 g dl^{-1}.

Figure 3 shows $[\eta]$ vs. M for the polybutadiene–tetrahydrofuran system. At low molecular weights $[\eta]$ approaches $[\eta]_\theta$ as expected. In the range where $[\eta] \approx [\eta]_\theta$ the values of $\alpha^2(c)$ calculated by equation (13) are approximately unity. Thus $c\ddagger$ can be estimated with equation (12) from the value of $[\eta]\ddagger$ where $[\eta]$ and $[\eta]_\theta$ first begin to diverge significantly:

$$c\ddagger = \frac{0.77}{[\eta]\ddagger} \qquad (15)$$

For polystyrene–toluene, $[\eta]\ddagger$ is approximately 0.06 dl g^{-1} giving $c\ddagger$ = 12 g dl^{-1}; for polybutadiene–tetrahydrofuran $[\eta]\ddagger \approx 0.07$ dl g^{-1} giving $c\ddagger$ = 11 g dl^{-1}. Thus, based on this rather simple application of the screening length principle, the expansion ratio becomes quite insensitive to concentration beyond about 10% polymer. It should be noted, however, that this value depends on the proportionality constant in equation (14) and thus, ultimately, on the particular criterion for overlap chosen in equation (3). With other overlap criteria the values of $c\ddagger$ range from about 5 g dl^{-1} to 20 g dl^{-1} (refs 9, 12). In any case the concentrated region, the region of sensibly constant chain dimensions, appears to encompass a wide range of concentrations in typical good solvent systems.

VISCOELASTIC c–M REGIMES

In undiluted linear polymers of low molecular weight the zero-shear viscosity η_0 is directly proportional to M. At high molecular weights η_0 is proportional to $M^{3.4}$. A molecular weight M_c which is characteristic of the polymer separates the two regions. This behaviour is attributed to the onset of chain entanglement[9–11]. The value of M_c is insensitive to temperature and increases with dilution. At high concentrations:

$$(M_c)_{\rm soln} \doteq M_c\rho/c \qquad (16)$$

where ρ is the polymer density. Characteristic molecular weights with similar properties are associated with the plateau modulus G_N^0 and the recoverable shear compliance J_e^0. With viscosity behaviour as the criterion for entanglement we can distinguish two c–M regimes:

$$cM < \rho M_c \text{ (not entangled)}$$

$$cM > \rho M_c \text{ (entangled)} \qquad (17)$$

For polystyrene M_c = 31 000 and ρ = 1.07 and for polybutadiene M_c = 5000 and ρ = 0.90, both at 25°C. Therefore, with concentrations measured in g dl^{-1} the products:

$$cM = 3.3 \times 10^6 \text{ (polystyrene)}$$

$$cM = 4.5 \times 10^5 \text{ (polybutadiene)} \qquad (18)$$

define the boundary between the entangled and non-entangled régimes for concentrated solutions of these polymers.

The nature of this entanglement boundary in semi-dilute solutions is unclear experimentally. In polymer–solvent systems where equation (1) is valid, the scaling theory predicts that osmotic pressure π is proportional to $c^{9/4}$ in the semi-dilute regime[6]. De Gennes suggests that G_N^0 should also be proportional to $c^{9/4}$ (ref 14), arguing that osmotic pressure and elastic modulus at short times should both be proportional to the concentration of binary polymer–polymer contacts. The characteristic molecular weight associated with plateau modulus, $(M_e)_{\rm soln}$, is proportional to $c/(G_N^0)_{\rm soln}$. Thus, if $(M_c)_{\rm soln}$ and $(M_e)_{\rm soln}$ have the same concentration dependence, the values of $(M_c)_{\rm soln}$ should increase more rapidly with dilution in the semi-dilute region than predicted

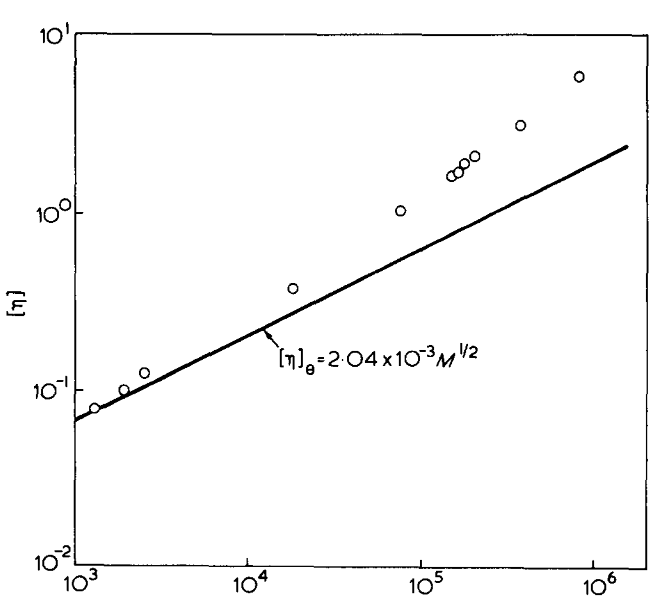

Figure 3 Intrinsic viscosity of polybutadiene in tetrahydrofuran. The $[\eta]$ vs. M line was obtained as the average of reported values for *cis-* and *trans*-polybutadiene[4] for a 50/50 *cis–trans* ratio

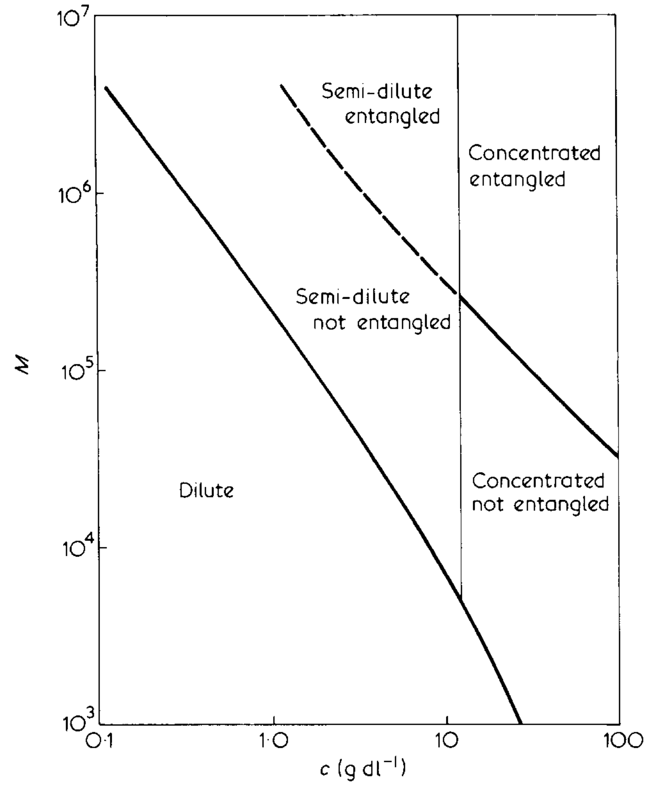

Figure 4 Concentration–molecular weight diagram of viscoelastic régimes for polystyrene in a good solvent

by equation (16). On the other hand, in θ-solvents the osmotic pressure should vary as the concentration of ternary contacts and thus be proportional to c^3. In this case, however, the binary contact concentration presumably varies as c^2, so the correspondence between π and G_N^0 is lost. For θ-solvents therefore, it seems reasonable to suppose that equation (16) applies throughout both the semi-dilute and concentrated regions.

Figures 4 and *5* are concentration–molecular weight diagrams showing the various régimes of behaviour expected for the polystyrene–toluene and polybutadiene–tetrahydrofuran examples. The boundary between the semi-dilute and concentrated regimes was calculated from equation (15) with $[\eta]^{\ddagger} = 0.06$ dl g^{-1} for polystyrene and $[\eta]^{\ddagger} = 0.07$ dl g^{-1} for polybutadiene. The boundary between the dilute and semi-dilute regimes (the locus of c^* vs. M) was calculated from equation (12) with intrinsic viscosity data. The boundary between the entangled and non-entangled régime was calculated from equation (18). The dashed continuations of these for semi-dilute solutions indicate merely the trend expected from the de Gennes prediction for good solvents.

DISCUSSION

Figures 4 and *5* distinguish five régimes for good solvent systems: dilute, semi-dilute but not entangled, semi-dilute entangled, concentrated but not entangled, and concentrated entangled. Viscoelastic properties in semi-dilute solutions (≤10% polymer in the systems examined here) can differ from one solvent to another owing to differences in the chain expansion factor. Some allowance for these solvent-related differences is probably necessary in seeking general empirical laws relating such properties to c and M. Thus, for example, the relative viscosity η_0/η_s of polystyrene in a θ-solvent appears to be virtually a unique function of the product $c[\eta]_\theta$ (ref 16). In good solvents such as toluene η_0/η_s increases less rapidly with $c[\eta]$ and small but systematic differences appear for samples of different molecular weight. If η_0/η_s in semi-dilute solutions is a function of coil overlap (measured in a θ-solvent by the product $c[\eta]_\theta$ at all concentrations since coil dimensions do not change) then the correlating variable in good solvents, $c[\eta]$, should be corrected for coil contraction at each concentration. The appropriate correlating variable is:

$$c[\eta]\left(\frac{\alpha(c)}{\alpha(0)}\right)^3$$

which, with equations (13) and (14) and $\alpha^3(0) = [\eta]/[\eta]_\theta$, becomes simply $0.77\,(M/M_s)^{1/2}$. For the case in which $[\eta] \propto M^a$ (Mark–Houwink relation), the variable becomes

$$0.77\left(\frac{c[\eta]}{0.77}\right)^{1/2a}$$

which of course reduces to $c[\eta]$ in the θ-solvent ($a = 0.5$). This approximate correction for variations in chain dimensions does appear to move the correlations for θ- and good solvents closer to a common curve, but how much improvement is obtained can only be determined from a detailed examination of data[8,16–18]. It does not, however, account for the increased deviations with molecular weight which appear in good solvent correlations[11].

Finally, *Figures 4* and *5* make evident the importance of distinguishing between entanglements of chains and simple chain overlap. There is clearly a large concentration–molecular weight domain in the semi-dilute region where overlap is extensive and yet the usual viscoelastic phenomena associated with chain entanglement are not expected.

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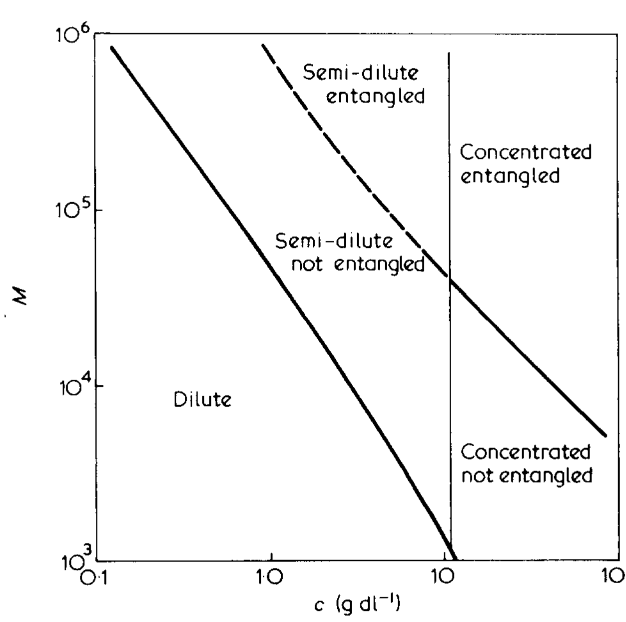

Figure 5 Concentration–molecular weight diagram of viscoelastic régimes for polybutadiene in a good solvent

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