Macromolecules 1980, 13, 623-626

A Scaling Analysis of Theories of the Viscoelastic Properties of Entangled Polymer Systems

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Received December 12, 1979

ABSTRACT: Various theoretical assumptions concerning the viscoelastic properties of entanglement limited polymer solutions are analyzed by using our deductive approach to the dynamical scaling theory of polymer solutions. Three different scaling assumptions concerning the entangled system are tested. The first model assumes, in effect, that the entanglements introduce a new dimensionless parameter which is important in the entanglement regime, but which is irrelevant in the dilute and semidilute regions where macroscopic manifestations of entanglement networks are not observed. The other two models assume that the coil overlap concentrations continue to be the scaling concentrations in the entangled regime just as they are in semidilute solutions. Both the perturbed and unperturbed coil overlap concentrations are tested as possible scaling concentrations. The analysis proceeds by inserting experimental molecular weight power law dependences for the plateau modulus, the viscosity, and the steady state compliance into the scaling relations to obtain predictions of the concentration power law dependences which are then compared with experimental values to determine the consistency of the assumptions of each of the models.

I. Introduction

The study of entangled polymer systems is central to a description of the viscoelastic properties of concentrated solutions and melts of high molecular weight polymers where the macroscopic manifestations of entanglement networks are observed.[1] These systems are characterized by a viscosity, η, which depends on molecular weight, M, as

$$\eta \propto M^{3.4} \tag{I.1}$$

They display a plateau modulus, $G_N{}^0$, for intermediate frequencies that corresponds to the elastic modulus of an entanglement network, and they have a steady state recoverable shear compliance, $J_e{}^0$, with the behavior

$$G_N{}^0 J_e{}^0 = \text{constant} \tag{I.2}$$

Theories have been proposed for η, $G_N{}^0$, and $J_e{}^0$ on varying levels of sophistication and with varying degrees of success, but no theory is available to simultaneously describe the molecular weight and concentration dependence of these three central quantities in the linear viscoelastic properties of entangled polymer systems. Furthermore, the most advanced molecular theories[1-5] consistantly obtain an M^3 power law for η, making the 3.4 power law even more perplexing.

The mathematical description of even a single entanglement is an enormous task, although approximate treatments are available.[6,7] However, the mathematical characterization of the properties of an entangled polymer network is substantially more difficult in view of the necessity for retaining the entanglements as topological constraints.[8,9] Nevertheless, Doi and Edwards[3] have made considerable progress with the derivation of constitutive equations for the melt by the use of models involving the motion of polymers in entanglement generated tubes.

Scaling theories of polymer solutions are somewhat less ambitious than full theories because they seek to determine the asymptotic long chain power law dependence of solution properties on the molecular weight and the polymer concentration. The scaling theories were introduced by de Gennes and co-workers as a simple heuristic vehicle for reproducing the results of intricate renormalization group calculations.[4,5] These arguments could then be applied to more complicated situations for which the renormalization group methods are either too complicated or inapplicable. We have provided a systematic derivation of the scaling theories of polymer solutions with the following important properties:[10-12]

(1) Equilibrium scaling relations[10] are derived directly from the expression for the partition function for a set of interacting *continuous* polymer chains at concentration c by the method of asymptotic dimensional analysis.

(2) The polymer molecular weight distribution may be taken to be monodisperse, if desired. This contrasts sharply with the exponential molecular weight distribution, $\exp(-M/M_0)$, inherent in the renormalization group method results upon which the de Gennes scaling method embarks.

(3) The theory utilizes the essential approximation of ignoring the presence of cutoffs to remove the infinite self-interaction terms. For polymer systems this appears to introduce errors in the exponent ν, associated with the root mean square chain size in good solutions, of only 1-2% with higher errors incurred when similar approximations are applied to Ising type systems.[13]

(4) The theory retains explicit dependences on *all* dimensional quantities. This feature has enabled the deriviation of relationships between molecular weight exponents for spatial dimensionalities which differ by unity, thereby generating these exponents *directly* from scaling.[10,11]

(5) The dynamical scaling theory[11,12] proceeds from the dynamical equations for interacting continuous chains and from the correlation function expressions for various solution properties.

(6) The utilization of combined scaling and effective medium type concepts has led to the derivation of non-power-law-type scaling relations,[12] specifically to the empirical Martin equation for the concentration dependence of the solution viscosity ranging from the dilute region well into the semidilute region.

Here we extend our scaling theory to the entangled regime to consider the concentration and molecular weight dependences of η, $G_N{}^0$, and $J_e{}^0$. Our aim here is to utilize the scaling theory and available experimental data as a vehicle for testing various physical assumptions concerning the nature of entangled systems with the belief that such information will prove useful in developing molecular theories of the viscoelastic properties of entangled systems. The testing procedure involves introducing the experimental molecular weight power laws into the scaling theory to obtain predictions of the concentration power laws which are then compared with experiment. Two basic

0024-9297/80/2213-0623$01.00/0

views of the entangled systems are contrasted. One approach assumes that the entanglement coupling introduces a new length (or molecular weight, etc.) scale to provide a new fundamental dimensionless parameter that characterizes the viscoelastic properties of entangled systems, while the second utilizes the properties of the semidilute region,[4,10] such as blob size and correlation length, for the entangled regime. The latter de Gennes approach essentially assumes that the coil overlap concentration retains physical importance into the entanglement regime, while the former treatment assumes that a new scaling concentration emerges for the entangled systems.

It is shown in section II that the new scale parameter approach is capable of being consistent with the majority of available data for η, G_N^0, and J_e^0. The c^2 dependence of G_N^0 emerges directly from the scaling theory. The observed molecular weight power law dependence of η and J_e^0 is utilized to obtain their power law variations with concentration in good agreement with experimental data. In section III we provide a more deductive treatment[10-12] of the de Gennes approach[4,5] to indicate how the overlap concentration assumption provides reasonable, though somewhat less successful, predictions, but only if the overlap concentration associated with swollen chains is used. This feature is somewhat unsatisfactory as many experiments consider concentrations up to the melt where the unperturbed (Θ condition) overlap concentration is more appropriate. Scaling theory with the unperturbed overlap concentration, however, is shown not to provide acceptable predictions.

II. Scaling Relations

The minimum description of entangled systems requires the introduction of certain essential characteristics of the entangled polymer network. We show that a scaling theory can be developed based upon the introduction of a single new dimensional parameter and still agree with the available experimental data.[1] This is a very important feature and a major motivation for a scaling theoretic investigation since it demonstrates that many apparently different theoretical formulations of entangled polymer systems might be capable of providing the same final description despite strong apparent differences between the theories. This parallels the situation involved in the description of transport coefficients of dilute gases where any two-parameter potential, having attractive and repulsive portions, can be adjusted to reproduce the experimental data.

The dimensional quantity we consider is the distance in space between entanglement junctions. This distance, α, is later combined into a dimensionless entanglement probability to make contact with experimental data. Having introduced a new length scale, it scales just as any length. Using the scale relations from Adler and Freed[11,12] and explicitly incorporating the frequency dependence into the functional form, we obtain the scaling law for the complex viscosity, $\eta(\omega)$, as

$$\frac{\eta(\omega)-\eta_0}{c\eta_0} = \frac{\zeta l^2N^2N_A}{\eta_0 M} f\left(\frac{cN_AN^{3/2}l^3}{M}, \frac{\zeta N^{1/2}}{\eta_0 l}, \frac{\alpha}{lN^{1/2}}, \frac{vN^{1/2}}{l^3}, \frac{\omega\zeta l^2N^2}{k_BT}\right) \tag{II.1}$$

Here the various symbols are defined as follows: η_0 is the solvent viscosity, c the polymer concentration, ζ the monomer friction coefficient, N the number of monomers, l the monomer (i.e., Kuhn) length, N_A Avagadro's number, M the chain molecular weight, v the excluded volume, ω the frequency, and k_BT the absolute temperature in energy units. f is the general scaling function which contains all dimensional quantities in the relevant dimensionless forms.

We consider first concentrated solutions where the draining parameter, $\zeta N^{1/2}/\eta_0 l$, is irrelevant as is the excluded volume interaction. The concentration enters in (II.1) in terms of the ratio of the volume of an unperturbed coil to the volume available per coil. In the entangled region the unperturbed coil volume is inappropriate as a scaling volume, so the entanglement length scale is used to construct a new dimensionless concentration from the first and third arguments of (II.1). Hence, the entanglement length scale must enter as the ratio of this length to the cube root of the volume per chain. Thus, the scaling function in (II.1) reduces to the simpler limit of

$$\frac{\eta(\omega)-\eta_0}{c\eta_0} = \frac{\zeta l^2N^2N_A}{\eta_0 M} f_s\left(\frac{cN_A\alpha^3}{M}, \frac{\omega\zeta l^2N^2}{k_BT}\right) \tag{II.2}$$

where the argument $cN_A\alpha^3/M$ results from combining the first and third variables in (II.1) in a fashion analogous to that introduced in the semidilute region.[4,5,10] The presence of the new dimensionless parameter $cN_A\alpha^3/M$ is a consequence of the assumption that a new scaling concentration emerges at the relevant quantity in the entanglement domain.

This dimensionless parameter, $cN_A\alpha^3/M$, must be related to the probability of entanglements which in turn is proportional to the contact probability.[1] The latter is obtained, following Graessley,[1] by noting that the number of contacts is proportional to c^2. The number of polymers per unit volume is proportional to c/M, so the number of intermolecular contacts per polymer is proportional to $c^2/(c/M) = cM$. In dimensionless form this becomes $cM/\rho M^*$ where ρ and M^* represent a reference concentration and molecular weight, respectively. ρ is customarily chosen as the density in the melt, while when appropriate numerical factors are appended, M^* becomes the empirical entanglement molecular weights M_c, M_e, and M_e' as reviewed by Graessley.[1] Equating $cN_A\alpha^3/M$ to the entanglement probability $\rho M^*/cM$ (apart from a numerical constant) implies that

$$\alpha = (\rho M^*/c^2N_A)^{1/3} \tag{II.3}$$

and that $\alpha \propto c^{-2/3}$ independent of molecular weight. Hence, (II.2) is rewritten in terms of the dimensionless entanglement probability as

$$\frac{\eta(\omega)-\eta_0}{c\eta_0} = \frac{\zeta l^2N^2N_A}{\eta_0 M} f_s\left(\frac{\rho M^*}{cM}, \frac{\omega\zeta l^2N^2}{k_BT}\right) \tag{II.4}$$

The complex shear modulus, $G(\omega)$, is given by

$$G(\omega) = G'(\omega) + iG''(\omega) = i\omega\eta(\omega) \tag{II.5}$$

The presence of a plateau modulus,

$$G'(\omega) = G_N^0 \text{ for } \omega_{\min} < \omega < \omega_{\max} \tag{II.6}$$

independent of frequency, implies that the imaginary part of the viscosity, $\eta''(\omega)$, behaves as

$$\eta''(\omega) = G_N^0/\omega \text{ for } \omega_{\min} < \omega < \omega_{\max} \tag{II.6a}$$

Hence, for $\omega_{\min} < \omega < \omega_{\max}$ the scaling function f_s, $\propto \omega^{-1}$. Using the fact that $\eta(\omega) \gg \eta_0$, we find that G_N^0 scales as

$$G_N^0 = \frac{cN_Ak_BT}{M} g_s^P\left(\frac{\rho M^*}{cM}\right) \tag{II.7}$$

As the plateau modulus is a (temporary) network property, it must be independent of the molecular weight M. This imposes a power law form

$$g_s^{p}(x) \propto x^{-1} \tag{II.8}$$

so we obtain

$$G_N^{\,0} \propto c^2RT/\rho M^* \tag{II.9}$$

where $R = N_Ak_B$ and the numerical proportionality factor is undetermined by scaling.

The solution viscosity is obtained for $\omega = 0$, $\eta(\omega) = \eta$, $\eta \gg \eta_0$ as

$$\eta = \frac{c\zeta l^2N^2N_A}{M}g_s^{r}(\rho M^*/cM) \tag{II.10}$$

The empirical $M^{3.4}$ power law (eq I.1) translates into the requirements of the power law dependence,

$$g_s^{r}(x) \propto x^{-2.4} \tag{II.11}$$

converting (II.10) into

$$\eta \propto \left[\frac{\zeta l^2N_A\rho M^*}{M_A^{\,2}}\right]\left(\frac{cM}{\rho M^*}\right)^{3.4} \tag{II.12}$$

where $M_A \equiv M/N$ and the constant numerical factor is undetermined by scaling. The −2.4 power law of g_s^{r} is indicative of a collective type behavior,[14] providing an essential barrier to a full theoretical description.

It is important to recognize that the microscopic effective unit friction coefficient ζ is concentration dependent, and this variation must be considered when comparing experimental data to (II.12). The Doi–Edwards theory also produces a scaling relation of the form of (II.10) when the distance between entanglements along the tube, a, is calculated with unperturbed chain dimensions.[3]

The steady state compliance, $J_e^{\,0}$, is defined by

$$J_e^{\,0} = \frac{1}{\eta^2}\lim_{\omega\to 0}\frac{G'(\omega)}{\omega^2} = i\frac{1}{\eta^2}\lim_{\omega\to 0}\frac{\eta''(\omega)}{\omega} \tag{II.13}$$

Thus, as $\omega \to 0$ we must have $\eta''(\omega) \propto \omega$ and (II.4) implies

$$\lim_{\omega\to 0}\frac{\eta''(\omega)}{\omega} = \frac{c\zeta l^2N^2N_A}{M}\,\frac{\zeta l^2N^2}{k_BT}\,g_s^{i}\!\left(\frac{\rho M^*}{cM}\right) \tag{II.14}$$

Introducing (II.14) and (II.10) into (II.13), using the power law from (II.12), and invoking the empirical relation (I.2) implies that g_s^{i} displays the power law

$$g_s^{i}(x) \propto x^{-3.8} \tag{II.15}$$

again indicative of a cooperative type behavior.

The scaling predictions of the concentration dependences of $G_N^{\,0}$, η, and $J_e^{\,0}$ emerging from (II.9), (II.12), and (II.15) are in general agreement with the experimental data reviewed by Graessley.[1] However, some recent isothermal experiments by Graessley[15] and co-workers on polybutadiene obtain power law concentration dependences for $G_N^{\,0}$, η, and $J_e^{\,0}$ with exponents of 2.26, 4, and −2.26, respectively. The $G_N^{\,0}$ and $J_e^{\,0}$ exponents, but not that for η, do coincide with de Gennes' scaling predictions.[5] The polybutadiene results may be indicative of different categories of entangled systems just as Θ and good solutions represent different varieties in the dilute regime, etc. It is, therefore, of greater interest to investigate the alternative scaling description that emerges from the use of the coil overlap concentration as the basic scaling concentration.

III. Scaling with Coil Overlap Concentration

Here we assume that the additional length scale, a, in (II.1) does not exist. In this case the scaling theory results for η in good and poor solvents have been given by de Gennes.[5] For completeness, below we apply our approach to η as well as to $G_N^{\,0}$ and $J_e^{\,0}$. Similar to the situation in section II, the draining parameter $\zeta N^{1/2}/\eta_0 l$ is taken to be irrelevant. In good solutions the appearance of the ratio of concentration to the unperturbed coil overlap concentration,

$$c_0^* \propto M/N_AN^{3/2}l^3 \tag{III.1}$$

is inappropriate, and concentration should appear in the form of c/c^*, where c^* is the perturbed coil overlap concentration,

$$c^* \propto N^{1-3\nu}(\upsilon l^{-3})^{3(1-2\nu)}l^{-3}M_AN_A^{\,-1} \tag{III.2}$$

and ν is the excluded volume index in the mean square end-to-end distance in $\langle \mathbf{R}^2\rangle \propto N^{2\nu}$. Given these assumptions, the good solution scaling relations for the complex frequency dependent viscosity become[12]

$$\frac{\eta(\omega) - \eta_0}{c\eta_0} = \frac{\zeta l^2N^2N_A}{\eta_0 M}f_g(c/c^*,\omega\zeta l^2N^2/k_BT) \tag{III.3}$$

Proceeding as before with c/c^* as the relevant dimensionless parameter instead of $cM/\rho M^*$, the molecular weight independence of $G_N^{\,0}$ yields

$$G_N^{\,0} \propto c^{3\nu/(3\nu-1)}\frac{RT}{M_A}\left(\frac{\upsilon}{l^3}\right)^{3(2\nu-1)/(3\nu-1)}\left(\frac{l^3N_A}{M_A}\right)^{1/(3\nu-1)} \tag{III.4}$$

Using the $\nu = {}^3/_5$ good solution limit implies that

$$G_N^{\,0} \propto c^{9/4}\frac{RT}{M_A}\left(\frac{\upsilon}{l^3}\right)^{3/4}\left(\frac{l^3N_A}{M_A}\right)^{5/4} \propto (J_e^{\,0})^{-1} \tag{III.4a}$$

in accord with the polybutadiene data. However, note that the $(\upsilon/l^3)^{3/4}(l^3N_A/M_A)^{3/4}$ term implies a solvent dependence and an extra temperature dependence over the usual RT factor which could be subject to experimental testing. For polybutadiene, Graessley[15] finds that the $G_N^{\,0}(c)$ data provide a single curve independent of solvent quality (solvents used are tetradecane, flexon, and low molecular weight (≈2500) polybutadiene). This is in contrast to the excluded volume dependence in (III.4a). Note that l is a function of temperature and that ζ likewise varies with concentration and strongly with temperature. These features must be considered in testing (III.4a), (III.5a), (III.7), or (III.8) against experiments.

The $M^{3.4}$ power law for the entangled viscosity then leads to the relation

$$\eta \propto c^{1+[2.4/(3\upsilon-1)]}N^{3.4}\left(\frac{\upsilon}{l^3}\right)^{7.2(2\nu-1)/(3\nu-1)}\frac{\zeta l^2N_A}{M_A}\left(\frac{l^3N_A}{M_A}\right)^{2.4/(3\nu-1)} \tag{III.5}$$

$$\eta \overset{\nu = 3/5}{\longrightarrow} c^4N^{3.4}(\upsilon/l^3)^{1.8}\frac{\zeta l^2N_A}{M_A}\left(\frac{l^3N_A}{M_A}\right)^3 \tag{III.5a}$$

again in accord with the polybutadiene data, but again with an extra particular temperature and solvent quality dependence emerging through the $(\upsilon/l^3)^{1.8}$ factor in (III.5a).

The agreement of the concentration dependence from (III.4a) and (III.5a) with the polybutadiene data is perplexing as the experiments extend into the melt,[1] and at the high concentration limit the excluded volume effect should be absent.[16] Then the $\upsilon N^{1/2}l^{-3}$ term in (II.1) should be dropped, and the Θ condition scaling relation for the frequency dependent complex viscosity becomes

$$\frac{\eta(\omega) - \eta_0}{c\eta_0} = \frac{\zeta l^2 N^2 N_A}{\eta_0 M} f_t\left(\frac{c N_A N^{3/2} l^3}{M}, \frac{\omega \zeta l^2 N^2}{k_B T}\right) \quad \text{(III.6)}$$

The scaling predictions for the concentration dependence then follow from (III.4) and (III.5) by using $\nu = {}^1/_2$ as

$$G_N^0 \propto (J_e^0)^{-1} \propto c^3 \frac{RT}{M_A}\left(\frac{l^3 N_A}{M_A}\right)^2 \quad \text{(III.7)}$$

$$\eta \propto c^{5.8} N^{3.4} \frac{\zeta l^2 N_A}{M_A}\left(\frac{l^3 N_A}{M_A}\right)^{4.8} \quad \text{(III.8)}$$

which yield concentration dependences that are incompatible with experimental data.

IV. Discussion

The scaling approach is used to assess the validity of various physical assumptions concerning the viscoelastic properties of entangled polymer systems. Known molecular weight power law dependences are introduced into the scaling theory to provide predictions for the concentration dependence which, in turn, is compared with experiment. This mode of analysis is applied to three models of the entangled polymer system.

The first model assumes, in effect, that for macroscopically entangled systems there exists a new dimensionless parameter which does not enter into the description of the viscoelastic properties of dilute and semidilute (i.e., nonentanglement limited) solutions. This dimensionless parameter is interpreted, following the review by Graessley,[1] in terms of the chain contact probability. The derived scaling theory concentration dependences of G_N^0, η, and J_e^0 are consistent with the experimental data reviewed by Graessley.[1]

The other two models follow the ideas of de Gennes[5] in assuming that the coil overlap concentration, c_0^* or c^*, represents the fundamental scaling concentration as it successfully does in the dilute and semidilute regimes.[5,10] Choosing the perturbed (swollen) chain overlap concentration, c^*, provides agreement with recent isothermal data on polybutadiene.[15] However, the high concentrations utilized in the experiment appear to require the use of the unperturbed chain overlap concentration, c_0^*, as the scaling concentration, and this approach yields scaling predictions which are in poor agreement with experimental values. It should be noted that the c^* scaling model produces an additional predicted solvent quality and temperature dependence of G_N^0, η, and J_e^0 through their dependence on the excluded volume, and this is a point which can be tested experimentally. Perhaps there are different possible types of entanglement systems, those where the contact probability provides the scaling concentration, and those for which the coil overlap concentration is the relevant variable. Except for polybutadiene, the available data currently favor the former.

Acknowledgment. I am grateful to Professors Bill Graessley and Masao Doi for helpful discussions and for making their work available to me prior to publication. This research is supported, in part, by National Science Foundation Grant DMR78-26630 (polymers program).

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Distribution Functions and Viscoelastic Properties of Perfect Random Nets

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Received January 16, 1980

ABSTRACT: Eigenvalue and relaxation time spectra, viscoelastic properties, mean square dimensions, and the distribution function of the radius of gyration are calculated for perfect networks. These nets consist of a number μ of f-functional junctions connected at random by monodisperse Gaussian chains of $n + 1$ statistical subunits. The dependence of network dimensions on chain length and junction number is determined and it is found that these nets have dimensions which are independent of junction number in the limit of large μ. The viscoelastic functions are calculated from the exact relaxation time spectra near the asymptotic limit $\mu \rightarrow \infty$. The results are similar to the Rouse-Mooney static junction theory but cooperative network modes are found which have relaxation times much longer than those of the interlinking chains. The frequency dependences of the storage and loss shear moduli are found to differ in detail from those of the Rouse–Mooney prediction.

Distribution Functions and Mean-Square Dimensions

Previous treatments of the Gaussian network problem have not attempted to account for chain and network cooperative contributions to the mean-square dimensions (MSD) and viscoelastic properties. The reason for this is clear enough; there are many complications in the description of elastic networks. These include the proper

0024-9297/80/2213-0626$01.00/0