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Correctly Averaged Non-Gaussian Theory of Rubberlike Elasticity. Application to the Description of the Behavior of Poly(dimethylsiloxane) Bimodal Networks

Carlos Menduiña and Juan J. Freire*

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain

Miguel A. Llorente

Departamento de Quimica General y Macromolēculas, Facultad de Ciencias, Universidad Nacional de Educaciōn a Distancia (UNED), 28040 Madrid, Spain

Thomas Vilgis[†]

Cavendish Laboratory, Cambridge CB3 0HE, England, U.K.

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ABSTRACT: A new theoretical relationship between the rubberlike elasticity of a polymer network and the distribution of the vector connecting junction points (or the end-to-end vector distribution function of the chain joining two of these points) is presented. In this approach the free energy of the chains is correctly averaged over the network structure, a difference with respect to older treatments in which a preaveraged deformation dependence is considered. The new theory and a slight modification in the previous procedure to analyze bimodal network data lead to a more satisfactory explanation of these data (presenting a pronounced upturn for high extensibilities due to non-Gaussian effects) in terms of molecular magnitudes.

Introduction

In a recent work,[1] some of us presented a method to relate the elastomeric properties of polymer networks with the chain length distribution. This method makes use of an analytical form for the end-to-end distance distribution function, $F(R)$, or the spherically symmetric part of the end-to-end vector distribution function, $F(\mathbf{R})$, in terms of coefficients determined by inference from the even moments $\langle R^{2p}\rangle$. ($\mathbf{R}$ represents the vector joining two connected junction points in the network structure, referred to a local system associated to the chain joining these points, and the broken brackets represent both orientational and conformational average with respect to an external system or the network structure.) Simultaneously, Mark and Curro[2,3] published a series of papers in which they approach the same problem through Monte Carlo generated distribution functions. Both types of theoretical calculations have an obvious experimental reference: the data corresponding to bimodal networks composed by short and long chains, for which an important deviation with respect to the behavior associated to a simple Gaussian distribution is clearly observed at high elongations,[4,5] so that a pronounced upturn in the stress–strain curves is shown, due to the limited flexibility of the short chains. However, the agreement between numerical calculations based in non-Gaussian theories and experimental data is only qualitative. In our opinion, there are two main problems from which the quantitative discrepancies may arise:

First, the theoretical relationship between elastic forces and distribution functions proposed in previous works[1-3] is based in an expression for the free energy in terms of the preaveraged end-to-end vector of the chain connecting two junction points

$$A(\alpha) = -k_{\mathrm{B}}T \ln F[\langle(\alpha\cdot\mathbf{R})^2\rangle^{1/2}] \tag{1}$$

where $F(\mathbf{R})$ is the actual distribution function of the fixed end-to-end points (cross-links). α is the deformation tensor. For practical purposes (see the next section) we define the radial distribution function in the usual manner

$$W(R) = 4\pi R^2 F(R) \tag{2}$$

The argument in the distribution function in eq 1 is the deformed and averaged end-to-end vector

$$\langle(\alpha\cdot\mathbf{R})^2\rangle = \sum_{i=1}^{3}\alpha_i^2\langle R_i^2\rangle = (\langle R^2\rangle/3)\sum_{i=1}^{3}\alpha_i^2 \tag{3}$$

which gives the characteristic deformation dependence.

If $F(\mathbf{R})$ is a simple Gaussian function of R, we find from eq 1 and 3 the free energy for the Gaussian network $A = (1/2)k_{\mathrm{B}}T\sum_{i=1}^{3}\alpha_i^2$. (If we would have allowed the cross-links to fluctuate in the James and Guth sense the only change would be a factor $^1/_2$ in the modulus.)

However the correct expression for the free energy is[6]

[†] Present address: Max-Planck Institut für Polymerforschung, D-6500 Mainz, FRG.

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$$A(\alpha) = -k_BT\langle \ln F(\alpha\cdot\mathbf{R})\rangle = -k_BT \int d^3\mathbf{R} \ln F(\alpha\cdot\mathbf{R})F(\mathbf{R}) \quad (4)$$

where the averages are taken on the actual topology of the amorphous system. The approximation made in the second part of eq 4 restricts the theory to networks comprised of fixed or nonfluctuating junctions.

For general problems the average of the logarithm is a difficult mathematical task, and the most advanced method to this purpose is the use of the replica trick that is described in ref 6 and applied to the theory of rubber elasticity elsewhere.[7] It can be immediately seen that if $F(\mathbf{R})$ is a Gaussian function we find again the expression for the free energy of a Gaussian network through the second part of eq 4. However if $F(\mathbf{R})$ is a more complicated function, the results obtained by use of eq 1 (preaveraged version) can differ remarkably from those obtained with the correct eq 4. Employing a simpler mathematical treatment, we will show here that eq 4 yields analytical formulas for the force when noncomplex but realistic forms of the distribution function are used. Therefore, the differences between eq 1 and eq 4 can be numerically studied.

The second problem in the theory concerns separation of the short- and long-chain contributions to the macroscopic deformation of bimodal networks. Unfortunately, this separation can only be performed in an approximate way, which includes several assumptions on the estimation of macroscopic averages from the system characteristics. In the present work we also incorporate a modification to our previous scheme for this separation. The modification seems to be justified and, moreover, together with the nonpreaveraged treatment introduced above, contributes to give a considerably more realistic description of the experimental data.

Theory

Nonpreaveraged Formulation of the Elastic Force. In the case of simple elongation and taking the external z axis as the stretching direction, α has the form

$$\alpha = \begin{pmatrix} \alpha^{-1/2} & 0 & 0 \\ 0 & \alpha^{-1/2} & 0 \\ 0 & 0 & \alpha \end{pmatrix} \quad (5)$$

so that the transformation through deformation of the end-to-end vector, from $R(R,\theta,\phi)$ to $R_D(R_D,\theta_D,\phi_D) \equiv \alpha\mathbf{R}$, can be written in polar coordinates as

$$R_D = R \cos \theta(\tan^2 \theta\alpha^{-1} + \alpha^2)^{1/2} \quad (6)$$

$$\theta_D = \arctan (\alpha^{-3/2} \tan \theta) \quad (7)$$

$$\phi_D = \phi \quad (8)$$

The elastic force can be calculated from eq 4 since for a network of N_T chains

$$f(\alpha) = (\partial\Delta A/\partial L)_{T,V} = (1/L^\circ)(\partial\Delta A/\partial\alpha)_{T,V} \quad (9)$$

where ΔA is the free energy due to deformation, i.e., $\Delta A = A(\alpha) - A(1)$, and L° is the length of the sample equilibrium. Dividing over the cross-sectional area gives the elastic force per unit area

$$f^*(\alpha) = (1/V)(\partial\Delta A/\partial\alpha)_{T,V} \quad (10)$$

Then, taking into account the relationship $N_Tk_BT/V = \rho RT/M_c$, where k_BT is the Boltzmann factor, ρ is the network density, and M_c is the molecular weight between cross-links, the explicit form for $f^*(\alpha)$, according to eq 4 and 10, is

$$f^*(\alpha) = (\rho RT/M_c) \int_0^\infty dR\, R^2F(R) \int_0^\pi \int_0^{2\pi} [\partial \ln F(R_D,\theta_D,\phi_D)/\partial\alpha] \sin\theta\, d\theta\, d\phi \quad (11)$$

Since $F(\boldsymbol{R})$ can be expanded as[8,9]

$$F(R) = \sum_{l,m}^{\infty} F_{l,m}(R)Y_{l,m}(\theta,\phi) \quad (12)$$

we get

$$\partial F(R_D,\theta_D,\phi_D)/\partial\alpha = \sum_{l,m}\{[\partial F_{l,m}(R_D)/\partial R_D] \times (\partial R_D/\partial\alpha)Y_{l,m}(\theta_D,\phi_D) + F_{l,m}(R_D)[\partial Y_{l,m}(\theta_D,\phi_D)/\partial\theta_D](\partial\theta_D/\partial\alpha)\} \quad (13)$$

(ϕ_D does not depend on α since it is an invariant through deformation.)

From eq 6 we get

$$\partial R_D/\partial\alpha = (R_D/2\alpha)(2 - \alpha^{-3} \tan^2 \theta)/(1 + \alpha^{-3} \tan^2 \theta) \quad (14)$$

On the other hand, the coefficients $F_{l,m}(R)$ can be expressed in terms of expressions as[9,10]

$$F_{l,m}(R) = P_{l,m}(R) \sum_{k=0}^{M_l} g_k^{(lm)}R^{2k} \quad (15)$$

with $M_l = M - l$ (M is the number of even moments available for the inference procedure) and

$$P_{l,m}(R) \propto \exp[-a_{l,m}R^2 - (b_{l,m}R^2)^2] \quad (16)$$

Then, one obtains

$$\partial F_{l,m}(R_D)/\partial\alpha = P_{l,m}(R_D) \times [\sum_{k=0}^{M_l} g_k^{(lm)}R_D^{2k+1}(-2a_{l,m} - 4b_{l,m}^2R_D^2) + \sum_{k=1}^{M_l} 2kg_k^{(lm)}R_D^{2k-1}] \quad (17)$$

In order to simplify the theory we introduce two approximations. First, we neglect the nonsymmetric terms $l \neq 0$ in eq 13. This is equivalent to using $F(R_D)$ instead of $F(\mathbf{R}_D)$ in eq 11. Moreover, we neglect the terms with $k \neq 0$ in eq 15 for $F_{0,0}(R)$. Then, $F_{0,0}(R) \approx P_{0,0}(R)$. The influence of the different coefficients $g_k^{(00)}$ with $k \neq 0$ was studied in our previous work[1] based in the preaveraged theory, and it was concluded that their influence in the stress–strain curves is not very important from the quantitative point of view, though they contribute in some extension to the precise definition of the curve forms. Then, the simple addition of a non-Gaussian term in R^4 (eq 16) is able to describe the curve upturn to first order. Also, we are now undertaking the numerical investigation of this influence for the present nonpreaveraged theory, and, moreover, we also plan to investigate in the future the influence of the $F_{l,m}(R_D)$ terms, i.e., the coefficients of the nonsymmetric part of $F(\boldsymbol{R}_D)$.

With these simplifications, i.e., assuming $F(R_D) \approx (4\pi)^{-1/2}F_{0,0}(R_D) \approx (4\pi)^{-1/2}P_{0,0}(R_D)$, we obtain from eq 2, 11, 13, 14, and 17

$$f^*(\alpha) = (\rho RT/2M_c) \int_0^\infty dR\; W(R)I(\alpha,R) \quad (18)$$

where

$$I(\alpha,R) = (1/2\alpha) \int_0^\pi (-2a_{00}R_D^2 - 4b_{00}^2R_D^4) \times (2 - \alpha^{-3} \tan^2 \theta)/(1 + \alpha^{-3} \tan^2 \theta) \sin\theta\, d\theta \quad (19)$$

Substituting R_D in terms of R, θ, and α through eq 6 and solving the integrals in eq 19, we get (see Appendix)

$$I(\alpha,R) = (4a_{00}R^2/3)(\alpha - \alpha^{-2}) + (4b_{00}{}^2R^4/15)(2\alpha^2 - 2/\alpha)(3\alpha + 4/\alpha^2) \quad (20)$$

so that, finally

$$f^*(\alpha) = (\rho RT/M_c)[(2/3)a_R(\alpha - \alpha^{-2}) + (2b_R{}^2/15)C_R(2\alpha^2 - 2/\alpha)(3\alpha + 4\alpha^{-2})] \quad (21)$$

where

$$a_R = a_{00}\langle R^2\rangle$$

$$b_R = b_{00}\langle R^2\rangle$$

and

$$C_R = \langle R^4\rangle/\langle R^2\rangle^2 \quad (22)$$

depend directly on the first and second moments of R that are evaluated according to the procedure described in previous papers.[1,10] (a_{00} and b_{00} are fitted so that $P_{0,0}(R)$ reproduces the moments $\langle R^2\rangle$ and $\langle R^4\rangle$.)

Equation 21 can be compared with the corresponding result of the preaveraged theory described in ref 1 (with $g_k = 0$ for $k = 0$), which can be expressed as

$$f^*(\alpha) = (2\rho RT/3M_c)(\alpha - \alpha^{-2})[a_R + (2b_R{}^2/3)(\alpha^2 + 2/\alpha)] \quad (23)$$

It can be observed that the leading term in $\alpha - \alpha^2$ is identical in both equations (in fact represents the Gaussian contribution to the elastic force according to the very simple Kuhn theory[11]). However, the perturbation term due to the non-Gaussian contributions expressed through $b_R{}^2$ is completely different. Of course, this difference affects mainly the region of high elongations, where the upturns are manifested. A numerical study of eq 21 and its comparison with eq 23 will be explicitly performed in the next section.

Treatment of Bimodal Networks. The non-Gaussian contributions to rubberlike elasticity have been only experimentally manifested at high elongations in measurements with bimodal networks[4,5] (for which crystallization effects are not apparent). In order to understand the stress–strain curves of such networks, an adequate separation between the contributions of short and long chains should be performed. This separation has been attempted in ref 1, where we assumed that the forces in the individual long and short network chains are equal: i.e., they act as if they are in series (the same assumption is also considered by Curro and Mark, who derived this condition by using the maximum entropy criterion). Our separation procedure is detailed in ref 1. It can be summarized through the following equation:

$$G = f^*_{\text{exp}}(\alpha_{\text{macro}}) - 2C_2(1 - \alpha^{-3}{}_{\text{macro}}) = (2/3)(1 - 2/F)(\rho RT v_{2c}{}^{2/3}/\bar{M}_n)(L^0/L_i^0)f_i'(\alpha_i), \qquad i = \text{s, l} \quad (24)$$

where the experimental data of elastic forces vs. macroscopic elongations are introduced as $f^*_{\text{exp}}(\alpha_{\text{macro}})$. $(1 - 2/F)$ represents the factor corresponding to the phantom limit (F is the functionality of the junction points), and the $2C_2$ term takes care of the departure from this limit according to the approximate Mooney–Rivlin treatment.[12] The factor $v_{2c}{}^{2/3}$ is introduced to take into account the conditions under which the network was formed, v_{2c} being the volume fraction of the polymer during the cross-linking reaction.[13] Subscripts s and l apply for short and long chains, respectively, and

$$f_i'(\alpha_i) = f_i^*(\alpha_i)/(2\rho RT/3M_{c,i}), \qquad i = \text{s, l} \quad (25)$$

(for $i = \text{l}$, $f_l'(\alpha_l)$ reduces to the term $(3/2)(\alpha_l - \alpha_l{}^{-2})$ since $a_R \approx {}^3/_2$ and $b_R{}^2 \approx 0$ for long chains approaching to the Gaussian limit).

Table I
Coefficients a_R, b_R, and C_R for Poly(dimethylsiloxane) Chains of Different Lengths

N	a_R	b_R	C_R
10	−18.1423	3.0556	1.0586
20	−2.1993	1.2271	1.2283
30	−0.1283	0.7743	1.3581

The data for $f^*_{\text{exp}}(\alpha_{\text{macro}})$ applied simultaneously to describe the short- and long-chain behavior through eq 24, together with a relationship between the short- and long-chain and macroscopic deformations, which we assume to be of the form

$$\alpha_{\text{macro}} = \phi_s{}^{1/3}\alpha_s + (1 - \phi_s{}^{1/3})\alpha_l \quad (26)$$

(ϕ_i is the volume fraction of the i chains in the sample), allow us to obtain α_s, α_l, and an estimation of the number-average molecular weight $\bar{M}_n$. For the networks that will be numerically studied in the next section, the term $2C_2$ was estimated in preliminary fittings (see Table IV of ref 1), and these numerical values are maintained here since they are small and a better estimation cannot influence much the final results.

An estimation of L_i^0/L^0 is needed to solve eq 24 and 26. In our previous work[1] we estimated this ratio from the corresponding values of the moments of short and long chains $\langle R^2\rangle_i$ (eq 32 of ref 1). However, this purely microscopic relationship between independent equilibrium dimensions does not seem coherent with the use of volume fractions to obtain the macroscopic deformation in eq 26. In fact, it seems more reasonable to estimate L_i^0/L^0 also from those fractions as

$$L_i^0/L^0 = \phi_i{}^{1/3}, \qquad i = \text{s, l} \quad (27)$$

This slight modification of the separation scheme previously outlined has an important quantitative effect on the final results, as it will be shown in the next section.

Numerical Calculations and Discussion

Calculations for $f'(\alpha)$. In order to study the numerical differences between the preaveraged and nonpreaveraged theories in the prediction of stress–strain curves, we have obtained numerical values for $f'(\alpha)$, defined from eq 21 and 25 for poly(dimethylsiloxane) chains represented by means of the rotational isomeric model with statistical weight parameters corresponding to t = 25 °C of N(number of bonds) = 10, 20, and 30. The values of a_R, b_R, and C_R are calculated from the moments $\langle R^2\rangle$ and $\langle R^4\rangle$ previously obtained[1] and are presented in Table I. The results for $f'(\alpha)$ are shown in Figure 1, where the values obtained from eq 23 (old preaveraged theory) are also plotted for the sake of comparison. It can be observed that the new nonpreaveraged theory predicts much more abrupt upturns, in qualitative accordance with the experimental data (a more detailed comparison with the data will be given below). Moreover, the new theory yields nonintercepting curves, the values of $f'(\alpha)$ corresponding to shorter chains being always higher than those of longer chains. The preaveraged theory, nonetheless, gives curves whose form cannot be easily analyzed in terms of chain length, except at high extensibilities, where again the higher $f'(\alpha)$ corresponds to the shorter chain. In summary, the plots of $f'(\alpha)$ reveal that the new nonpreaveraged theory is able to predict results that follow more realistic patterns. In any case, differences between the results derived from both types of theories are very significant, and therefore, a revision of the qualitative and quantitative conclusions

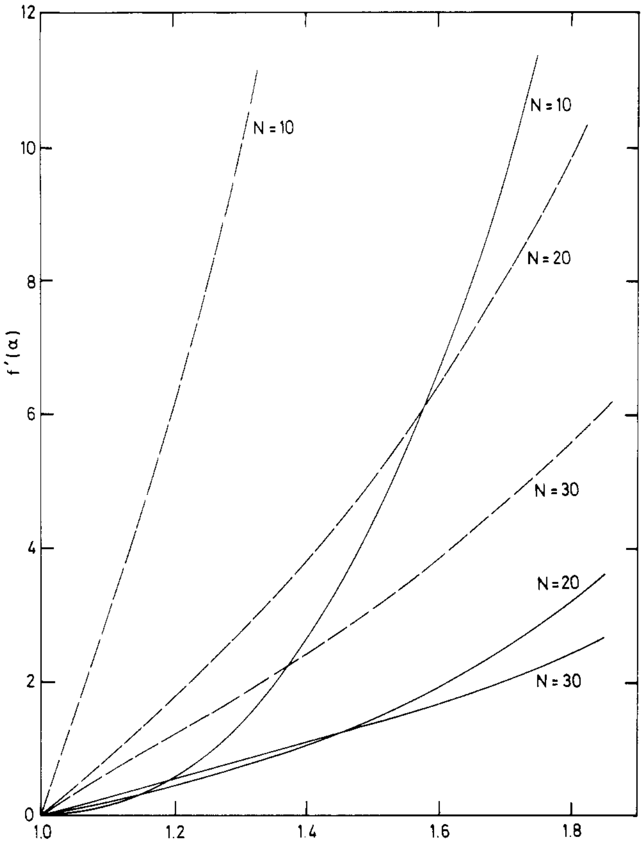

Figure 1. $f'(\alpha)$ vs. α for poly(dimethylsiloxane) chains of different lengths: (---) from eq 21 (new theory); (—) from eq 23 (old theory[1]).

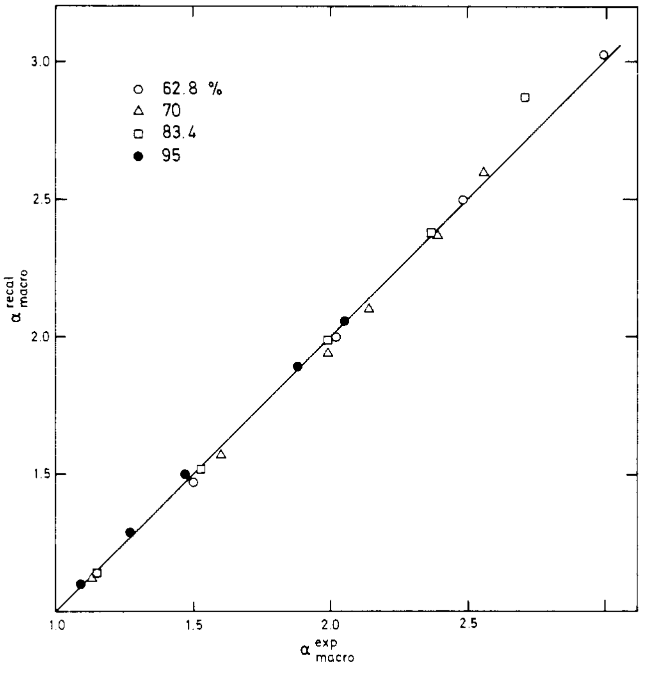

Figure 2. $\alpha_{\rm macro}$(recal) vs. $\alpha_{\rm macro}$(exptl) (see text) for data corresponding to samples with molecular weight of 18 500 + 1 100. (Molar compositions of short chains as indicated.) (—) $\alpha_{\rm macro}$(recal) = $\alpha_{\rm macro}$(exptl).

previously outlined by comparison with experimental data is clearly needed.

Fittings of Experimental Data. The data of Mark et al.[4,5] for bimodal networks of different compositions and short chain lengths, which were analyzed in our previous work,[1] are also employed as reference for the present

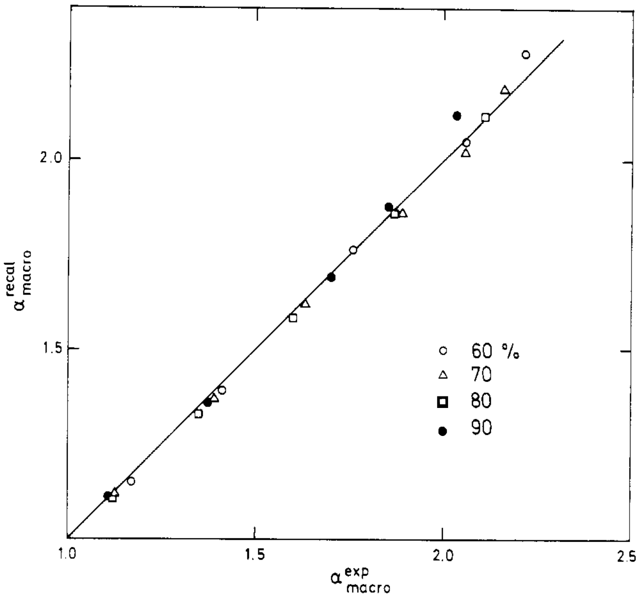

Figure 3. Same as Figure 2 but for molecular weight networks of 18 500 + 660.

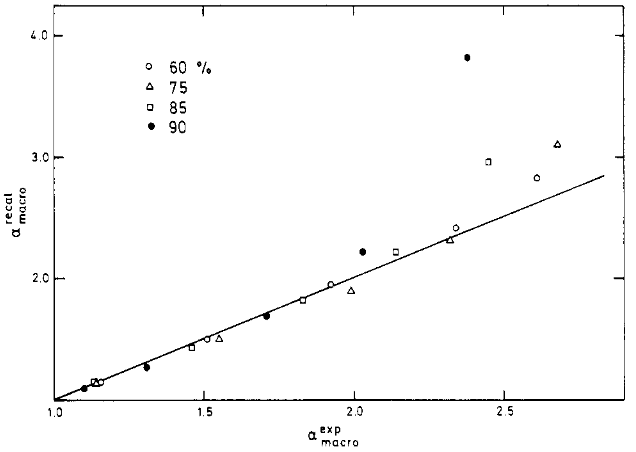

Figure 4. Same as Figure 2 but for molecular weight networks of 18 500 + 220.

theoretical results. Employing eq 24 for short and long chains and eq 26 (with the adequate experimental values of the physical constants and using eq 27 to obtain L_i^0/L^0), we have calculated the values of α_s, α_l, and $\bar{M}_n$ that best reproduce the different values of $f^*_{\rm exp}(\alpha_{\rm macro})$. α_s and α_l are fitted for each experimental point, while $\bar{M}_n$ is fitted with all the different data corresponding to a given network sample.

In Figures 2–4 we present the experimental values of $\alpha_{\rm macro}$ plotted together with the values of $\alpha_{\rm macro}$ recalculated from eq 26 by using the fitted values of α_s and α_l. The coincidence of both experimental and recalculated values along the straight line $\alpha_{\rm macro}$(exptl) = $\alpha_{\rm macro}$(recal) for the different data of a given sample indicates a good numerical fitting of $\bar{M}_n$ over all the sample points. Only at high extensibilities in the case of the networks composed by the short chain of lowest molecular weight (18 500 + 220) this coincidence is not found. It should be stressed that this particular network with extremely short chains could not be even treated with the old procedure since the fittings gave unphysical results. Then, our new numerical fittings can be considered satisfactory for the most representative cases.

The fitted values of $\bar{M}_n$ can be compared with those used to prepare the networks. This comparison serves as a test on the performance of the separation procedure. In Table

Table II
Values of $\bar{M}_n$ Calculated by Fitting with the Old and New Procedures and Expected from Preparation

% short chains	$10^{-3}\bar{M}_n$[a]	$10^{-3}\bar{M}_n$[b]	$10^{-3}\bar{M}_n$[c]
	mol wt = 18 500 + 1 100		
62.8	5.1	10.6	7.6
70.0	3.7	8.8	6.3
83.4	2.7	8.8	4.0
95.0	2.0	10.0	2.0
	mol wt = 18 500 + 660		
60.0	3.9	8.6	7.8
70.0	2.4	6.9	6.0
80.0	1.7	6.3	4.2
90.0	2.7	5.0	2.4
	mol wt = 18 500 + 220		
60.0		6.6	7.8
75.0		4.8	4.8
85.0		4.0	3.0
90.0		3.5	2.0

[a] Old procedure (ref 1). [b] Present work calculations. [c] Expected from preparation.

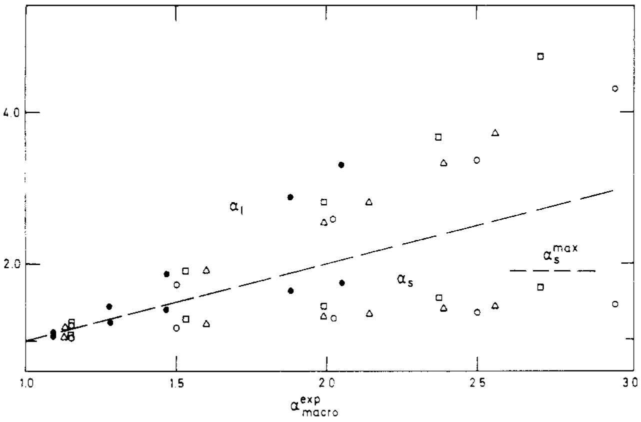

Figure 5. Deformations of long and short chains as a function of the experimental macroscopic deformation for samples with molecular weight of 18 500 + 1 100. The dash line corresponds to affine deformation. Molar compositions of short chains: (○) 62.8%, (△) 70.0%, (□) 83.4%, and (●) 95%.

II we have summarized the results for $\bar{M}_n$ obtained with the old and new treatments together with those expected from preparation. It should be pointed out that our new treatment yields values of $\bar{M}_n$ considerably higher than those obtained in our previous fittings with the old theory and, in general, they are also higher than the expected values. This latter discrepancy can be justified as a consequence of noncomplete linking effects in the preparation procedure, except in the systems with a very high proportion of short chains, for which the fitted values of $\bar{M}_n$ are too high. Nevertheless, the small fitted values of $\bar{M}_n$ obtained in the most typical cases with the old treatment (about half of the expected value) are much more difficult to explain. Therefore, it seems that the use of the new nonpreaveraged new theory, together with the modified way to estimate L_i^0/L^0, leads to fittings that yield considerably more realistic values of $\bar{M}_n$ than our old treatment, so that the new theory only fails for network compositions close to 100% short chains. It should be remarked that the independent use of either the new nonpreaveraged theory or the new estimation of L_i^0/L^0 leads to a more modest improvement in the prediction of $\bar{M}_n$, and only the simultaneous introduction of both modifications is able to give what we consider as a satisfactory agreement for most samples.

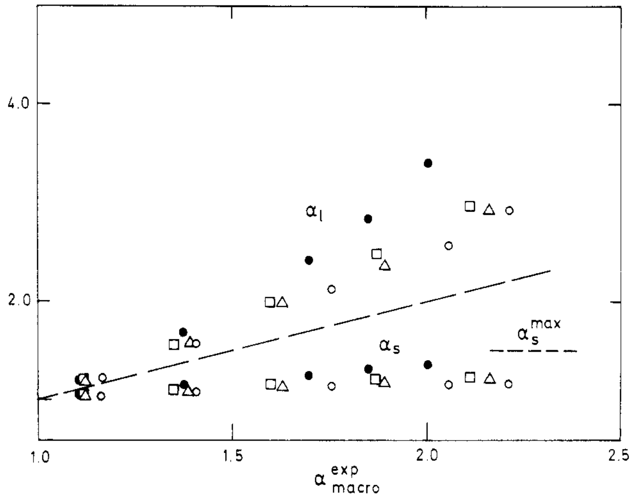

Figure 6. Same as Figure 5 but for molecular weight networks of 18 500 + 660. Molar compositions of short chains: (○) 60%, (△) 70%, (□) 80%, and (●) 90%.

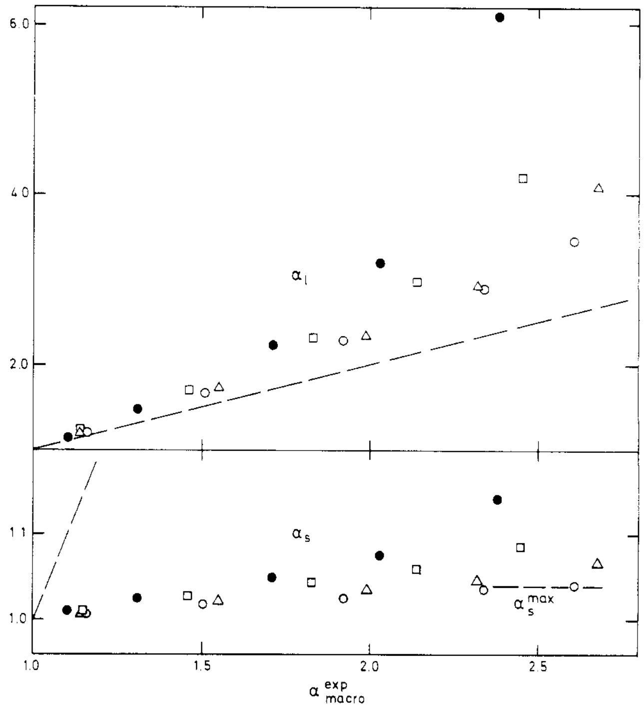

Figure 7. Same as Figure 5 but for molecular weight networks of 18 500 + 220. Molar compositions of short chains: (○) 60%, (△) 75%, (□) 85%, and (●) 90%.

In Figures 5–7 the fitted values of α_s and α_l for the different values of α_{macro}(exptl) are shown. With respect to the same type of plots obtained with the old treatment (see Figures 12 and 13 of ref 1) we should point out that the separation between the values of α_s and α_l is now clearer, even at small extensibilities (where the old procedure gave some confusing results). Another difference is that the new values of α_s are smaller than the result corresponding to the chain maximum extensibility, α_s(max) (except those corresponding to high extensibilities in the very short chain network, molecular weight of 18 500 + 220, for which fittings are not good as commented above). However, the values of α_s obtained with the old procedure for the intermediate system (molecular weight 18 500 + 660) were above α_s(max). Then, the new treatment is again shown to yield a considerably more coherent pattern of fitted results than those previously obtained. Notwithstanding, some of the earlier conclusions can be now confirmed. Thus, it seems clear that the long chains deform much more than the short ones, the latter approaching

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their maximum extensibility limit very rapidly.

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Appendix

Substituting eq 6 in eq 19, we get

$$I(\alpha,R) = I_1(\alpha,R) + I_2(\alpha,R) \tag{A1}$$

where

$$I_1(\alpha,R) = -a_{00}\alpha R^2\int_0^\pi \cos^2\theta(2-\alpha^{-3}\tan^2\theta)\sin\theta\,\mathrm{d}\theta \tag{A2}$$

and

$$I_2(\alpha,R) = -2b_{00}{}^2\alpha^3R^4\int_0^\pi \cos^4\theta(1+\alpha^{-3}\tan^2\theta)\times (2-\alpha^{-3}\tan^2\theta)\sin\theta\,\mathrm{d}\theta \tag{A3}$$

and, through straightforward simplifications, we get

$$I_1(\alpha,R) = -a_{00}R^2\left[2\alpha\int_0^\pi \cos^2\theta\sin\theta\,\mathrm{d}\theta - \alpha^{-2}\int_0^\pi \sin^3\theta\,\mathrm{d}\theta\right] \tag{A4}$$

together with

$$I_2(\alpha,R) = -2b_{00}R^4\left[2\alpha^3\int_0^\pi \cos^4\theta\sin\theta\,\mathrm{d}\theta + \int_0^\pi \cos^2\theta\sin\theta\,\mathrm{d}\theta - \alpha^{-3}\int_0^\pi \sin^5\theta\,\mathrm{d}\theta\right] \tag{A5}$$

The involved integrals are simply solved so that the results for I_1 and I_2 are written as the first and second terms on the right side of eq 20.

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Transient Viscoelastic Properties of Linear Polymer Solutions

Yoshiaki Takahashi,* Yoshinobu Isono,[†] Ichiro Noda, and Mitsuru Nagasawa

Department of Synthetic Chemistry, Nagoya University, Chikusa-ku, Nagoya 464, Japan.

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ABSTRACT: Shear and normal stress developments after stepwise increases of shear rate from a steady shear rate $\dot\gamma_1$ to a higher one $\dot\gamma_2$ were observed with a Weissenberg rheogoniometer Type R-17 in linear polystyrene solutions. The initial parts of the stress-development curves at different $\dot\gamma_2$ compose a single line if $\dot\gamma_1$ is kept constant, and the initial slope becomes lower with increasing $\dot\gamma_1$. It was concluded that the original quasi-network structure of polymer solutions remains unchanged until a certain critical strain is accumulated in the solution. The difference in the initial slope at different $\dot\gamma_1$ may be caused by a change in the effective entanglement density with $\dot\gamma$. It is also pointed out that the additivity of responses in viscoelastic behavior of polymer solutions does not hold in nonlinear regions.

Introduction

In concentrated solutions and melts of linear polymers the polymer molecules are entangled with each other, forming a quasi-network structure. The entanglements may be dissolved and re-formed continuously, and the structure of the solution may be represented by the equilibrium entanglement density. The effective entanglement density is changed by external stimuli given to the polymer solution, such as shear rate.[1–3] It was pointed out in previous papers[4,5] that the structure cannot be changed at the instant when an external stimulus is given to the solution, but changes with a time lag. It is as if the quasi-network is ruptured when a certain strain has accumulated in the solution. This speculation was experimentally supported by observing the stress developments in a polymer solution when a steady shear flow is instantly given to the solution. The initial slopes of the transient viscosity vs. time plots at various shear rates agreed with that at the limit of zero shear rate, independent of shear rate.[4–7]

Under steady shear flow, polymer solutions have a quasi-network structure characterized by an effective density of entanglements, which decreases with increasing shear rate. It may, therefore, be reasonable to predict that the steady structure of polymer solutions at $\dot\gamma_1$ would not be changed to that at $\dot\gamma_2$ at the instant when the shear rate is instantly changed from $\dot\gamma_1$ to a higher value $\dot\gamma_2$ but that the rupture of the original structure would occur with a certain time lag. An aim of this work is to test the idea of the network-rupture model by observing stress development after a stepwise increase of shear rate from a value $\dot\gamma_1$ to a higher value $\dot\gamma_2$.

Moreover, the viscoelastic properties of polymer solutions and melts are phenomenologically described by various types of constitutive equations, usually by those of the so-called single-integral type with a memory function $\mu(t - t')$ or an aftereffect function $\phi(t - t')$, where t and t' are the present and past time, respectively.[8,9] These

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[†] Present address: Department of Material Science and Technology, Technological University of Nagaoka, Nagaoka 949-54, Japan

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