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A Note on the Chain Entanglement in Concentrated Polymer Solutions

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A crude form of the relaxation spectrum for concentrated polymer solutions is presented, which is compatible, though not quantitatively, with recent experimental results of the steady-shear viscosity and compliance.

INTRODUCTION

This is an English version of our old note which was published in Japanese some years ago.[1] Not a few experimental results have been accumulated in our laboratory since then, and we now conceive that in the fully entangled state of polymers, the steady-shear compliance J_e^0 is proportional to the inverse cubic power of polymer weight concentration c rather than the inverse square power.[2,3] Thus, the following analysis which is based on the inverse square dependence of J_e^0 on c has to be modified at least in this respect. Nevertheless, we decided to present this note in its original form, hoping that it still might have some value for elucidating a gross structure of the relaxation spectrum of polymer concentrates. It is one of our purposes to show that the apparently complicated dependence of J_e^0 on c as illustrated in Fig. 2 is compatible with a very simple combination of the wedge-type and the box-type spectra for the relaxation modes.

STEADY-SHEAR VISCOSITY AND COMPLIANCE

The slow relaxation properties of polymer concentrates may be characterized in terms of two parameters, the steady-shear viscosity η and the steady-shear compliance J_e^0. As for the former, it has long been recognized that***

$$\eta = AM \quad \text{for } M \leq M_c \tag{1a}$$

$$\eta = BM^{3.5} \quad \text{for } M > M_c \tag{1b}$$

where M is the molecular weight of the polymer, and A, B, and M_c are constants determined by the polymer concentration c.[4] The above two equations can be built in a simple two-term equation

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*** Rigorously speaking, η should be regarded as the viscosity of the state of a constant friction coefficient ζ.

$$\eta = AM + BM^{3.5} \quad (2).$$

The big difference between two exponents, 1 and 3.5, assures a sharp transition from the behavior of Eq. (1a) to that of Eq. (1b) in agreement with experimental results. We can always locate in the double logarithmic plot of η against M a critical molecular weight M_c at which two straight lines with slopes 1 and 3.5 intersect quite sharply. This transition has a tendency to become gradual as the polymer concentration c is decreased, but still there is no difficulty to assess M_c. The values of M_c determined in this way are proportional to the reciprocal of c in most systems, and we have for example a relationship

$$cM_c = 3.6 \times 10^4 \quad (3)$$

for polystyrene solutions in Aroclor.[5] Here c is expressed in gram per cubic centimeter. This equation suggests that the solvent acts merely as a diluent for the polymer.

On the other hand, the behavior of J_e^0 as function of M and c has long been in controversy. Recent experimental results obtained for narrow distribution polymers seem to support a unified view that

$$J_e^0 = \alpha(M/cRT) \quad \text{for small values of M and c} \quad (4a)$$

$$J_e^0 = \beta/c^{\nu} \quad \text{for large values of M and c} \quad (4b)$$

where R is the gas constant, T is the absolute temperature, and α, β, and ν are constants independent of M and c. However, there still remains some controversy unsettled among investigators if one looks at more detailed behavior of J_e^0. For example, some investigators have shown that ν in Eq. (4b) is approximately two, while we prefer to set it as $\nu=3$, as already mentioned in the beginning of this note. But we will not go further into this problem.

Graessley and Segal have shown that their experimental data can be represented by a two term equation of the reciprocal of J_e^0:[6]

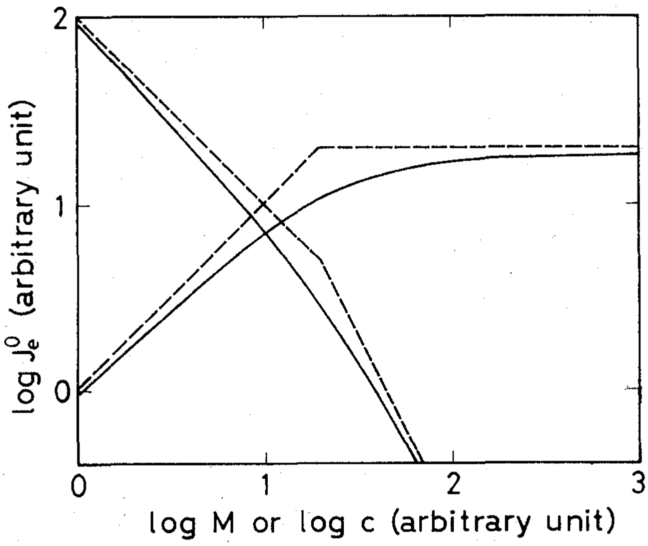

Fig. 1. The molecular weight- and concentration-dependences of J_e^0 as calculated from Eq.(5b). The broken lines show their asymptotes.

$$\frac{1}{J_e^0}=\frac{cRT}{\alpha M}+\frac{c^2}{\beta} \tag{5a}$$

or

$$J_e^0=\left(\frac{\alpha}{1+\alpha_2 cM}\right)\frac{M}{cRT}, \qquad \alpha_2\equiv\frac{\alpha}{RT\beta} \tag{5b}.$$

For small values of the product cM such that $cM \ll 1/\alpha_2$, this equation reduces to Eq. (4a), while for large values of cM, it reduces to Eq. (4b). This equation is, in a sense, analogous to Eq. (2), but it predicts only a gradual change between two limiting types of behavior, Eqs. (4a) and (4b), as illustrated in Fig. 1. Any sharp transition can hardly be observed on neither the log J_e^0 *vs.* log M curve nor the log J_e^0 *vs.* log c curve, in contrast to the case of the log η *vs.* log M curve. Porter *et al.* have also reported the data which are in agreement with Eq. (5).[7] But other groups of investigators have found that the change in the behavior of J_e^0 occurs somewhat more sharply at around a certain critical value of

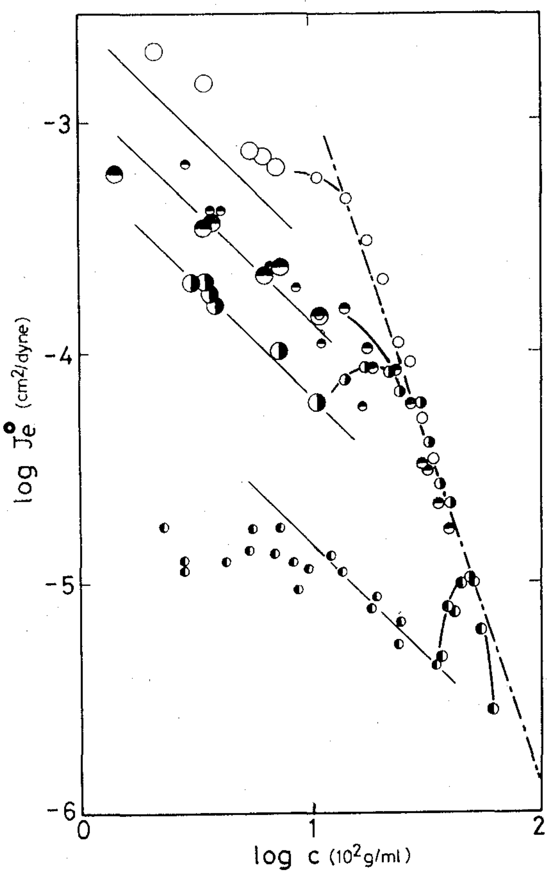

Fig. 2. The concentration dependence of J_e^0 obtained for narrow-distribution polystyrenes in Aroclor.[2] Molecular weights of the polymers are 1.80×10^6 (open circles), 8.60×10^5 (top-filled), 4.11×10^4 (right-filled), 9.72×10^4 (left-filled, medium circles), and 8.20×10^4 (left-filled, small circles). Thin solid line corresponds to $J_e^0=0.4\ M/cRT$ for each sample and the dashed line is drawn with a slope -3.

molecular weight M_J. For example, Onogi *et al.* have mentioned that in the case of polystyrene, M_J is approximately equal to the corresponding quantity M_c for the viscosity,[8] and Odani *et al.* have found after an extensive survey of the existing data that M_J is twice or three times as large as M_c is.[9] This last view implies that the so-called Rouse behavior of Eq. (4a) persists beyond M_c over a certain range of M, though not over the whole range as often assumed in the earlier view. In addition, the concentration dependence of J_e^0 revealed by us shows a complicated profile as illustrated in Fig. 2, which is essentially different from that given in Fig. 1.

Under these circumstances, it may be of some value to note that a set of experimental results selected from the above is compatible with a very simple form of the relaxation spectrum.

RELAXATION SPECTRUM

Define a parameter M_e which represents an average molecular weight between entanglement coupling points along a polymer chain, and put

$$y = M/M_e \tag{6}$$

Since the product cM_e, just like cM_c in Eq. (3), must be a constant characteristic of a given polymer-diluent system at least approximately, the reduced variable y is proportional to M when c is fixed, and to c when M is fixed.

When $M < M_e$, each polymer chain will be free from entanglement, and the relaxation spectrum $H(\tau)$ may be expressed as

$$H(\tau) = \frac{1}{2}\left(\frac{cRT}{M}\right)\left(\frac{\tau_1}{\tau}\right)^{1/2} \tag{7}$$

$$\tau_1 = \left(\frac{\zeta a^2}{6\pi^2 kT}\right)\left(\frac{M}{m_0}\right)^2 \tag{8}$$

Here τ_1 represents the longest relaxation time in the Rouse theory.[10] Other notations in Eq. (8) have its usual meanings: ζ is the friction coefficient of a segment, m_0 is its molecular weight, a is the average-statistical length, and k is the Boltzmann constant. The viscosity η, the normal stress coefficient θ, and the steady-shear compliance J_e^0 are related to $H(\tau)$ as

$$\eta = \int_0^\infty H(\tau)d\tau \tag{9}$$

$$\frac{\theta}{2} = \int_0^\infty H(\tau)\tau d\tau \tag{10}$$

$$J_e^0 = \frac{\theta}{2\eta^2} \tag{11}$$

respectively. Thus, substitution of Eq. (7) into Eqs. (9) to (11) yields

$$\eta = \frac{cRT}{M}\tau_1 \propto cM \tag{12}$$

$$J_e^0 = \frac{1}{3}\frac{M}{cRT} \tag{13}$$

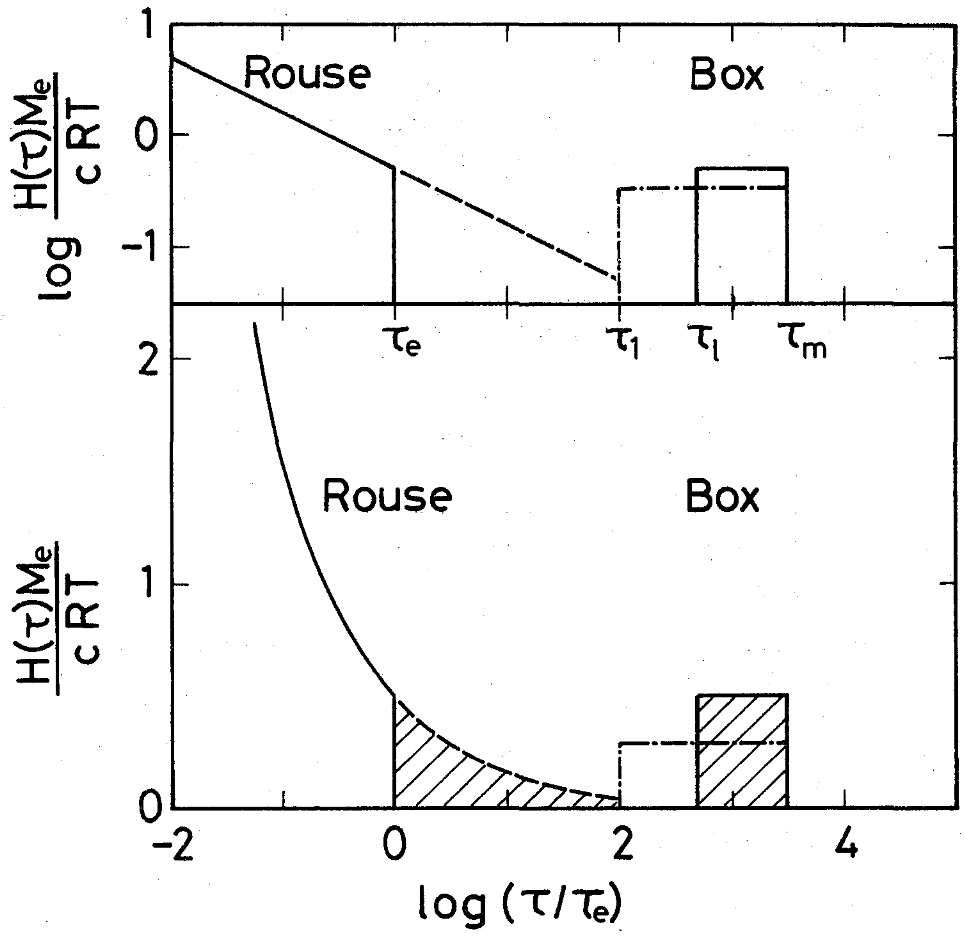

Fig. 3. The assumed model of the relaxation spectrum $H(\tau)$ for a system with $M=10\ M_e$. The solid line for the box corresponds to $h=2.0$, and the chain line to $h=3.5$.

The numerical factor 1/3 in Eq. (13) is different from the correct value 0.400 because of the use of the approximate continuous form, Eq. (7), in place of the original discontinuous spectrum. But we ignore such a difference as this.

When $M>M_e$, the Rouse-type spectrum may be applied only to the molecular motions having τ smaller than τ_e:

$$\tau_e=\left(\frac{\zeta a^2}{6\pi^2 kT}\right)\left(\frac{M_e}{m_0}\right)^2=\frac{\tau_1}{y^2} \tag{14}$$

This part of the spectrum which is of the wedge type is schematically shown in Fig. 3 by the solid line. On the other hand, the molecular motions involved in the dotted trapezoid are subjected to the entanglement coupling interactions, and they will be shifted towards longer times. Since no established theory is available for these modes of molecular motions, we simply assume the box-type spectrum for them, and put

$$H(\tau)=\frac{1}{2}\left(\frac{cRT}{M}\right)\left(\frac{\tau_1}{\tau}\right)^{1/2} \qquad 0<\tau<\tau_e \tag{15a}$$

$$H(\tau)=\frac{1}{h}\left(\frac{cRT}{M_e}\right) \qquad \tau_1<\tau<\tau_m \tag{15b}$$

The maximum relaxation time τ_m must be put

$$\tau_m=y^{3.5}\tau_e \tag{16}$$

to recover Eq. (1b) from Eqs. (9) and (15a, b). The lower bound τ_1 of the box spectrum may be determined with the aid of the auxiliary condition that

$$\int_{\tau_e}^{\tau_1} H_{Rouse}\ d\ \ln\ \tau=\int_{\tau_1}^{\tau_m} H_{Box}\ d\ \ln\ \tau \tag{17}$$

This is an analogy of the famous Debye assumption in the theory of specific heat, and represents the conservation of the degrees of freedom in molecular motions during the process of entanglement formation. Thus, we obtain

$$\begin{aligned}\tau_1&=\tau_m \exp\left[-h\left(1-\frac{1}{y}\right)\right]\\ &=\tau_e y^{3.5} \exp\left[-h\left(1-\frac{1}{y}\right)\right]\end{aligned} \tag{18}$$

Furthermore, τ_1 must be larger than τ_e, otherwise some modes of molecular motions will result in the shift of wrong direction. This condition leads to the condition that

$$h\leq 3.5 \tag{19}$$

Within this limit, we can assign any value for the parameter h. Thus two possible forms of the box-type spectrum are illustrated in Fig. 3 by the solid and the chain lines, where y is put 10, and h is put 2 and 3.5.

The viscosity η and the steady-shear compliance J_e^0 are readily obtained by substituting Eqs. (15a, b) into Eqs. (9) to (11). The results are

$$\eta=\frac{cRT}{M_e}\tau_e\left[1+\frac{y^{3.5}}{h}\left\{1-\exp\left[-h\left(1-\frac{1}{y}\right)\right]\right\}\right] \tag{20}$$

$$J_e^0=\frac{M_e}{3cRT}F(y) \tag{21}$$

$$F(y)\equiv\frac{1+(3/2h)y^7\{1-\exp[-2h(1-y^{-1})]\}}{[1+h^{-1}y^{3.5}\{1-\exp[-h(1-y^{-1})]\}]^2} \tag{22}$$

Eq. (20) is essentially a two-term equation similar to Eq. (2). On the other hand, Eq. (21) is different from Eq. (5b). The molecular weight dependence of J_e^0 is represented by F(y), while the concentration dependence by $F(y)/y^2$.

Figure 4 illustrates the M-dependence of η, and the M- and c-dependences of J_e^0 calculated by Eqs. (20) and (21). The log η *vs.* log M curve shows a sharp turn at about $M_c=1.7\ M_e$ (h=3.5) and 1.6 M_e (h=2) as expected. The log J_e^0 *vs.* log c curve displays a maximum qualitatively in agreement with the behavior shown in Fig. 2. But the slope of the branch for high concentrations is −2, which is not in agreement with our experimental value, −3. The log J_e^0 *vs.* log M curve also shows a slight maximum at the shoulder part, and it makes sharp the connection of the horizontal branch and the Rouse branch of the curve. The lower end of the horizontal branch is located around $2\,M_c$,

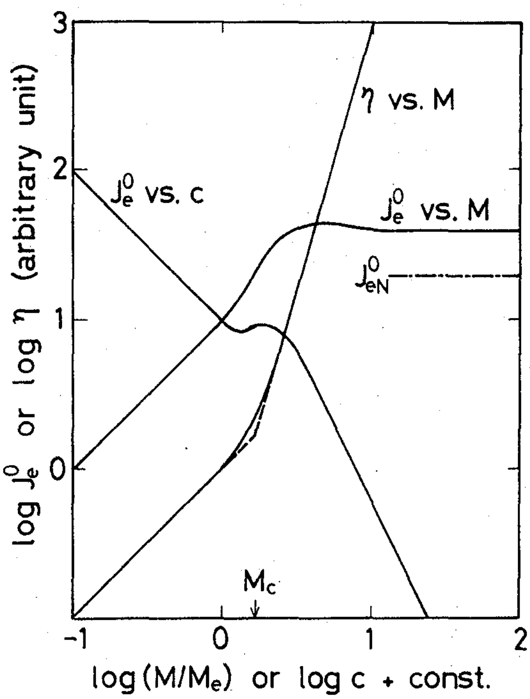

Fig. 4. The molecular weight dependence of η and the molecular weight- and concentration-dependences of J_e^0 as calculated from Eqs. (20) to (24).

which is practically in agreement with M_J determined by Odani *et al.*[9]

The so-called entanglement compliance J_{eN}^0 may be obtained as

$$J_{eN}^0=\frac{M_e}{cRT} \qquad \text{independent of h} \tag{23}$$

This is to be compared with

$$\lim_{y\to\infty} J_e^0=\frac{h}{2}\left[\frac{\exp(2h)-1}{(\exp h-1)^2}\right]\frac{M_e}{cRT} \tag{24}$$

Thus, the ratio of this limiting value of J_e^0 to J_{eN}^0 is about 2 when h=3.5. However, if we calculate the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, by standard procedures, the minimum appearing in the $G''(\omega)$ *vs.* ω curve is too deep in comparison with the observed results. This is undoubtedly originated from the complete removal of relaxation modes from the region lying between τ_e and τ_1. In real systems, there must remain a considerable number of modes in this region as a result of the distribution of the entanglement spacing. However, it may be nonsensical to embelish further a crude model as the present.

Finally, we must refer to the work of Janeschitz-Kriegl.[11] He has also shown that J_e^0cRT/M shows a maximum at around a critical concentration or molecular weight. His spectrum $H(\tau)$ consists of two wedges which are separated by a distance in the time scale, and it predicts J_e^0 to be proportional to M in both regions of small M and large M.

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