(7) D. B. V. Parker, *Eur. Polym. J.*, 5, 93 (1963).
(8) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuck, *J. Am. Chem. Soc.*, **86**, 1046 (1964).
(9) G. A. Olah, S. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962).
(10) J. Kuo, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1973.
(11) T. Higashimura, O. Kishiro, and T. Takeda, *J. Polym. Sci., Polym. Chem. Ed.*, 14, 1089 (1976).
(12) J. Skura and R. W. Lenz, submitted for publication.

Nonlinear Viscoelasticity of Concentrated Polymeric Liquids

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ABSTRACT: Following Doi and Edwards, the topological constraints imposed on a polymer molecule by surrounding molecules are described by means of a harmonic potential which confines the molecule in a "tube" of a certain radius. In reviewing this theory, a number of equations are rederived by a different method. The result of the calculation defines the free energy of the molecule in the tube and this leads in a straightforward manner to the tensile force in the molecule and to the lateral pressure exerted by it. In contrast to the assumption made by Doi and Edwards, it is assumed that a deformation of the system gives rise to a new tube radius. Its magnitude is determined by the equilibrium between the lateral pressure exerted by the molecule and the elastic response of the surrounding medium. This model gives results that are intermediate between the extreme cases of constant tube radius assumed by Doi and Edwards and constant segment volume assumed by Marrucci and de Cindio. It depends on the constitutive properties of the system which one of the limits is approached. Moreover, the model explains in a natural way the experimentally observed maximum in plots of elongational viscosity vs. stretching rate.

The nonlinear viscoelastic behavior of concentrated polymeric liquids, either melts or solutions, has long been described by the use of a strict analogy with the classical theory of rubber-like elasticity. Instead of permanent junction points of the chain network made by the chemical cross-links, impermanent junctions due to entanglements were supposed. The chains of the network were assumed to follow affinely the external deformation, and only the renewal rate of the impermanent junctions remained to be established. By taking a constant renewal rate, Lodge[1] derived the following equation for the stress tensor

$$\sigma = \int_{-\infty}^{t} \mathbf{C}_t^{-1}(t')\mu'(t-t')\,\mathrm{d}t' \qquad (1)$$

where $\mathbf{C}_t(t')$ is the "history" of the Cauchy deformation tensor and μ' is called the memory function.

Subsequent modifications of Lodge's theory, by the use of different assumptions on the rate of junction renewal, gave rise to equations similar to eq 1 but with a different memory function, which also depended on some scalar measure of the deformation history. In any case, the tensorial form of the stress tensor was dictated by $\mathbf{C}^{-1}$, which is a consequence of the assumption of affine deformation.

A novel approach was recently taken by Doi and Edwards[2-5] on the basis of the "reptation" idea of de Gennes.[6] The fundamental assumption is that long linear flexible macromolecules in concentrated systems can only diffuse along their own length, the lateral movements being effectively hindered by the topological constraints made by the other chains. With appropriate additional assumptions, Doi and Edwards derived the following constitutive equation

$$\sigma = \int_{-\infty}^{t} \mathbf{Q}_t(t')\mu'(t-t')\,\mathrm{d}t' \qquad (2)$$

where $\mathbf{Q}$ is a tensor quite different from $\mathbf{C}^{-1}$.

Equation 2 shows many interesting features which are at variance with those derived by means of eq 1. For example, in a shear flow the tensor $\mathbf{Q}$ predicts a nonzero negative value for the second normal stress difference, in agreement with experiments, while the tensor $\mathbf{C}^{-1}$ gives zero for that quantity. Also, eq 2 "naturally" predicts a shear rate dependent viscosity while in order to obtain the same result from eq 1 it is necessary to adopt a memory function which, in one way or another, depends on the deformation history.

Although the approach used by Doi and Edwards is undoubtly sound and the general picture of the physics involved is extremely appealing, it appears that one of the assumptions made in the derivation is open to question. The matter has already been considered in a recent paper[7] where it is shown that the relaxation behavior of a molten polymer at high extensions agrees better with a variant of the theory which was obtained in ref 7 by modifying the assumption in question. On the other hand, relaxation data obtained in concentrated solutions[8] seem to agree much better with the predictions by Doi and Edwards.[3]

In this paper we shall further examine this matter and offer a possible solution. The motivations for this analysis are briefly indicated as follows. In the first place, the assumption made in ref 3 is in itself a doubtful one, for which the authors themselves develop only a "plausible" argument. At first sight, the alternative advanced in ref 7 looks more consistent with the overall model but, when carefully inspected, it also presents nonnegligible difficulties. Second, either assumption leads to results which should apply universally, i.e., independently of any characteristics of the particular system, whereas the actual behavior of different concentrated polymeric liquids indicates that differences, even qualitative ones, indeed exist. Finally, some of the predictions of the theory by Doi and Edwards appear unsatisfactory. We refer in particular to the behavior in elongational flow which is considered in ref 5. It is there predicted that the elongational viscosity

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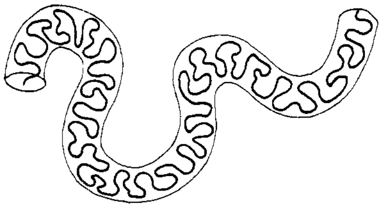

Figure 1. The chain and the tube which confines it.

never exceeds three times the zero-shear viscosity whereas there exists experimental evidence to the contrary.

In the following, we shall first briefly reexamine the model in general terms. We shall then consider the thermodynamic properties of a chain laterally constrained by the other chains, which present new aspects compared to the case of a free chain. By appropriately reformulating the assumptions about the effect of the deformation on these constraints, we shall then derive an expression for the stress tensor. The case of an elongational flow will finally be considered as an example.

Generalities about the Model

The general approach is the same as that used by Doi and Edwards and consists of studying the behavior of a single polymer chain belonging to the system with the rest of it accounted for by means of appropriate actions or restrictions exerted upon the given chain.

The fundamental restriction is that determined by the impossibility for the chain to move sideways any significant distance without "cutting" other chains. The model accounts for this restriction by assuming that the chain is confined within a tube-like region of appropriate diameter such as that schematically represented in Figure 1. One should not think that the tube is occupied only by the given chain. Segments of other chains will also be present in the tube since the tube is representative of the topological confinement of the chain, not of the ordinary intermolecular forces. Indeed, the determination of the diameter of this tube from first principles is still an open problem.

The thermal movement of the chain consists of a fast "wriggling" motion inside the tube which also determines a slow diffusion of the whole chain along the axis, called a "reptation" by de Gennes.[6] In ref 2 and 6, it is shown that rearrangements of the chain inside the tube will take place within a time proportional to M^2 while the diffusion of the chain out of the tube, to generate a new one, takes a time—called the disengagement time—which is proportional to M^3. With respect to these motions, the tube geometry can be considered as fixed. In a recent paper,[9] Klein has shown that the characteristic time for a significant change in the tube geometry would be proportional to M^5.

When the system is deformed, the tube geometry is altered by the deformation and the chain within it "reacts" by a sequence of two events which have a different time scale. First, the chain will rearrange itself within the deformed tube. Then it will diffuse out of the tube to create a new one. The second process, being the slowest one, is that which essentially determines the time dependence of the viscoelastic response. The modality of tube deformation as well as the fast rearrangement of the chain within the tube are what determine the tensorial dependence of the stress upon the applied deformation.

It is mainly the latter problem that is considered in this paper. We shall assume throughout that the behavior of the chain is Gaussian. A consistency test will be made on the results which shows under what conditions this assumption is indeed satisfied.

Equilibrium Properties of a Chain in a Tube

When a chain of infinite length is confined within a tube of assigned diameter, there exists an equilibrium line density of chain monomers along the tube. This has been calculated by Doi and Edwards[3] by the use of a harmonic potential as a means of representing the tube confinement. The relevant equations are here reproduced with the inclusion of the numerical constants which are needed in the following.

If x and y are Cartesian coordinates in a cross section of the tube with the origin at the center, the harmonic potential V is written as

$$\frac{V}{kT} = \frac{w^2}{6}(x^2 + y^2) \tag{3}$$

The results needed for the following are derived in the Appendix by a method different from that of Doi and Edwards. We quote, first of all, the result for the ensemble average

$$\langle x^2 + y^2 \rangle = b/w \tag{4}$$

where b is the monomer length. It has been found convenient to define a tube "radius", a, according to the definition

$$a^2 = 2\langle x^2 + y^2 \rangle \tag{5}$$

which means that the parameter in the harmonic potential is given by

$$w = 2b/a^2 \tag{6}$$

We note further that eq A2 in the Appendix defines the probability of finding n monomers in a length l of the tube, i.e.,

$$P_l(n) \propto n^{-1/2} \exp\left(-\frac{3l^2}{2b^2n} - \frac{2b^2}{3a^2}n\right) \tag{7}$$

If this is maximized with respect to n, one gets

$$n = \frac{3a^2}{8b^2}\left\{\left(1 + \frac{16l^2}{a^2}\right)^{1/2} - 1\right\} \tag{8}$$

if $l/a \gg 1$, eq 8 simplifies to

$$n/l = 3a/2b^2 \tag{9}$$

which corresponds to neglecting the pre-exponential term in eq 7. (It may be noted that if $l/a \ll 1$, eq 8 gives $l^2 = \langle Z^2 \rangle = nb^2/3$, which is the classical result for a free chain.)

Equation 9 gives the equilibrium line density of monomers along the tube as calculated by Doi and Edwards, who also show that, since the relative fluctuation of this quantity is very small, n/l is indeed a well-defined thermodynamic property.

However, the significance of eq 7 is really a much more comprehensive one, as it defines the Helmholtz free energy of a chain made up of n monomers in a length l of tube. Neglecting the pre-exponential factor, we write

$$A = kT\left(\frac{3l^2}{2b^2n} + \frac{2b^2n}{3a^2}\right) \tag{10}$$

Consequences of this form of the free energy, which includes the effect of the topological constraints due to neighboring chains, are expected to play a role also in the behavior of cross-linked rubbers. This matter will be taken up in a later paper.

The derivative of A with respect to l, at constant n and a, gives the tension F along the tube axis

$$F = \frac{3kT}{b^2}\frac{l}{n} \tag{11}$$

In spite of the similarity with the classical equation giving the tension in a chain fixed at both ends, eq 11 has a somewhat different meaning since l is a curvilinear distance along the tube rather than the end-to-end distance of the chain. A better descriptive relation is obtained if eq 9 is substituted into eq 11, giving

$$F = 2kT/a \tag{12}$$

Equation 12 directly relates the chain tension to the tube radius only. There is nothing hypothetical about the force F. It is the usual manifestation of a free energy change which of course depends upon the constraints of the system, in this case the radius of the confining wall. Strictly speaking, eq 12 applies to an infinitely long chain. If the chain has a finite length, as is always the case, this force exists through most of the chain and vanishes toward the free ends where, in view of the larger topological freedom of these ends, the tube radius may be thought to grow locally toward infinity.

The longitudinal tension is not the only force which is active in the constrained chain. The chain also exerts a pressure, p, on the tube wall. This is obtained from the derivative of A with respect to a, at constant l and n

$$-kT\frac{4b^2n}{3a^3} = -p2\pi al \tag{13}$$

which, by the use of eq 9, gives

$$p = \frac{kT}{\pi a^3} \tag{14}$$

Needless to say, since the derivative of A with respect to n, at constant l and a, is zero at equilibrium, eq 12 and 14 could also be obtained by first substituting eq 9 into eq 10 which gives

$$A = \frac{2kT}{a}l \tag{15}$$

and then by taking the partial derivatives of A with respect to l and a, respectively.

We shall see in the following that the chain pressure on the tube wall, given by eq 14, plays an important role in determining the mechanical behavior of the polymeric liquid. Of course, at equilibrium the pressure that the chain exerts on the topological constraints which form the tube wall is balanced by an equal reaction that these constraints exert upon the chain.

The Subdivision of the Tube in Segments

For the sake of subsequent calculations, it is convenient to subdivide the tube which entraps the chain into a sequence of segments. The length of these segments is chosen in such a way that the directions of consecutive segments be completely uncorrelated. In other words, we treat the tube itself as a random coil made of freely jointed segments. Each segment is represented by a vector $\mathbf{r}$, which gives both the length and the orientation of the segment.

If the chain is made up of a total number of monomers n_t, at equilibrium we shall write

$$Nr^2 = n_t b^2 \tag{16}$$

where N is the number of segments in which the tube containing the given chain is divided. Equation 16 expresses the obvious fact that the square end-to-end distance of the chain coincides with that of the tube. We have assumed that the square end-to-end distance of a chain in a concentrated system obeys free chain Gaussian statistics. There is experimental evidence to this effect for melts[10] and even for concentrated solutions in good solvents,[11] in the latter case provided b is made concentration dependent to account for excluded volume effects over short distances.

If we now call n the number of monomers contained in a tube segment, eq 9 provides a relationship between n and r, i.e.,

$$n = \frac{3a}{2b^2}r \tag{17}$$

and, since

$$n_t = Nn \tag{18}$$

eq 16, 17, and 18 give

$$r = 3a/2 \tag{19}$$

$$N = 4n_t b^2/9a^2 \tag{20}$$

Equations 19 and 20, by giving r and N as a function of a, uniquely determine the subdivision of the tube in randomly oriented segments under equilibrium conditions.

The Stress Tensor

The basic element for calculating the stress tensor will be the subchain contained in a tube segment. The tensile force in a subchain is given by

$$\mathbf{F} = \frac{2kT}{a}\frac{\mathbf{r}}{r} \tag{21}$$

where, together with eq 12, we have used $\mathbf{r}/r$ to indicate the direction.

We shall use eq 21 also under nonequilibrium conditions with the only proviso that a may be different from a_0. (*From here on, all values relative to true equilibrium conditions will be indicated by the subscript zero.*)

The justification for using an equilibrium relation, eq 12, under non-equilibrium conditions is based on the time scale effect previously described. The time needed by the chain to reach a temporary equilibrium within a tube which has been modified by the deformation is much shorter than that needed to escape out of the deformed tube toward a condition of complete equilibrium. The stress tensor is then given by

$$\sigma = cN\langle \mathbf{Fr}\rangle = 2kTcN\left\langle \frac{\mathbf{rr}}{ar}\right\rangle \tag{22}$$

where c is the number of macromolecules per unit volume.

There now remains to be established how the distributions of $\mathbf{r}$ and a, as well as N, are modified by the deformation process. However, the latter quantity can easily be related to the former two. Since the line density of monomers will also rapidly reach a temporary equilibrium in the deformed tube, we may write eq 17 and 18 as

$$\langle n\rangle = \frac{3}{2b^2}\langle ar\rangle \qquad n_t = N\langle n\rangle \tag{23}$$

from which

$$N = \frac{2}{3}n_t b^2\frac{1}{\langle ar\rangle} \tag{24}$$

The stress equation then becomes

$$\sigma = \frac{4}{3}kTcn_t b^2\frac{1}{\langle ar\rangle}\left\langle \frac{\mathbf{rr}}{ar}\right\rangle \tag{25}$$

Finally, by defining the dimensionless quantities

$$\alpha = a/a_0 \qquad \rho = r/r_0 \qquad \rho = \rho(\mathbf{r}/r) \tag{26}$$

eq 25 is written as

$$\sigma = 3kTcN_0\frac{1}{\langle\alpha\rho\rangle}\left\langle\frac{\rho\rho}{\alpha\rho}\right\rangle \tag{27}$$

where N_0 is given by eq 20. Of course, at equilibrium $\alpha = \rho = 1$ and the distribution of ρ is random so that σ is an isotropic tensor.

The Effect of the Deformation on the Tube Geometry

The effect of the deformation upon the geometry of the topological constraints which form the tube wall is better seen as occurring in two steps.

First the tube is modified affinely with the external deformation, both longitudinally and transversally. The longitudinal affine deformation is obtained by taking, for each tube segment,

$$\rho = \mathbf{E}\cdot\mathbf{u} \tag{28}$$

where $\mathbf{E}$ is the deformation tensor and $\mathbf{u}$ the unit vector along the original direction of the tube segment.

If for the sake of semplicity we keep a cylindrical symmetry of the tube segments, the affine deformation of the tube cross section requires that α becomes

$$\alpha' = \rho^{-1/2} \tag{29}$$

However, the transverse dimension of the tube cannot remain at the value determined by eq 29. According to eq 14, a change in tube diameter alters the chain pressure and therefore a tube expansion (or contraction) is required in order to reestablish equilibrium, again a temporary one, between the chain and the surrounding constraints.

More in detail, since for arbitrary deformation the tube segments always elongate on the average (i.e., $\langle\rho\rangle > 1$, see, e.g., Appendix B of ref 3), the tube diameter decreases ($\langle\alpha'\rangle < 1$) and the chain pressure correspondingly increases. Therefore, the chain will tend to expand back, by pushing against the tube wall. The surrounding medium will resist this expansion and a balance will be found at an appropriate value of α.

In the next section we shall calculate this value of α. Before doing so, we comment briefly on the assumptions which have been made previously on the tube deformation problem.

Doi and Edwards, together with eq 28, simply assumed $\alpha = 1$ throughout. The justification for this assumption was based on an admittedly weak argument about the chain tension.[3] The stress tensor was then related to a tensor $\mathbf{Q}$ given by (see eq 27)

$$\mathbf{Q} = \frac{1}{\langle\rho\rangle}\left\langle\frac{\rho\rho}{\rho}\right\rangle \tag{30}$$

At the other extreme, Marrucci and de Cindio[7] assumed an α value given by eq 29, obtaining a stress proportional to

$$\mathbf{Q}' = \frac{1}{\langle\rho^{1/2}\rangle}\left\langle\frac{\rho\rho}{\rho^{1/2}}\right\rangle \tag{31}$$

which has the unpleasant property of diverging at large deformations.

As shown in the following, the assumption proposed in this paper leads to an intermediate result between eq 30 and 31, which approaches one or the other depending on the extent of the deformation as well as on the constitutive properties of the polymeric liquid.

We further remark that the assumption of affine deformation of the tube in the longitudinal direction, eq 28, should not be confused with the assumption of affine deformation of the chains which is made in rubber-like models. In the present case the chain monomers are free to "slide" along the tube and, when the tube is deformed, they rapidly do so in order to reestablish a temporary equilibrium with the modified surroundings.

The Tube Expansion Problem

The value of α is determined by solving the problem of the expansion of a cylindrical cavity inside a continuum in which stresses develop according to eq 27. Since in eq 27 α appears again as an unknown, one can anticipate that the equation to be solved will be of the implicit type.

We assume that the cavity and the surrounding material has cylindrical symmetry and that the displacements only occur in the radial direction. The force balance equation at any point in the continuum is written as

$$R\frac{\mathrm{d}\sigma_{RR}}{\mathrm{d}R} = \sigma_{\theta\theta} - \sigma_{RR} \tag{32}$$

where R and θ are cylindrical coordinates and σ_{RR} and $\sigma_{\theta\theta}$ are physical components of the stress.

By assuming that the material is incompressible, the equation of continuity is derived as follows. Assume that all points originally located at R' have been displaced to R and call λ the local value of the expansion ratio R/R'. The condition of constant volume requires that the shell comprised between R' and $R' + \mathrm{d}R'$ has reduced its thickness to a value $\mathrm{d}R$ such that

$$\mathrm{d}R/\mathrm{d}R' = 1/\lambda \tag{33}$$

Since, by definition of expansion ratio

$$\frac{R + \mathrm{d}R}{R' + \mathrm{d}R'} = \lambda + \mathrm{d}\lambda \tag{34}$$

we obtain

$$\frac{\mathrm{d}\lambda}{\mathrm{d}R} = -\frac{\lambda^3 - \lambda}{R} \tag{35}$$

The stress difference $\sigma_{\theta\theta} - \sigma_{RR}$ appearing in eq 32 uniquely depends on λ, the dependence being determined by the stress constitutive equation of the continuum. We call $g(\lambda)$ this function. Combining eq 32 and 35 to eliminate R and integrating then gives

$$-\sigma_{RR} = \int_1^{\lambda}\frac{g(\zeta)}{\zeta^3 - \zeta}\,\mathrm{d}\zeta \tag{36}$$

At the boundary with the cavity, the value of λ is given by

$$\lambda = \alpha/\alpha' \tag{37}$$

where α' is given by eq 29 and α is the unknown. At the same boundary, the stress σ_{RR} must balance the pressure increment of the chain which is calculated from eq 14 as

$$\Delta p = \frac{kT}{\pi}\left(\frac{1}{a^3} - \frac{1}{a_0^3}\right) = \frac{kT}{\pi a_0^3}\left(\frac{1}{\alpha^3} - 1\right) \tag{38}$$

Equation 36 then gives

$$\frac{kT}{\pi a_0^3}\left(\frac{1}{\alpha^3} - 1\right) = \int_1^{\alpha/\alpha'}\frac{g(\zeta)}{\zeta^3 - \zeta}\,\mathrm{d}\zeta \tag{39}$$

Equation 39 determines α as a function of α' once $g(\lambda)$ is specified. To this end, we simplify eq 27 somewhat, by rearranging the averages there appearing in the form

$$\sigma = 3kTcN_0 \frac{\langle \rho\rho \rangle}{\langle \rho^2 \rangle \langle \alpha \rangle^2} \tag{40}$$

By using arguments similar to those made in ref 3, one can surmise that this rearrangement does not lead to serious errors.

For the case of a cylindrical expansion, eq 40 gives

$$g(\lambda) = 3kTcN_0 \frac{\lambda^2 - \lambda^{-2}}{\frac{1}{3}(\lambda^2 + \lambda^{-2} + 1)} \frac{1}{\alpha^2} \tag{41}$$

where the ensemble average for α is understood. It is also understood that α is a (still unknown) function of λ. We also have

$$\rho = \langle \rho^2 \rangle^{1/2} = \{\tfrac{1}{3}(\lambda^2 + \lambda^{-2} + 1)\}^{1/2} \tag{42}$$

and thus

$$\alpha' = \{\tfrac{1}{3}(\lambda^2 + \lambda^{-2} + 1)\}^{-1/4} \equiv m(\lambda) \tag{43}$$

Equation 39 then gives

$$\frac{1}{\alpha^3} - 1 = B \int_1^{\alpha/m} f(\zeta)\, d\zeta \tag{44}$$

with

$$f(\lambda) = \frac{3}{2} \frac{\lambda^2 + 1}{\lambda(\lambda^4 + \lambda^2 + 1)} \frac{1}{\{\alpha(\lambda)\}^2} \tag{45}$$

$$B = 6\pi c N_0 a_0^3 \tag{46}$$

Equation 44 is the integral equation which, together with eq 43 and 45, determines the function $\alpha(\lambda)$ and thus, through eq 41, $g(\lambda)$. An explicit solution to these equations is found by considering that, as discussed in the next section, B is in general a very large number.

It is apparent that, for $B \rightarrow \infty$, the solution of eq 44 is

$$\alpha(\lambda) = m(\lambda) \tag{47}$$

If B is large, eq 47 will hold true at small values of λ, while deviations will progressively appear as λ increases. Expanding all functions around $\lambda = 1$ gives in fact

$$m(\lambda) = 1 - \tfrac{1}{3}\epsilon^2$$

$$\alpha(\lambda) = 1 - \frac{1}{3} \frac{B}{B + 3} \epsilon^2 \tag{48}$$

where $\epsilon = \lambda - 1 \ll 1$. However, it can be shown that, for values of λ which give rise to an appreciable difference between $\alpha(\lambda)$ and $m(\lambda)$, the value of the decreasing function $f(\lambda)$ has already become negligibly small. This enables us to calculate the integral in eq 44, using the following approximate form for $f(\lambda)$

$$f(\lambda) \simeq \frac{3}{2} \frac{\lambda^2 + 1}{\lambda(\lambda^4 + \lambda^2 + 1)} \frac{1}{\{m(\lambda)\}^2} = \frac{1}{\lambda^2} \left(\frac{3}{4} \frac{\lambda^4 + 2\lambda^2 + 1}{\lambda^4 + \lambda^2 + 1} \right)^{1/2} \simeq \frac{1}{\lambda^2} \tag{49}$$

Thus eq 44 becomes

$$\frac{1}{\alpha^3} - 1 = B\left(1 - \frac{m}{\alpha}\right) \tag{50}$$

One should now substitute $\alpha(\lambda)$ from eq 50 into eq 41 and then integrate eq 39. However, the simplification adopted above can be applied directly to eq 39 which then becomes identical with eq 50 with α' substituted for m. The solution of eq 39 is then

$$\frac{1}{\alpha} = \left(\frac{B + 1}{2} + \beta \right)^{1/3} + \left(\frac{B + 1}{2} - \beta \right)^{1/3}$$
$$\beta = \left\{ \left(\frac{B}{3\rho^{1/2}} \right)^3 + \left(\frac{B + 1}{2} \right)^2 \right\}^{1/2} \tag{51}$$

where, from eq 29, $\rho^{-1/2}$ has been substituted for α'.

Equation 51, by relating α to ρ, represents the solution of the tube deformation problem in the radial direction for large values of B.

Limiting properties of the solution are

$$\lim_{\rho \to \infty} \alpha = (B + 1)^{-1/3} \simeq B^{-1/3} \tag{52}$$

$$\lim_{\rho \to 1} \alpha \simeq \rho^{-1/2} \tag{53}$$

It is also apparent that, for $B \rightarrow 0$, the exact solution is $\alpha = 1$, a property which is shared by eq 51, even though this equation was derived for large values of B.

The Constitutive Parameter B

The value of the constant B defined by eq 46 can be estimated as follows. We first substitute for N_0 the expression given by eq 20, obtaining

$$B = \frac{8\pi}{3} c n_t b^2 a_0 \tag{54}$$

Next we consider that the product cn_t gives the monomer concentration, which can be written as

$$cn_t = \phi / v_m \tag{55}$$

where ϕ is the volume fraction occupied by the polymer and v_m is the volume of a monomer. By calling d the lateral dimension of the monomer, we write

$$v_m = \frac{\pi}{4} d^2 b \tag{56}$$

so that finally

$$B = \frac{32}{3} \phi \frac{b a_0}{d^2} \tag{57}$$

In a melt $\phi = 1$ and, since $b \gg d$ and $a_0 \gg b$, we conclude that B is a large number, of order 10^2–10^3 at the very least.

In a solution, decreasing the polymer concentration increases a_0. The overall effect is that B decreases, since

$$a_0 \propto c^{-\gamma} \tag{58}$$

where $\gamma < 1$. [$\gamma = {}^3/_4$ according to a scaling theory[11] and $\gamma = {}^3/_5$ by a mean field theory.[12]] However, the effect is rather small. Even if $\gamma = {}^3/_5$, reducing the polymer concentration to $\phi = 0.01$ implies a decrease of B with respect to the melt of less than a factor of 10. We shall further comment on this result later in the paper.

Equation 52 shows that B determines the minimum value of α which is obtained at large deformations. We are now in the position to verify whether or not the Gaussian assumption is satisfied also in the extreme conditions corresponding to eq 52. We recall that the results obtained are based on the assumption that

$$bw \ll 1 \tag{59}$$

which allows us to derive eq A2 of the Appendix and implies also that the chain is Gaussian because the number of monomers per unit length, n/l, will then remain much larger then b^{-1}. In other words, $n \gg l/b$, which is the condition for Gaussian behavior.

Inequality 59 is equivalent to

$$b^2 \ll a^2 \tag{60}$$

Under the limiting conditions of eq 52, by the use of eq 57, we obtain

$$\frac{32}{3}\phi\frac{b^2}{d^2} \ll \frac{a_0{}^2}{b^2} \qquad (61)$$

We expect that inequality 61 is satisfied in most cases, also when $\phi = 1$. We further note that, even if inequality 61 is not satisfied, the deviations from the Gaussian behavior should not be very large. Indeed, there should exist a sort of self-compensating effect by which, since deviations from the Gaussian behavior give rise to larger forces, the increased pressure on the tube wall should more effectively displace the wall itself.

Rheological Predictions

We have shown that, soon after a concentrated polymeric liquid has been suddenly deformed, the stress tensor is given by eq 27 with ρ determined by eq 28 and α by eq 51. During the subsequent relaxation, the stress tensor obeys the equation

$$\sigma = 3kTcN_0\frac{1}{\langle\alpha\rho\rangle}\left\langle\frac{\rho\rho}{\alpha\rho}\right\rangle\mu(t) \qquad (62)$$

where $\mu(t)$ represents the average fractional amount of polymer chain which at time t has not yet diffused out of the deformed tube. In fact, that part which has abandoned the deformed tube and has generated a new underformed, randomly-oriented tube does not contribute to the deviatoric part of the stress tensor.

A fundamental question to be answered is whether or not $\mu(t)$ depends upon the extent of the deformation. On this problem, we tentatively adopt the viewpoint expressed in ref 7 by which, in spite of the fact that the tube length is altered by the deformation, the disengagement time of the chain remains essentially constant. The entire problem is to some extent a matter of conjecture, as can be seen from the following argument.

The disengagement time is proportional to L^2/D where D is the curvilinear diffusivity and L is the arc length of the tube, which is inversely proportional to a. Further $D = kT/\zeta$, where ζ is a friction factor that is commonly set proportional to n_t. In fact, assuming Stokes resistance, one might expect ζ to be proportional to bn_t, because b is a measure for the size of the monomer. Now, in the Doi–Edwards version of the theory, a and therefore L remain constant, and this leads to a disengagement time independent of the deformation. If, on the other hand, the value of a decreases with deformation, the arc length L and consequently the disengagement time would increase.

We venture to suggest that the difficulty may lie in the assumption that D is inversely proportional to bn_t. It seems at least as acceptable to assume that D is inversely proportional to aN, where N is the number of subchains. This considers the friction as due to the motion of subchains rather than monomers and, in a way, is more in keeping with the spirit of the model because the readjustment of the number of monomers in the individual subchains is very fast compared to the process of reptation.

Now, the number of subchains per molecule is $N = 2n_tb^2/3ar$ (eq 24). Thus D would become proportional to r and therefore the disengagement time becomes inversely proportional to a^2r, i.e., it stays constant or even decreases with increasing deformation. Although this argument is by no means conclusive, it throws at least some doubt on the assertion that the disengagement time remains constant only when a remains constant.

If $\mu(t)$ does not depend on deformation, more complex situations other than a stress relaxation can simply be treated by means of a superposition principle. The stress tensor at any given time is obtained by summing the contributions, each given by eq 62, of the various deformation increments which have occurred at all previous times. An integration by parts then gives

$$\sigma = 3kTcN_0\int_{-\infty}^{t}\mathbf{Q}_t{}^*(t')\mu'(t-t')\,\mathrm{d}t' \qquad (63)$$

with

$$\mu'(t) = -\mathrm{d}\mu(t)/\mathrm{d}t \qquad (64)$$

$$\mathbf{Q}^* = \frac{1}{\langle\alpha\rho\rangle}\left\langle\frac{\rho\rho}{\alpha\rho}\right\rangle \qquad (65)$$

where now ρ is calculated on the basis of the deformation tensor between t' and t. Equation 63 differs from that by Doi and Edwards[4] insofar as the function $\alpha(\rho)$ has been included in the tensor $\mathbf{Q}^*$.

We shall not examine the predictions of eq 63 for all possible cases of rheological interest. We anticipate that most of them are qualitatively similar to those obtained by Doi and Edwards.[5] Quantitatively, the results depend upon the function $\mu(t)$, which can be obtained from experiments of linear viscoelasticity, as well as on the value of the constitutive parameter B, which in principle could also be determined from independent experiments.

The only case which is considered here is that of a uniaxial elongational flow under conditions of steady state, which better describes the novel qualitative features introduced by the present theory.

Although not strictly necessary, we simplify eq 65 by writing

$$\mathbf{Q}^* \simeq \frac{\langle\rho\rho\rangle}{\langle\rho^2\rangle}\frac{1}{\alpha^2} \qquad (66)$$

and focus our attention on the process with relaxation time τ, i.e.,

$$\mu(t) = \exp\left(-\frac{t}{\tau}\right) \qquad (67)$$

The elongational viscosity is then given by

$$\frac{\eta_{\mathrm{el}}}{3\eta_0} = \frac{1}{\Gamma\tau}\int_0^{\infty}\frac{\lambda^2-\lambda^{-1}}{\lambda^2+2\lambda^{-1}}\frac{1}{\alpha^2}\exp\left(-\frac{t}{\tau}\right)\mathrm{d}\left(\frac{t}{\tau}\right) \qquad (68)$$

where Γ is the rate of stretching and η_0 is the zero-shear viscosity. The time-dependent stretch ratio λ is given by

$$\lambda = \exp(\Gamma t) \qquad (69)$$

and α is obtained from eq 51 by first calculating ρ as

$$\rho = \left(\frac{\lambda^2+2\lambda^{-1}}{3}\right)^{1/2} \qquad (70)$$

The integral of eq 68 has been calculated numerically for $B = 10^3$ and 10^2 at several values of $\Gamma\tau$. The results are reported in Figure 2, which shows that, as $\Gamma\tau$ increases, the ratio $\eta_{\mathrm{el}}/3\eta_0$ first increases becoming larger than the Trouton value, $\eta_{\mathrm{el}}/3\eta_0 = 1$, and then progressively decreases approaching the behavior given by

$$\lim_{\Gamma\tau\to\infty}\frac{\eta_{\mathrm{el}}}{3\eta_0} = B^{2/3}\frac{1}{\Gamma\tau} \qquad (71)$$

The presence of a maximum is easily understood on the basis of the functional behavior of $\alpha(\rho)$. As $\Gamma\tau$ increases, the time average value of ρ increases. For moderately large values of ρ, $\alpha(\rho)$ coincides with $\rho^{-1/2}$ and thus tensor $\mathbf{Q}^*$ coincides with $\mathbf{Q}'$ of eq 31. In elongational flow, $\mathbf{Q}'$ would

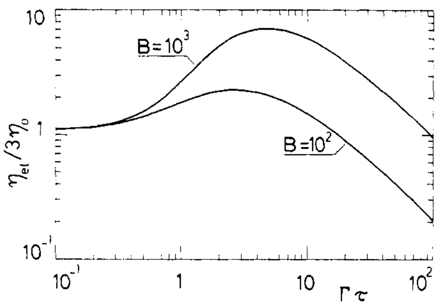

Figure 2. The elongational viscosity vs. the stretching rate. The parameter B is defined through eq 57.

rapidly diverge with increasing $\Gamma\tau$ and thus η_{el} starts deviating from the Trouton value in excess of that value. However, by further increasing the average value of ρ, $\alpha(\rho)$ levels off at the value given by eq 52 and thus tensor $\mathbf{Q}^*$ approaches the behavior of tensor $\mathbf{Q}$ of Doi and Edwards, eq 30. The tensile stress reaches a constant value and the elongational viscosity drops proportionally to Γ^{-1}.

Most experimental data of elongational flow are transient flow results. The most reliable steady state data are those obtained on low density polyethylene by various techniques summarized in ref 13. Although the polymer is branched and it is therefore questionable whether the theory applies to it, it is remarkable that the behavior of the elongational viscosity is indeed that "naturally" predicted by the present theory. Older results on polystyrene also show the same behavior.[14]

Concluding Remarks

One of the interesting aspects of the theory which has been presented is that the predicted results may be qualitatively different, depending on the constitutive parameter B. In particular, when B decreases as it does in progressively less concentrated solutions, the behavior predicted by Doi and Edwards is approached.

However, as previously noted, the dependence of B on concentration is rather weak and it is perhaps not sufficient to explain the differences in behavior which are observed. This may be due to an effect which has been purposely left out in the previous calculations in order to avoid excessive complications.

In treating the chain expansion problem, we have assumed that the surrounding material is incompressible. Now, the material which actually opposes the chain expansion is made up only of those chains which form the topological constraint, while segments of other chains as well as the solvent act as a diluent in this process.

Since density and concentration are of course uniform throughout, when the chain pushes aside the topological constraints, diluent material is drawn into the tube. This shows that treating the resisting material as an incompressible continuum is an incorrect assumption. Rather, a behavior similar to that of a swollen rubber should be invoked.

We have not performed calculations about this effect but it should be apparent that it works in the direction of enhancing the difference between melts and concentrated solutions since, by reducing the polymer concentration, the resisting material becomes progressively more compressible.

We note finally that, in case of solutions in good solvents, excluded volume effects on a local scale should be appropriately accounted for.

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Appendix

Consider a sequence of $n + 1$ monomers somewhere near the middle of a very long chain. These monomers are numbered 0, 1, ..., n. The monomer 0 is located in the plane $z = 0$ while the nth monomer lies in the plane $z = l$. Each of these $n + 1$ monomers is subject to the harmonic potential given in eq 3. The free energy A of this chain is obtained from

$$\exp\left(-\frac{A}{kT}\right) = \int \cdots \int \Pi_j (\mathrm{d}^3\mathbf{r}_j) \exp\left\{-\frac{3}{2b^2}\Sigma_j \tau_j^2 - \frac{1}{kT}\Sigma_j V_j\right\} \quad \text{(A1)}$$

where $\tau_j = \mathbf{r}_j - \mathbf{r}_{j-1}$ and b is the effective monomer length for the free chain; V_j is given by eq 3 when $0 \leq j \leq n$ but is zero for all other monomers; the integral is extended over the position $\mathbf{r}_j$ of all the monomers.

This integral is a product of three integrals which extend over the x, y, and z coordinates, respectively. That over the z coordinates is well known.[15] The integral over the x or y coordinates is of the form

$$\int \cdots \int \Pi_j (\mathrm{d}x_j) \exp(-\sum_{j,k} c_{jk} x_j x_k)$$

which is proportional to $C^{-1/2}$, where C is the determinant of the coefficients c_{jk}. Evaluating this determinant one finds that

$$\exp\left(-\frac{A}{kT}\right) = Kn^{-1/2} \exp\left(-\frac{3l^2}{2nb^2} - \frac{bwn}{3}\right) \quad \text{(A2)}$$

provided $bw/3 \ll 1$ and, at the same time, $\exp(-nbw/3) \ll 1$. The constant K is independent of n and of l.

On the same basis it can be shown that the probability of finding the nth monomer at the position x_n, y_n, l is proportional to[16]

$$n^{-1/2} \exp\left\{-\frac{3l^2}{2nb^2} - \frac{w}{2b}(x_n^2 + y_n^2)\right\} \quad \text{(A3)}$$

from which it follows that

$$\langle x_n^2 + y_n^2 \rangle = \frac{2b}{w} = \langle x_0^2 + y_0^2 \rangle \quad \text{(A4)}$$

It is also possible to find the averages

$$m_k = \langle x_k^2 + y_k^2 \rangle \quad \text{(A5)}$$

for arbitrary values of k ($0 \leq k \leq n$). To simplify the notation, we introduce the parameter

$$s = bw/3, \text{ i.e., } s \ll 1 \text{ and } \exp(-ns) \ll 1 \quad \text{(A6)}$$

If, following Doi and Edwards in Appendix A of ref 3, we fix the coordinates (x_0, y_0) and (x_n, y_n) at zero, it is found that

$$m_k = \frac{b^2}{3s} \frac{\cosh ns - \cosh (n - 2k)s}{\sinh ns} \qquad (0 \leq k \leq n) \quad \text{(A7)}$$

When plotted against k, this defines a spindle-shaped body, having its widest extension at $k = n/2$. If n is sufficiently large to make $ns \gg 1$, this body assumes the shape of a cigar, namely

$$m_k = b/w \quad \text{(A8)}$$

for all k except those close to 0 or n.

If, on the other hand, we fix the zeroth monomer at the origin, but for the nth monomer require only that $z_n = l$, it is found that

$$m_k = \frac{b^2}{3s} \frac{\sinh ns - \sinh (n - 2k)s}{\cosh ns} \tag{A9}$$

which for large values of ns is again almost flat at level $m_k = b/w$, except near $k = 0$ and near $k = n$, but this time m_k increases near $k = n$ to become equal to twice the average value in the rest of the tube. The same is true for m_0 when we require only that the zeroth monomer is in the plane $z = 0$. This explains why the average in eq A4 is twice as large as that in eq A8.

Finally, it may be mentioned that more general results, when $ns \gg 1$, can be obtained also for arbitrary values of s, for example

$$m_k = \frac{b}{w}\left\{1 + \left(\frac{bw}{6}\right)^2\right\}^{-1/2} \tag{A10}$$

but it falls outside the scope of the present work to pursue this case further.

References and Notes

(1) A. S. Lodge, "Elastic Liquids", Academic Press, New York, 1964.
(2) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1789 (1978).
(3) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1802 (1978).
(4) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1818 (1978).
(5) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **75**, 38 (1979).
(6) P. G. de Gennes, *J. Chem. Phys.*, **55**, 572 (1971).
(7) G. Marrucci and B. de Cindio, *Rhenol. Acta*, in press.
(8) M. Fukuda, K. Osaki, and M. Kurata, *J. Polym. Sci., Part A*, **13**, 1563 (1975).
(9) J. Klein, *Macromolecules*, **11**, 852 (1978).
(10) J. P. Cotton, D. Decker, H. Benoit, B. Farnoux, J. Higgins, G. Jannink, R. Ober, C. Picot, and J. Des Cloizeaux, *Macromolecules*, **7**, 863 (1974).
(11) M. Daoud, J. P. Cotton, B. Farnoux, J. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. de Gennes, *Macromolecules*, **8**, 804, (1975).
(12) S. F. Edwards, quoted in ref 2.
(13) H. M. Laun and H. Münstedt, *Rhenol. Acta*, **17**, 415 (1978).
(14) R. L. Ballman, *Rheol. Acta*, **4**, 137 (1965).
(15) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).
(16) Equation A5 of ref 3 contains a misprint in the second exponential term.

A Neutron Scattering Study of the Chain Trajectory in Isotactic Polystyrene Single Crystals

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ABSTRACT: The trajectory of a chain in well-charcterized isotactic polystyrene (IPS) single crystals has been examined by means of small-angle neutron scattering (SANS). Both the variation of mean dimensions with molecular weight and asymptotic behavior have been studied. The results are consistent with a sheet-like conformation along the 330 crystallographic plane.

Small-angle neutron scattering (SANS) has recently been used extensively to study the trajectory of a chain in bulk semicrystalline polymer. The first results obtained on polyethylene samples[1,2] rapidly quenched from melt to room temperature were compatible with those of the Flory model for which only small portions of the chain are incorporated sequentially in several crystalline lamellae. However, from the recent studies that we performed on semicrystalline isotactic polystyrene[3] (IPS), we have concluded that the conformation depends strongly on the chain mobility in the original amorphous medium. As suggested by Flory,[4] two parameters can be considered: the long relaxation time τ_m of the chains in the amorphous state and the time τ_p needed for the crystalline growth front to go through the dimension of one amorphous chain. This last parameter is evaluated according to

$$\tau_p \sim R_g/G \tag{1}$$

where R_g is the radius of gyration of the amorphous macromolcules and G the radial crystalline growth rate. In bulk polyethylene the relation $\tau_p << \tau_m$ is always valid, and therefore Flory[4] predicted that the thermal motions of units of the chain can affect only limited arrangements leading to a globally Gaussian chain made of amorphous subunits and small crystallized portions. In contrast, for IPS crystallized at 180 °C from the amorphous state the relations $\tau_m \sim \tau_p$ and $\tau_m >> \tau_p$ can be easily obtained by only using **H** matrices of different molecular weights.[5] SANS experiments[3] revealed indeed the existence of a schematic conformation possessing a long crystallized sequence folded along the 330 plane with two amorphous wings for the first situation ($\tau_m \sim \tau_p$) and the Flory type conformation for the second situation ($\tau_m >> \tau_p$). These results were supported both by the evolution of the mean dimensions with crystallinity and by the asymptotical scattering behavior.

As a consequence, one can reasonably expect a total incorporation of the chain forming a slab along the 330 crystallographic plane in self-seeded monocrystals grown from dilute solutions. Indeed, the long relaxation time in solution is rather small whereas the growth rate of single crystals is slow leading to $\tau_m \ll \tau_p$. Such an assumption has been confirmed by Sadler and Keller[6] from SANS experiments on polyethylene. For IPS, Keith, Vadimsky, and Padden[7] suggested a similar model by taking into account the regular hexagonal shape of the single crystals as seen by electron microscopy.

It is the purpose of this paper to describe SANS experiments carried out on IPS single crystals in order to confirm the earlier interpretation.

Experimental Section

1. **Materials.** Both hydrogenated (IPSH) and deuterated (IPSD) polymers were synthesized according to the Natta me-

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