

Limiting Shear Dependence of the Intrinsic Viscosity of Deformable Polymer Molecules*†

H. VAN OENE,‡ *Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada*

Synopsis

Previous theories of the shear dependence of the intrinsic viscosity of deformable polymer molecules are reviewed. Most of these theories, except those of Cerf and Kuhn and Kuhn, predict that for a polymer homologous series the shear dependence $[\eta]/[\eta]_0$ can be expressed in terms of the reduced parameter $(M[\eta]_0/RT)\eta_s q$. Such a representation is not in agreement with experimental findings. In this paper a phenomenological model is presented in terms of the Oldroyd rheological equations of state. This model allows one to take into account the finite deformation of the molecule. In terms of this model finite deformation leads to a retarded elasticity, which can be described in terms of the recoverable shear but which does not influence the shear viscosity. The retarded elasticity results, however, in a shift of the $[\eta]/[\eta]_0$ versus $(M[\eta]_0/RT)\eta_s q$ curve along the reduced stress coordinate. This shift is proportional to the molecular weight and independent of the solvent viscosity. Comparison with experiment shows the existence of the predicted shift factor for series of measurements on fractions of polystyrene in a good solvent. The one series of measurements in a theta solvent reveal that in such a solvent the shift vanishes. The implications of this finding are discussed. The shift factor is also shown to have many properties in common with the inner viscosity as defined by Cerf and experimentally evaluated by Leray from the velocity-gradient dependence of the extinction angle.

Introduction

Since the early theories of Kuhn^{1,2} and Peterlin^{3,4} showed that the structural viscosity often observed in even dilute solutions of polymer molecules could be described in terms of an orientation of a rigid, asymmetric particle (dumbell, ellipsoid) with respect to the direction of the velocity gradient, many attempts have been made to refine these model theories so as to be applicable to solutions of deformable polymer molecules.⁵⁻¹⁴

If orientation is the only cause of shear dependence, the predictions of the pertinent theory can be summarized as follows. The shear dependence

* Based in part on a thesis submitted to the faculty of graduate studies of the University of Alberta, Edmonton, Alberta, Canada, in partial fulfillment of requirements for the degree of Doctor of Philosophy, May 1963.

† Presented at the 12th High Polymer Forum, St.-Marguerite, P. Q., Canada, May 27-29, 1964.

‡ Present address: Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada.

expressed by means of the ratio $[\eta]/[\eta]_0$, where $[\eta]_0$ is the intrinsic viscosity at zero shear and $[\eta]$ the intrinsic viscosity at finite shear, is an even function of the parameter q/D_{rot} , where q is the velocity gradient, and D_{rot} the rotational diffusion coefficient. For polymer molecules the rotational diffusion is given by $RT/M[\eta]_0\eta_s$,¹⁵ hence $q/D_{\text{rot}} = (M[\eta]_0/RT)\eta_s q$, and

$$[\eta]/[\eta]_0 - 1 = \int \{ (M[\eta]_0/RT)\eta_s q \}^{2n} \quad (1)$$

where M is the molecular weight of the polymer, R the gas constant, T the temperature, η_s the viscosity of the solvent, and n a whole number > 1 . The coefficients in the power series depend only on the asymmetry of the molecules. For rigid ellipsoids these functions have been calculated by Scheraga.¹⁶ Experimentally the rigid ellipsoid case is well verified.¹⁷

The question of whether or not additional shear dependence, due to the deformability of the molecule is to be expected, or whether or not deformability in itself will give rise to shear dependence of $[\eta]$, has been treated in a number of different ways with conflicting results.

Kuhn and Kuhn⁵ introduced the coefficient of inner viscosity. This coefficient is related to the resistance to deformation of the polymer coil; more precisely, it is the resistance opposing a rate of change of the end-to-end distance of the polymer molecule. This resistance to deformation will make the diffusion coefficients associated with motion of the segments in the radial direction (D_{rad}), i.e., the direction of the end-to-end vector \mathbf{h} , differ from the diffusion coefficient associated with the motion of the segments in a tangential direction (D_{tang}), which motion is only opposed by the viscous forces of the solvent. Because of the inequality of the diffusion coefficients, shear dependence results and is a function of $(D_{\text{tang}}/D_{\text{rad}}) - 1$.

In the Kuhn and Kuhn theory, the latter quantity is proportional to $1/M[\eta]_0$. Hence, as the molecular weight of the polymer increases, the shear dependence due to the deformability of the molecule vanishes rapidly. Since this effect is superimposed over the effect of orientation, this theory would imply that if the shear-dependence is considered at constant $q/D_{\text{rot}} = (M[\eta]_0/RT)\eta_s q$ a polymer molecule with a higher molecular weight should show less shear dependence as expressed by the magnitude of $[\eta]/[\eta]_0$. This is in good agreement with the data of Lohmander and Svensson.¹⁸ Nevertheless, it is difficult to ascertain whether there is quantitative agreement with the Kuhn and Kuhn theory.

Copick¹⁰ and Peterlin and Copick⁹ point out that for a given end-to-end vector \mathbf{h} the configurations of the polymer molecule are not spherically symmetric. The asymmetry of the configuration will result in anisotropic hydrodynamic interaction, and hence the radial and tangential diffusion coefficients will be unequal. The shear dependence in their theory can be expressed as:

$$[\eta]/[\eta]_0 = 1 - 53/50\xi \{ (M[\eta]_0/RT)\eta_s q \}^2 \quad (2)$$

where $\xi = 1 - (D_{\text{rad}}/D_{\text{tang}}) = 0.14$ for a Gaussian coil, i.e., a constant

related to the average configuration of the molecule and independent of the molecular weight. A similar theory has been developed by Ikeda,¹¹ who obtains by a different method of averaging the much smaller value of 0.0196 for ξ . These theories, therefore, predict that as the molecular weight increases, the shear dependence increases also, which prediction is in good agreement with experimental evidence,^{7,19,20} but they also predict that for a polymer homologous series the shear dependence should be expressible as an unique function of q/D_{rot} , which is not in agreement with experiment. The recent data of Lohmander et al.^{18,20,21} show clearly that the shear dependence is not a simple reduced function of $(M[\eta]_0/RT)\eta_s q$, neither at extremely low shear rates nor at intermediate and high shear rates.

Essentially, the theories of Kuhn and Kuhn,⁵ Peterlin and Copick,⁹ and Ikeda¹¹ deal with the change in gross hydrodynamic resistance or changes in hydrodynamic interaction between the segments of the polymer molecule on deformation. In both theories the resulting expressions differ from the rigid particle theories, where shear dependence arises as a result of orientation only in the numerical values which multiply the parameter q/D_{rot} .

With the aid of a different model for the intrinsic viscosity it is possible to analyze in greater detail the influence of deformability or the elasticity of the molecule on flow behavior. The model most widely used is the one due to Rouse²² and Zimm.²³ In this model the polymer is replaced by an equivalent array of Hookean springs. The deformation of this set of springs can be analyzed by means of a normal mode analysis and is described by p principal modes of deformation, each associated with a relaxation time τ_p . The relaxation spectrum is determined from the configuration of the molecule. The shear viscosity can be written down immediately, with the aid of the Maxwell definition of viscosity:²²

$$\eta = \eta_s + (cN/M)kT\Sigma\tau_p \quad (3)$$

where η is the viscosity of the solution, η_s is the viscosity of the solvent, c is concentration (in grams/milliliter), and M is molecular weight.

The Rouse-Zimm (R-Z) theory itself is mainly concerned with the interpretation of so-called "dynamic" experiments. In a dynamic experiment the polymer solution is subjected to a periodic force with variable frequency ω . The R-Z theory then predicts *inter alia* the existence of a complex dynamic viscosity, given by:

$$\eta^* = \eta_1 + i\eta_2$$

where

$$\eta_1 = \eta_s + (cRT/M)\Sigma\tau_p/(1 + \omega^2\tau_p^2) \quad (4)$$

and:

$$\eta_2 = (cRT/M)\Sigma\omega\tau_p/(1 + \omega^2\tau_p^2)$$

The real part of the complex dynamic viscosity is proportional to the energy dissipated, the imaginary part is proportional to the energy stored.

At zero frequency the real part becomes equal to the steady flow viscosity, and the imaginary part vanishes.

Since no shear dependence of the intrinsic viscosity is obtained from the R-Z theory itself,²³ various additional assumptions have been incorporated into the original R-Z theory, with the aid of which it is possible to predict the shear dependence of the intrinsic viscosity. The resulting theories^{7,8,12,13} are, however, not in agreement with each other. Nevertheless it is instructive to discuss these modifications in some detail.

As Debye²⁴ showed, in steady shear the molecule in solution is subjected to a steady rotation with a frequency equal to $1/2q$. This rotation causes the molecule to be alternately stretched and pushed. If one now were to choose a coordinate system fixed in the molecule performing the same (rigid) rotation as the polymer molecule, then in this coordinate system the forces experienced by the molecule are periodic and hence one could take the effect of the velocity gradient on the shear viscosity to be equivalent to that of frequency on the dynamic viscosity.

Following this line of argument Bueche⁸ and Takemura¹² obtained expressions for the shear dependence of the intrinsic viscosity. In Takemura's theory this expression is given as:

$$[\eta]/[\eta]_0 = \Sigma(\tau_p/1 + q^2\tau_p^2)/\Sigma\tau_p \quad (5)$$

or to order q^2

$$\begin{aligned} [\eta]/[\eta]_0 &= 1 - \Sigma\tau_p^2q^2 \\ &= 1 - a(M[\eta]_0/RT)\eta_0q^2 \end{aligned} \quad (6)$$

where $a_{\text{Rouse}} = 0.400$, $a_{\text{Zimm}} = 0.200$.

Bueche's expression is slightly different. Moreover Bueche introduces a shielding parameter in order to obtain agreement with dilute solution data.

However, there are a number of difficulties inherent in the above argument. Pao¹³ raises the question as to whether it is sensible to speak of complete rotations of the deformed dynamical states, an assumption implicit in the theory of Bueche and Takemura. If by sufficiently rapid internal adjustment of the segments the deformed states could relax to the undeformed state in the time it takes the molecule to complete only a fraction of a rotation, then the species in solution for which one wants to calculate the intrinsic viscosity would be substantially undeformed, be almost spherical and show hardly any shear dependence. Since the deformation of the molecule can be described in terms of the magnitude of the displacement gradient, Pao¹³ introduces a "recoverable" displacement gradient δ , given by:

$$\delta = \sum_{p=1}^N q(\tau_p^2/1 + q^2\tau_p^2)/\sum_{p=1}^N (\tau_p/1 + q^2\tau_p^2) \quad (7)$$

Pao's theory results in a shear dependence of the form:

$$[\eta] = \frac{RT}{100\eta M_s} \left\{ \sum_{p=1}^N \frac{\tau_p}{1 + q^2\tau_p^2} + \frac{\sum_{p=1}^N [q\tau_p^2/(1 + q^2\tau_p^2)]}{\sum [\tau_p/(1 + q^2\tau_p^2)]} \right\} \quad (8)$$

$$[\eta]_0 = (RT/100M\eta_s)\Sigma\tau_p$$

which, to order q^2 can be expressed as:

$$[\eta]/[\eta]_0 = 1 - q^2\Sigma\tau_p^2\{1 - [\Sigma\tau_p^2/(\Sigma\tau_p)^2]\} \quad (9)$$

the quantity $\Sigma\tau_p^2/(\Sigma\tau_p)^2$ is a constant equal to 0.400 or 0.200, depending on whether Rouse²² or Zimm²³ relaxation times are used.

Comparison of the Takemura and Pao formulae reveal that both theories predict a possible reduced representation of the shear dependence by means of a plot of $[\eta]/[\eta]_0$ versus $(M[\eta]_0/RT)\eta_s q$. This, as already noted is not in agreement with experimental findings. It is noteworthy, however, that Pao's recoverable displacement gradient shifts the Takemura curve to higher reduced velocity gradient but leaves its shape essentially unchanged.

Cerf's treatment^{6,7} of inner viscosity in terms of the R-Z theory is rather different. He writes the rates of deformation of the principal modes of deformation as the sum of a pure rate of deformation and a rigid rotation:

$$s_p' = s_{p,d'} + s_{p,\omega'}$$

where s_p' is the rate of deformation of the p th mode, $s_{p,d'}$ is the pure rate of deformation of the p th mode, and $s_{p,\omega'}$ is the rigid rotation of the p th mode. Since a rigid rotation leaves the deformation unchanged he associated an inner viscosity with the pure rate of deformation term only.

The addition of the term $\Phi(s_p' - s_{p,\omega'})$ to the diffusion equation, then, leads to a shear dependence of the form:

$$[\eta]/[\eta]_0 = \sum_{p=1}^N [1 + (\tau_p' - \tau_p)^2 q^2] / [1 + (\tau_p'^2 - \tau_p^2) q^2] \quad (10)$$

where τ_p is the R-Z relaxation time, $\tau_p' = \tau_p(1 + \rho_p\nu_p)$ and ρ_p is the p th coefficient of inner viscosity. To order q^2 this yields

$$[\eta]/[\eta]_0 = 1 - 2\Sigma\tau_p(\tau_p' - \tau_p)q^2 \quad (11)$$

If $\tau_p = \tau_p'$, then the shear dependence vanishes completely. Moreover the shear dependence cannot be expressed as an unique function of q/D_{rot} because the inner viscosity term depends on molecular weight.⁷ Cerf's inner viscosity term could be deduced from shear dependence data alone, but the evidence can be obtained more directly from the velocity gradient dependence of the extinction angle. This dependence is:

$$\chi/q = 1/2(\Sigma\tau_p\tau_p'/\Sigma\tau_p) - a, (M[\eta]_0/RT)\eta_0 + b(\mathfrak{F}\langle h^2\rangle/RT) \quad (12)$$

where χ is the extinction angle, a , b are numerical coefficients, \mathfrak{F} is the coefficient of inner viscosity, and $\langle h^2 \rangle$ is the end-to-end distance of the undeformed polymer molecule.

The last term is the inner viscosity term, which is independent of the solvent viscosity and proportional to $\langle h^2 \rangle$.

The streaming birefringence results of Leray²⁵ provide strong support for the Cerf theory. However, Leray found that the inner viscosity term is proportional to the molecular weight of the molecule, hence indicating that not the actual end-to-end distance of the molecule appears in eq. (12) and also that the inner viscosity is independent of the concentration.

Recently Peterlin¹⁴ has examined the effect of the change in hydrodynamic interaction between segments on deformation of the molecule. This theory predicts an eventual increase in viscosity as the shear stress becomes very large. It also predicts that a plot of $[\eta]/[\eta]_0$ versus q/D_{rot} will not reduce the shear dependence for a polymer homologous series, even though at low shear stresses this effect is small. Judging from Lohmander's data¹⁹ the upturn of the intrinsic viscosity seems to be overestimated by this theory by about a factor of 50. In the low stress region the predictions of the recent Peterlin theory are essentially the same as those of the earlier theory of Peterlin and Copick.⁹

From this brief summary of the various theories which deal specifically with the shear dependence of the intrinsic viscosity of deformable molecules, the following points of view emerge. (1) The shear dependence is essentially similar to that observed with rigid asymmetric particles. The only difference is that with flexible molecules the asymmetry is not that of shape but due to the resistance to deformation which causes the two diffusion coefficients D_{rad} and D_{tang} to be unequal. For a perfectly flexible molecule these two coefficients are equal,²⁶ and hence the shear dependence vanishes. The asymmetry may be also thought of as an inherent property of the configuration of the molecule itself.^{9,11}

(2) In the framework of the Rouse-Zimm theory no shear dependence is obtained,²³ unless one makes an assumption about the equivalence of frequency and velocity gradient as was done by Takemura.¹² In order to obtain some measure of agreement with the experimental data an additional assumption is required pertaining to shielding of segments by segments,⁸ or similarly one can introduce a retardation time.^{6,13}

The only theory which predicts correctly the gross features of the limiting shear dependence on the intrinsic viscosity, i.e., the nonreducibility of a plot of $[\eta]/[\eta]_0$ versus $(M[\eta]_0/RT)\eta_s q$ is Cerf's theory and probably the early Kuhn and Kuhn theory, as interpreted in the above discussion.

In this paper a phenomenological description is given of the flow behavior of a liquid in which the elastic effects associated with the deformability of the solute can be characterized in terms of a relaxation and retardation time. The particular treatment is due to Reiner²⁷ and Oldroyd.²⁸ Attention is focussed on the fact that if in flow the molecule is deformed, the shear stress has to maintain this deformation. If the net deformation of the solute can be expressed by means of a Kelvin element, a simple theory results in which the nonreducibility of the $[\eta]/[\eta]_0$ versus $(M[\eta]_0/RT)\eta_0 q$ plot is a direct consequence of the finite deformation of the polymer

molecule. At least qualitatively, the proposed theory is confirmed by experiment.

Description in Terms of a Rheological Equation of State

As a model for the rheological behavior of a dilute solution of deformable polymer molecules we will choose the generalized Maxwell liquid, first proposed by Jeffreys.²⁹ Its applicability to dilute suspensions of elastic spheres was demonstrated by Fröhlich and Sack;³⁰ Oldroyd³¹ used it to describe the flow behavior of emulsions and also derived earlier²⁸ the various possible generalizations of this liquid. In its simple form, the liquid can be represented by the equation:

$$s + \dot{s}T_{\text{rel}} = 2\eta_L(\dot{d} + T_{\text{ret}}\dot{d}) \quad (13a)$$

where s is the shear stress; \dot{d} , the shear rate; T_{rel} a relaxation time; T_{ret} a retardation time, and η_L the observed shear viscosity. It is a liquid characterized by a relaxation time and a retardation time. As it stands, the equation is not a "proper" rheological equation of state, unless one further specifies how the time derivatives are to be taken.^{28,32} Oldroyd's theory leads to an equation of the form:

$$\sigma_{ik} \left[1 + \lambda_1 \frac{\mathfrak{D}}{\mathfrak{D}t} \right] = 2\eta_0 e_{ik} \left[1 + \lambda_2 \frac{\mathfrak{D}}{\mathfrak{D}t} \right] \quad (13b)$$

where σ_{ik} is the stress tensor; e_{ik} , the velocity gradient tensor; λ_1 , a relaxation time; λ_2 , a retardation time; η_0 , the zero shear viscosity; and $\mathfrak{D}/\mathfrak{D}t$, a symbol for the generalized convected time derivative. Nevertheless an important distinction due to Reiner²⁷ can already be made between two possible phenomenological representations which both admit to a description in terms of eq. (13).

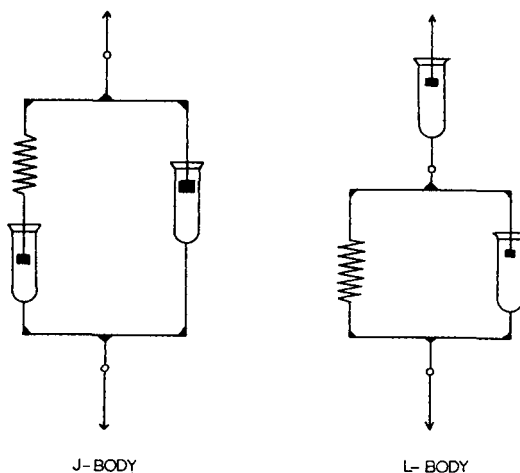


Fig. 1. Diagram of J-body and L-body (after Reiner²⁷).

If viscous contributions are represented by Newtonian dashpots and elastic contributions by Hookean springs, then according to Reiner²⁶ there are two ways of connecting the two dashpots and one spring, required to represent a body whose mechanical and flow behavior are represented by eq. (13); the one is called L-body (named after Lethersich³³) the other is called the J-body (named after Jeffreys²⁹). The L-body is essentially a liquid, the J-body a "relaxing" gel. The two representations are illustrated in Figure 1.

The L-body is characterized by the parameters:

$$\begin{aligned} T_{\text{rel}} &= (\eta_N + \eta_K)/\mu \\ T_{\text{ret}} &= \eta_K/\mu \end{aligned} \quad (14)$$

where μ is the modulus of elasticity of the Hookean spring; η_N is a Newtonian viscosity, and η_K the solid viscosity of the Kelvin element. It has a shear viscosity equal to the viscosity of the Newtonian dashpot only:

$$\eta_L = \eta_N$$

This Newtonian viscosity includes the viscous resistance of the solute due to the size and shape of the particle.³⁰

The J-body is characterized by the parameters:

$$\begin{aligned} T_{\text{rel}} &= \eta_M/\mu \\ T_{\text{ret}} &= \eta_N/(\eta_N + \eta_M) \end{aligned} \quad (15)$$

where η_M is viscosity of the Maxwell element and μ the modulus of elasticity of the Hookean spring. It has a shear viscosity equal to the sum of the viscosity of the Maxwell element and the viscosity of the Newtonian dashpot:

$$\eta_L = \eta_N + \eta_M$$

The J-body representation is usually considered to be also applicable to dilute solutions of deformable polymer molecules.^{22,34} It would appear, however, that the L-body description is more pertinent for present purposes. It specifically applies to a liquid in which, according to Reiner,²⁷

"When the solvent is subjected to continuous deformation or flow in which the suspended particles participate, forces are exerted by the solvent upon the 'springs' which are extended and compressed, and which they can resist elastically. The elasticity of the dispersed system accordingly resides in the solute; when the flow stops, extended springs contract etc. and the internal stresses of the system disappear. Because of the viscous resistance of the solvent this takes time and thus simulates a relaxation time."

Independent of the specific interpretation of the relaxation and retardation time, the generalization by Oldroyd^{23,32,35} of eq. (13a) to a proper rheological equation of state enables one to write down explicitly the stress system required to maintain a steady shear flow. The Oldroyd equations

predict in general the occurrence of normal stresses; moreover, these equations predict in addition a dependence of the shear viscosity on the magnitude of the velocity gradient.^{28,32,35} For the initial shear dependence of the viscosity Oldroyd obtains approximately:

$$\eta/\eta_0 = 1 + \lambda_1(\lambda_2 - \lambda_1)K^2 \quad (16)$$

where K is the magnitude of the velocity gradient, λ_1 is a relaxation time, and λ_2 is a retardation time.

No shear dependence is found if λ_1 is equal to λ_2 . If one identifies λ_1 with τ_p and λ_2 with τ_p' , then the shear dependence predicted by the Oldroyd equations is identical to that predicted by eq. (11), which follows from Cerf's theory.

From the Oldroyd equations one can also derive a quantity s , called the recoverable shear, defined as:

$$s = (t_{11} - t_{22})/2t_{12} = (\lambda_1 - \lambda_2)K \quad (17)$$

This quantity occurs frequently in the literature concerned with the experimental evaluation of functions arising in rheological equations of state, and can be regarded as a measure of network strain.³⁶

According to Philippoff,³⁷ the recoverable shear can also be expressed as:

$$s = J_e t_{12} = (1/G)t_{12} \quad (18)$$

where J_e is the equilibrium elastic compliance, G the shear modulus, and t_{12} the shear stress. Proof of this equality has recently been furnished by Coleman and Markovitz³⁸ for so-called second-order fluids. Hence the quantity s can be regarded also as a reduced measure of finite deformation since it is equal to the ratio of the shear stress and shear modulus, in the same way as the ratio of the velocity gradient and rotational diffusion coefficient q/D_{rot} is a reduced parameter for the degree of orientation of a particle. On the basis of extensive experimental evidence, Philippoff³⁷ also concludes that s , as defined above, is equal to:

$$s = 2 \cot 2\chi \quad (19)$$

where χ is the extinction angle measured in a streaming birefringence experiment.

The name, recoverable shear, is used for s , since it is also a measure of that part of the deformation of the liquid which is recovered if the flow stops, as evidenced by the fact that s can be evaluated from recoil experiments.³⁷

The stress dependence of the recoverable shear provides an experimental criterion for distinguishing between the L-body and J-body and description. For the J-body, the recoverable shear according to the eqs. (15) and (17) is given by the expression:

$$s = [\eta_M/(\eta_N + \eta_M)](t_{12}/\mu) = (1 - 1/\eta_r)^2(t_{12}/\mu) \quad (20)$$

Hence the slope of the plot of s versus the shear stress depends on the relative viscosity and, therefore, also on the concentration of the solution. For the range $2 > \eta_r > 10$, this slope should change by about a factor of three; in the range $10 > \eta_r > 100$, it changes by about 20%.

The recoverable shear for the L-body can be written as

$$s = (\eta_N q / \mu) = (t_{12} / \mu) \quad (21)$$

In this case the slope of a plot of s versus the shear stress is independent of the relative viscosity or the concentration of the solution. Such behavior is in very good agreement with the corresponding experimental results of Philippoff et al.³⁹ for a series of polyisobutylene solutions ranging in concentration from 0.25 to 100% polyisobutylene.

Unfortunately the data obtained by Oldroyd, Toms, and Strawbridge⁴⁰⁻⁴² who determined λ_1 and λ_2 separately, do not allow for an unambiguous distinction between the L-body and J-body representation, because, if the viscosity of the Maxwell element in the J-body is very much larger than the solvent viscosity η_N , then both the L-body and the J-body representation yield essentially the same result, i.e., λ_2 is independent of the viscosity and the concentration of the solution. The lack of a concentration dependence of λ_2 as contrasted with the pronounced concentration dependence of λ_1 is one of the striking findings in the investigation of Oldroyd, Strawbridge, and Toms.

Application to the Flow of Dilute Polymer Solutions

In the previous section a general phenomenological framework was discussed for the description of flow of deformable particles. One particular model, the L-body, was found to be consistent with experimental findings. The characteristic of the L-body is that the "elastic" properties of the liquid are described in terms of a Kelvin element. Hence, at constant stress one can write the total stress acting on the liquid as the sum of the stress associated with the dashpot, which determines the shear viscosity, and the elastic stress, associated with the Kelvin element, which does not contribute to the shear viscosity. Hence:

$$\text{Total shear stress} = \text{flow stress} + \text{elastic stress}$$

This relationship would not hold for the J-body, since in this instance one has the relationship:

$$\text{Total stress} = \text{flow stress} = \text{elastic stress}$$

A more physical description of the L-body type liquid would therefore be the following:

In flow the shear stress gives rise to a velocity gradient. Due to the presence of the particles, the stream lines are disturbed, and hence the deformable particles possess an intrinsic viscosity due primarily to their shape and size. The deformation of the molecules may make the molecules more asymmetric and may change the hydrodynamic interaction between

the segments within the molecule. Both these effects will cause a shear dependence of the intrinsic viscosity as was shown by Kuhn and Kuhn,⁵ Peterlin and Copick,⁹ Ikeda,¹¹ and Peterlin.¹⁴ In the theories cited, these two effects of deformability, can be described in terms of the "reduced" parameter q/D_{rot} , and both of these effects are, therefore, primarily associated with the magnitude of the velocity gradient.

As such, the fact that the molecule is deformed is in a sense secondary. However, these theories do not take into account the energy required to maintain the deformation of the molecule which energy is stored in the liquid and recoverable if the flow stops. Therefore, the only direct effect of deformation on the flow behavior of the L-body liquid is that not the whole applied shear stress will be available to maintain a certain velocity gradient. If the elastic part of the stress is interpreted as the shear stress required to maintain the deformation of the polymer molecule, then this term can be calculated with the aid of an appropriate rheological equation of state.⁴³⁻⁴⁵ Using the Rouse model, which is essentially a Maxwell liquid and which rheological equation of state can be obtained from the Olroyd equations by putting λ_2 equal to zero, Ikeda⁴⁶ obtains the following expressions for the stress system, required to maintain a steady flow:

$$\begin{aligned}\sigma_{11} &= (2cRT/M)q^2\Sigma\tau_p^2 - p \\ \sigma_{12} - \sigma_{12}^\circ &= (cRT/M)q\Sigma\tau_p \\ \sigma_{22} &= \sigma_{33} = -p \\ \sigma_{23} &= \sigma_{31} = 0 \\ \sigma_{12}^\circ &= \eta_s q\end{aligned}\tag{22}$$

The recoverable shear is, therefore, given by:

$$s = (\sigma_{11} - \sigma_{22})/2(\sigma_{12} - \sigma_{12}^\circ) = [\Sigma\tau_p^2/(\Sigma\tau_p)^2]\Sigma\tau_p q\tag{23}$$

As already pointed out it is useful to consider the recoverable shear as a reduced measure of the deformability of the molecule just as the parameter q/D_{rot} can be regarded as a reduced measure for the degree of orientation of the polymer molecule.

Since the elastic term arises from the inherent deformability of the molecule which is determined to a large extent by the configurational entropy, the elastic term should be independent of the solution viscosity. Hence the relaxation times to be used in evaluating the recoverable shear should be those associated with the deformation of the single polymer molecule. A possible choice would be the relaxation times with the deformation of a single, un-entangled polymer molecule in bulk. For the Rouse model, Ferry⁴⁷ obtains:

$$\tau_p = \langle\langle h_0^2 \rangle\rangle/6\pi^2 (M\xi_0/M_0)(1/RT)(1/p^2)\tag{24}$$

where M_0 is the molecular weight of the monomer and ξ_0 is the monomeric friction coefficient; because of the Gaussian configuration of the polymer molecule ξ_0 is inversely proportional to the molecular weight.

If this choice is made, then the expression for s becomes:

$$s = 0.400(\beta\langle h_0^2 \rangle / RT)q \quad (25)$$

where

$$\beta = \xi_0 M / M_0$$

On the basis of this interpretation of the L-body, it is possible to write down at once the following expression for the extinction angle. This expression will contain two terms, the one associated with the flow stress and hence with the velocity gradient due to orientation and the other associated with the elastic stress, which contribution according to Philippoff^{37,45} is equal to the recoverable shear:

$$\chi = aq/D_{\text{rot}} + s$$

or

$$\chi = a_1(M[\eta]_0/RT)\eta_s q + 0.400(\beta\langle h_0^2 \rangle / RT)q \quad (26)$$

This expression has the same form as eq. (12) derived by Cerf.⁶ One could, therefore, identify the inner viscosity term derived by Cerf with the recoverable shear as calculated for a simple Maxwell element. If this identification is made, the experimental findings of Leray²⁵ with respect to the lack of concentration dependence and the proportionality with respect to molecular weight of the inner viscosity term appearing in eq. (12) can be clarified to a considerable extent.

The independence of concentration follows since the term represents the resistance to deformation of the molecule only. In dilute solutions one would not expect entanglements to make any contribution to the shear modulus of the system. This follows also directly from the data of Philippoff et al.³⁹ on the stress dependence of the recoverable shear of polyisobutylene solutions referred to previously and the theory of Yamamoto.⁴⁸

The proportionality with respect to molecular weight arises in the Cerf theory^{6,7} by replacing the end-to-end distance of the molecule at rest with the unperturbed, Gaussian, end-to-end distance. This replacement is justified by a recent result of Ptitsyn.⁴⁹ Ptitsyn analyzes the effect of excluded volume on the shear modulus in deformation. He finds that if the forces acting on the polymer molecule are small, then the modulus is proportional to the actual end-to-end distance. If, however, the forces acting on the molecule are large enough to orient the molecule as well, the modulus becomes proportional to the unperturbed end-to-end distance, regardless of the non-Gaussian configuration of the polymer chain.

The main result from this analysis of the flow behavior of solutions containing deformable molecules is that this flow behavior cannot be described in terms of a reduced stress of the form q/D_{rot} , but that the reduced stress

has to contain an additional deformation term. This follows directly from eq. (16) for the shear dependence and eq. (17) for the recoverable shear, which equations were derived from the Oldroyd equations.

Because of the Kelvin element associated with the L-body description, the reduced stress governing the shear dependence of the viscosity is again the sum of two terms: (1) an inelastic term, associated with the dashpot which determines the shear viscosity, representing the effect of the velocity gradient on the flow behavior such as orientation, anisotropic hydrodynamic interaction, etc.; (2) an elastic term, which is associated with the finite deformation of the molecule and which has been identified with the recoverable shear. It is only this term which has been calculated from an appropriate rheological equation of state.

This functional form of the reduced stress can also be inferred from the constancy of the stress optical coefficient in a matching solvent,⁵⁰ as this constancy implies that the shear dependence is given by:

$$\eta/\eta_0 = \sin 2\chi$$

The shear dependence, therefore, has the same functional dependence on total stress as the extinction angle. Hence the following experimental criterion for finite deformation can be derived.

If the polymer molecule is rigid, the shear dependence of the intrinsic viscosity can be expressed as an unique, reduced function in terms of the parameter $(M[\eta]_0/RT)\eta_s q$.

If the polymer molecule is deformable, the reduced stress should contain a term of the form:

$$(M[\eta]_0/RT)\eta_s q + 0.400\beta(\langle h_0^2 \rangle/RT)q$$

or

$$(M[\eta]_0/RT)[1 + (0.400\beta K/[\eta]_0)(1/\eta_s)]t_{12}$$

where $t_{12} = \eta_s q$ is the maximum shear stress and K is the proportionality constant in the relationship $\langle h_0^2 \rangle = KM$.

Since from experiment only the maximum value of the shear stress t_{12} can be determined, and not the actual value of the shear stress, associated with the flow (the inelastic dashpot in the L-body description), our analysis implies that finite deformation gives rise only to a shift equal to the recoverable shear of the shear dependence (velocity gradient dependence) curve along the reduced stress coordinate $(M[\eta]_0/RT)t_{12}$, but does not affect the shape of the $[\eta]/[\eta]_0$ versus $(M[\eta]_0/RT)t_{12}$ plot.

The existence of such a shift factor can be verified in the following manner.

Consider the molecule to be rigid. In this case the effect of orientation can be analyzed in terms of the Scheraga calculations of the shear dependence of rigid ellipsoids of arbitrary axial ratio. For rigid molecules, the scale factor which has to be added to the value of $\log t_{12}$ in order to shift the $\log([\eta]/[\eta]_0)$ versus $\log t_{12}$ curve on to the $\log([\eta]/[\eta]_0)$ versus $\log q/D_{\text{rot}}$

curve is equal to $\log M[\eta]_0/RT$. For deformable molecules, however, this scale factor is given by:

$$(M[\eta]_0/RT)[1 + (0.400\beta K/[\eta]_0)(1/\eta_s)]$$

which contains a term inversely proportional to the solvent viscosity. This dependence is most clearly exhibited by a plot of $(RT/[\eta]_0)$ (shift factor) versus $1/\eta_0$, which plot should extrapolate to the molecular weight of the polymer molecule.

Discussion

The shear dependence of the intrinsic viscosity of four different fractions of polystyrene in four different solvents and at a number of different temperatures was measured in multibulb capillary viscometers. The viscometers have been described previously⁵¹ as well as the various shear corrections to the measured flow-times.⁵²

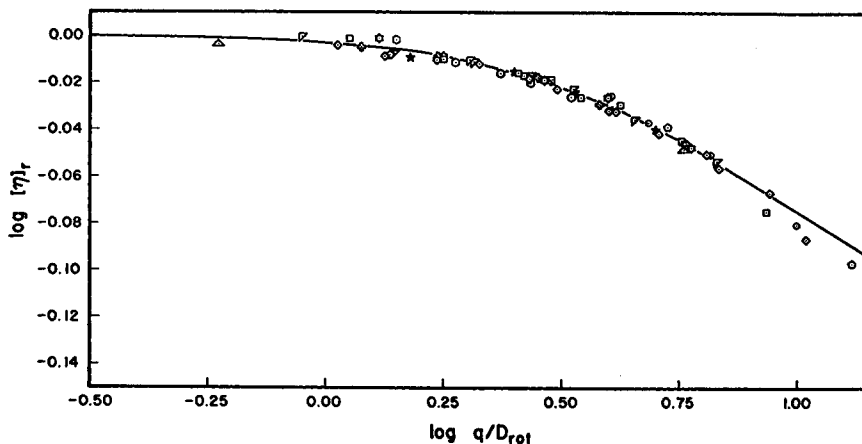


Fig. 2. Plot of $\log [\eta]/[\eta]_0$ vs. $\log \tau$ shifted horizontally so as to coincide with the reduced curve representing the shear dependence of a rigid ellipsoid with axial ratio three: (\odot) T_5 in toluene at 60°C.; (\diamond) T_5 in toluene at 40°C.; (\circ) T_5 in benzene at 20°C.; (\ominus) T_5 in cyclohexane at 35°C.; (\square) T_5 in benzene at 55°C.; (Δ) T_7 in benzene at 25°C.; (\triangleleft) T_7 in benzene at 40°C.; (\oplus) T_7 in benzene at 55°C.; (\star) $F_1A_1A_1$ in benzene at 25°C.; (\otimes) $F_1A_1A_1$ in benzene at 40°C.

In Figure 2 all the results obtained are plotted as $\log [\eta]/[\eta]_0$ versus $\log t_{12}$ and are all shifted so as to fit into the drawn curve, which is the Scheraga curve for the orientation of an ellipsoid with axial ratio equal to three. It is seen that this curve fits the data very well. The data obtained at the highest shear stress (about 10–15 dynes/cm.²) seem to deviate from this curve, which may not be too surprising since the whole stress range can most certainly not be described in terms of the orientation of an ellipsoid with fixed axial ratio. It is encouraging, however, that this relatively low stress range is fitted so well by a $p = 3$ curve.

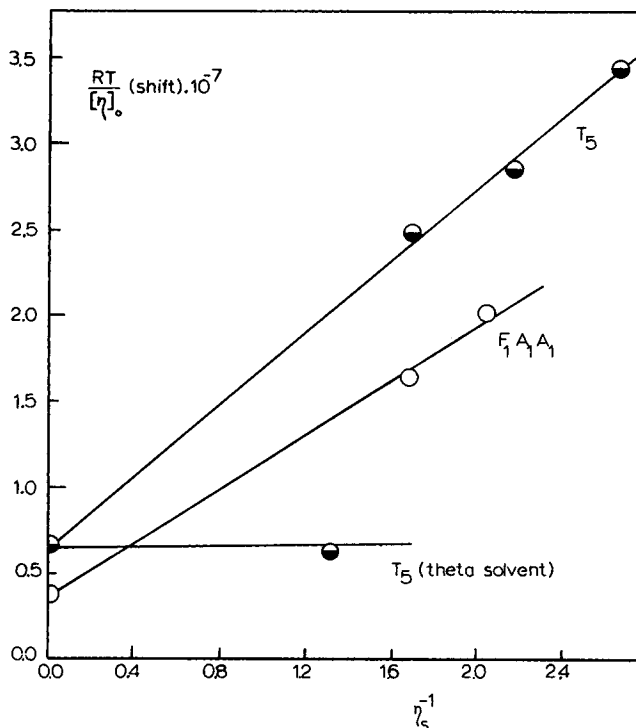


Fig. 3. Plot of $(RT/[\eta]_0)$ shift vs. $1/\eta_s$ for fractions T_5 and $F_1A_1A_1$. The intercept corresponds to the molecular weight calculated from $[\eta]_0$ in benzene from data of Leray.²⁵

The quantities $(RT/[\eta]_0) \times \text{shift}$ are listed in Table I and are plotted versus $1/\eta_s$ in Figure 3. These plots should extrapolate to the molecular weight of the particular fraction. The points indicated on the intercept are the values of the molecular weight obtained from intrinsic viscosities and molecular weights of polystyrene fractions in benzene with a molecular weight larger than one million listed by Leray.²⁵ This procedure was followed, since the intrinsic viscosity–molecular weight relationships for polystyrene in various solvents established in the literature diverge greatly in the high molecular weight region. Moreover in good solvents the $[\eta]$ – M relationships may be curved.⁵⁴ The molecular weights calculated from the data of Leray²⁵ are, however, in good agreement with the $[\eta]$ – M relationship recently proposed by Altares et al.⁵⁵

It is seen that the lines extrapolate to their respective intercepts and hence confirm the proposed relationship.

The most interesting curve is that of fraction T_5 . Only for this fraction were measurements available of the shear dependence under theta conditions. The experimental data were obtained from earlier work of Soues.⁵⁶ It is seen that the shift factor is not dependent on the solvent viscosity but has the value of the intercept, as would be the case if no net deformation

TABLE I
Shift Factors and the Intrinsic Viscosity at Zero Shear Rate for
Fractions T₅, T₆, T₇, and F₁A₁A₁

Fraction	Log shift factor	Temp., °C.	$[\eta]_0$, g./dl.	Solvent	η_0 , cpoise ^a	$(RT/(\text{shift})[\eta]_0) \times 10^{-7}$	$M \times 10^{-6b}$
Fraction T ₅	+1.212	35	2.35	Cyclohexane	0.761	0.667	6.84
	-0.0344	20	10.50	Benzene	0.6487	2.51	
	-0.013	40	9.22	Toluene	0.4650	2.91	
	-0.083	60	9.14	Toluene	0.390	3.51	
Fraction T ₆	-0.127	40	10.30	Benzene	0.4923	1.89	6.50
	+0.104	55	10.32	Benzene	0.412	2.08	
Fraction T ₇	+0.296	25	8.50	Benzene	0.6028	1.48	5.02
	+0.241	40	8.44	Benzene	0.4923	1.77	
	+0.279	55	8.47	Benzene	0.412	1.81	
Fraction F ₁ A ₁ A ₁	+0.350	25	6.60	Benzene	0.6028	1.67	3.81
	+0.273	40	6.67	Benzene	0.4923	2.05	

^a Data obtained from J. Timmermans.⁵³

^b Calculated from values of $[\eta]$ and M given by Leray.²⁶

of the molecule were present. In the analysis given above this can only be interpreted if the recoverable shear were to vanish in a theta solvent.

The vanishing of the recoverable shear is not predicted by anyone of the equations derived on the basis of the Rouse-Zimm model. As stated previously, the R-Z model represents essentially a simple Maxwell liquid which treats of relaxation only. The Maxwell liquid as generalized by Oldroyd, however, considers both relaxation and retardation. For an Oldroyd liquid the recoverable shear can vanish, provided the relaxation time and the retardation time are equal.

The vanishing of the recoverable shear indicates that the net deformation of a Gaussian molecule, when averaged over complete rotation, is nil. In this sense the result of Zimm²³ and the early theory of Peterlin,²⁶ which both predict no shear dependence due to deformability for an ideally flexible polymer molecule, seem to be borne out by experiment. Therefore, the shear dependence observed in a theta solvent is associated with inelastic effects only.

Although a rigid ellipsoid curve is used for fitting the data, similar results would have been obtained if the theory of Peterlin and Copick⁹ had been employed, since the coefficient of $(q/D_{rot})^2$ is for both curves very similar (0.120 for the rigid ellipsoid curves and 0.148 in the Peterlin-Copick theory).

Independent of any model is the finding that the curves representing the shear dependence of the intrinsic viscosity, measured in good solvents,

are systematically displaced from the shear dependence as measured in a theta solvent and that this displacement can be interpreted as arising from the finite deformation of the polymer coil in a good solvent. By coincidence, perhaps, it turns out that the choice of a rigid ellipsoid curve fits the shear dependence observed in the theta solvent with a scale factor equal to the molecular weight of the polymer.

The predictions of the L-body formalism seem also to apply to the velocity-gradient dependence of the extinction angle, insofar as the inner viscosity term found by Leray²⁵ has all the properties predicted from a model where this term is interpreted as arising from the finite deformation of the molecule. Independent verification of the vanishing of the "inner viscosity" term in the velocity-gradient dependence of the extinction angle under theta conditions would provide strong corroboration for the model proposed in this paper.

On the basis of these experimental results it follows, that for a treatment of the effect of finite deformation on the shear dependence of the intrinsic viscosity one has to consider both relaxation and retardation processes, and that an Oldroyd liquid interpreted as an L-body provides a better representation of finite deformation in flow than the usually considered Maxwell liquid, for which the recoverable cannot vanish.

A separate calculation of the recoverable shear in terms of the appropriate relaxation and retardation times will not be attempted. The data show that under theta conditions these two times are equal. From Ptitsyn's theory it follows that the modulus governing the deformation of the molecule is not influenced by excluded volume effects; hence, any dependence of the recoverable shear on the thermodynamic properties of the solvent will be reflected in the value of the monomeric friction coefficient β .

One comment should be made on the effect of polydispersity. If the proposed model is interpreted strictly as a deformed ellipsoid model, then the shear dependence observed is due to the asymmetry of the molecules induced by the deformation. As such, the asymmetry then enters only as a scale factor, since smaller spheres will be deformed into smaller ellipsoids, but the axial ratio will be the same, regardless of size. Hence polydispersity will not influence the shape of the $[\eta]/[\eta]_0$ versus $(M[\eta]_0/RT)\eta_0q$ curve. However, the recoverable shear term is strongly dependent on the molecular weight distribution [J_e is proportional to $(M_z M_{z+1})/M_w$]; the shift factor, therefore, will be very sensitive to the molecular weight distribution.

In conclusion it may be pointed out that the effect on entanglements can be readily incorporated in the treatment given above. Entanglement effects are primarily associated with the velocity-gradient dependence of the solution viscosity. Appropriate rheological equations of state have been given by Lodge⁵⁷ and Yamamoto.⁴⁸ The theory of the latter author is also applicable to liquids possessing a non-Newtonian shear viscosity. Both theories treat entanglements in terms of a simple Maxwell model. Since the recoverable shear in the Yamamoto theory is given by the same expression given earlier in eqs. (23) and (25), it follows that entanglements

have no influence on the stress dependence of the flow behavior. The entanglements are, therefore, considered as sufficiently loose so as not to impose a restriction on the deformation of the polymer molecule. In this respect deformation is simpler than flow, which of course is greatly influenced by entanglements, since flow involves relative motion of molecules rather than relative motion of connected segments as in deformation.

Hence, even in the presence of entanglements of the type considered by Lodge and Yamamoto, the stress dependence of the intrinsic viscosity should be the same as the stress dependence of η_{sp}/c , since the recoverable shear is independent of concentration. Such behavior has been described earlier by van Oene and Cragg¹² and can be inferred from the lack of concentration dependence of the inner viscosity observed by Leray.²⁴

It is a pleasure to acknowledge the encouragement and assistance which the author received from Professor L. H. Cragg during the course of this investigation. Professor Reiner's permission to use Figure 1 is gratefully acknowledged.

Financial support in the form of a National Research Council of Canada studentship (1959-1960) and a Shell Oil Fellowship (1960-1961) is also gratefully acknowledged.

This research in general has been supported by a grant of the National Research Council of Canada to Professor L. H. Cragg.

References

1. Kuhn, W., *Z. Physik. Chem.*, **A161**, 1, (1932).
2. Kuhn, W., *Kolloid-Z.*, **68**, 2, (1934).
3. Peterlin, A., *Z. Physik*, **111**, 232 (1938).
4. Peterlin, A., *Kolloid-Z.*, **86**, 230 (1939).
5. Kuhn, W., and H. Kuhn, *Helv. Chim. Acta*, **28**, 97 (1945); *ibid.*, **28**, 1533 (1945); *ibid.*, **29**, 71, 609, 830 (1946).
6. Cerf, R., *Compt. Rend.*, **243**, 1875 (1956); *J. Polymer Sci.*, **23**, 125 (1957); *J. Phys. Radium*, **19**, 122 (1958).
7. Cerf, R., *Advan. Polymer Sci.*, **1**, 382 (1959).
8. Bueche, F., *J. Chem. Phys.*, **22**, 1570 (1954).
9. Peterlin, A., and M. Copick, *J. Appl. Phys.*, **27**, 434 (1956).
10. Copick, M., *J. Chim. Phys.*, **53**, 440 (1956).
11. Ikeda, Y., *J. Phys. Soc. Japan*, **12**, 378 (1957).
12. Takemura, T., *J. Polymer Sci.*, **27**, 549 (1958).
13. Pao, Y.-H., *J. Chem. Phys.*, **25**, 1294 (1956); *J. Appl. Phys.*, **28**, 591 (1957); *J. Polymer Sci.*, **61**, 413 (1962).
14. Peterlin, A., *J. Chem. Phys.*, **33**, 1799 (1960); *Kolloid-Z.*, **182**, 110 (1962); *J. Chem. Phys.*, **39**, 224 (1963).
15. Frisch, H. L., and R. Simha, in *Rheology, Theory and Applications*, Vol. I, F. R. Eirich, Ed., Academic Press, New York, 1956, Chap. 14.
16. Scheraga, H. A., *J. Chem. Phys.*, **23**, 1526 (1956).
17. Yang, J. T., *J. Am. Chem. Soc.*, **80**, 1783 (1958); *ibid.*, **83**, 1316 (1961).
18. Lohmander, U., and A. Svensson, *Makromol. Chem.*, **65**, 202 (1963).
19. Sharman, L. J., R. H. Sones, and L. H. Cragg, *J. Appl. Phys.*, **24**, 703 (1953).
20. Lohmander, U., *Makromol. Chem.*, **72**, 159 (1964).
21. Lohmander, U., and R. Strömberg, *Makromol. Chem.*, **72**, 143 (1964).
22. Rouse, P. E., *J. Chem. Phys.*, **21**, 1272 (1953).
23. Zimm, B. H., *J. Chem. Phys.*, **24**, 269 (1956).
24. Debye, P., *J. Chem. Phys.*, **14**, 636 (1946).
25. Leray, J., *J. Chim. Phys.*, **57**, 323 (1960).

26. Peterlin, A., *J. Polymer Sci.*, **8**, 621 (1952).
27. Reiner, M., in *Handbuch der Physik*, S. Függe, Ed., Band VI, Springer Verlag, Berlin, 1958, p. 467.
28. Oldroyd, J. G., *Proc. Roy. Soc. (London)*, **A200**, 523 (1950).
29. Jeffreys, H., *The Earth*, Cambridge, 1929.
30. Fröhlich, H., and R. Sack, *Proc. Roy. Soc. (London)*, **A185**, 415 (1946).
31. Oldroyd, J. G., *Proc. Roy. Soc. (London)*, **A218**, 122 (1953).
32. Oldroyd, J. G., *Proc. Roy. Soc. (London)*, **A245**, 278 (1958).
33. Lethersich, W., *J. Soc. Chem. Ind.*, **61**, 101 (1942).
34. Giesekus, H., *Rheol. Acta*, **1**, 2 (1958).
35. Oldroyd, J. G., *Quart. J. Mech. Appl. Math.*, **4**, 271 (1951).
36. Pilpel, N., *Trans. Faraday Soc.*, **51**, 1307 (1955).
37. Philippoff, W., *J. Appl. Phys.*, **28**, 1118 (1951).
38. Coleman, B. D., and H. Markovitz, *J. Appl. Phys.*, **35**, 1 (1964).
39. Brodyan, J. G., F. H. Gaskins, and W. Philippoff, *Trans. Soc. Rheol.*, **1**, 109 (1957).
40. Oldroyd, J. G., D. J. Strawbridge, and B. A. Toms, *Proc. Phys. Soc.*, **B64**, 44 (1951).
41. Toms, B. A., and D. J. Strawbridge, *Trans. Faraday Soc.*, **49**, 1225 (1953).
42. Toms, B. A., *Rheol. Acta*, **1**, 137 (1958).
43. Rivlin, R. S., in *Rheology, Theory and Applications*, Vol. I, F. R. Eirich, Ed., Academic Press, New York, 1956, Chap. 10.
44. Mooney, M., *J. Polymer Sci.*, **34**, 599 (1959).
45. Philippoff, W., *Trans. Soc. Rheol.*, **5**, 163 (1961).
46. Ikeda, Y., *Repts. Prog. Polymer Phys. Japan*, **1**, 66 (1958).
47. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 156.
48. Yamamoto, M., *J. Phys. Soc. Japan*, **12**, 1148 (1958).
49. Ptitsyn, O. B., *Polymer Science USSR*, **1**, 259 (1960); *Vysokomol. Soedin*, **1**, 715 (1959).
50. Philippoff, W., *J. Polymer Sci.*, **57**, 141 (1962).
51. Cragg, L. H., and H. van Oene, *Can. J. Chem.*, **39**, 203 (1961).
52. van Oene, H., and L. H. Cragg, *J. Polymer Sci.*, **51**, 209 (1962).
53. Timmermans, J., *Physico-chemical Constants of Pure Organic Compounds*, Elsevier, New York, 1950.
54. Kurata, M., and W. H. Stockmayer, *Advan. Polymer Sci.*, **3**, 196 (1963).
55. Altares, T., D. P. Wyman, and V. R. Allen, *J. Polymer Sci.*, **24**, 4533 (1964).
56. Sones, R. H., M. Sc. Thesis, McMaster University, 1952.
57. Lodge, A. S., *Trans. Faraday Soc.*, **52**, 120 (1956).

Résumé

On a passé en revue les théories antérieures sur la relation entre le cisaillement et la viscosité intrinsèque des macromolécules déformables. La plupart de ces théories excepté celles de Cerf et Kuhn et Kuhn, prédisent que pour un polymère de séries homologues la dépendance du cisaillement $[\eta]/[\eta]_0$ peut être exprimée en fonction du paramètre réduit $(M[\eta]_0/RT)\eta_{0g}$. Une telle représentation n'est pas en accord avec les résultats expérimentaux. Dans ce texte, un modèle phénoménologique est représenté en fonction des équations rhéologiques d'état d'Oldroyd. Ce modèle permet de tenir compte de la déformation finie de la molécule. En fonction de ce modèle, une déformation finie conduit à une élasticité retardée, qui peut être décrite en fonction du cisaillement récupérable mais qui n'influence pas la viscosité lors du cisaillement. L'élasticité retardée cependant provoque un déplacement de la courbe $[\eta]/[\eta]_0$ en fonction de $(M[\eta]_0/RT)\eta_{0g}$ le long de la coordonnée de la tension réduite. Ce déplacement est proportionnel au poids moléculaire et est indépendant de la viscosité du solvant. Une comparaison avec l'expérience montre l'existence du facteur de déplacement prévu pour

une série de mesures sur des fractions de polystyrène dans un bon solvant. La seule série de mesures dans un solvant thêta montre que dans un tel solvant le déplacement s'annule. On discute des conséquences de cette découverte. On montre aussi que le facteur de déplacement a beaucoup de propriétés en commun avec la viscosité-*"interne,"* définie par Cerf et expérimentalement évaluée par Leray à partir de la dépendance de l'angle d'extinction sur le gradient de vitesse.

Zusammenfassung

Es wird ein Überblick über die Theorie für die Scherabhängigkeit der Viskositätszahl deformierbarer Polymermoleküle gegeben. Die meisten Theorien mit Ausnahmen derjenigen von Cerf und Kuhn-Kuhn, kommen zu dem Ergebnis, dass in polymerhomologen Reihen die Scherabhängigkeit $[\eta]/[\eta]_0$ durch den reduzierten Parameter $(M[\eta]_0/RT)\eta_{\infty}q$ ausgedrückt werden kann. Eine solche Darstellung steht jedoch mit den experimentellen Befunden nicht in Übereinstimmung. In der vorliegenden Mitteilung wird ein phänomenologisches Modell auf Grundlage der rheologischen Zustandsgleichung von Oldroyd angegeben. Dieses Modell gestattet eine Berücksichtigung deren endlichen Deformation des Moleküls. Mit diesem Modell führt eine endliche Deformation zu einer verzögerten Elastizität, welche als rückbildbare Scherung beschrieben werden kann, und welche die Scherviskosität jedoch nicht beeinflusst. Die verzögerte Elastizität führt zu einer Verschiebung der $[\eta]/[\eta]_0-(M[\eta]_0/RT)\eta_{\infty}q$ -Kurve entlang der reduzierten Spannungsordinate. Diese Verschiebung ist dem Molekulargewicht proportional und von der Lösungsmittelviskosität unabhängig. Ein Vergleich mit dem Experiment zeigt die Existenz eines solchen Verschiebungsfaktors bei einer Messreihe Polystyrolfraktionen in einem guten Lösungsmittel. Eine Messreihe in einem Thetalösungsmittel lässt erkennen, dass in einem solchen Lösungsmittel die Verschiebung verschwindet. Die Bedeutung dieses Befundes wird diskutiert. Weiters wird gezeigt, dass der Verschiebungsfaktor viele Eigenschaften der von Cerf definierten und von Leray aus der Abhängigkeit des Auslöschungswinkels vom Geschwindigkeitsgradienten ermittelten inneren Viskosität gemeinsam haben.

Received January 28, 1965