On the viscosity of chain polymers

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Simple considerations of the molecular-weight dependences of the intrinsic viscosity and melt viscosity of chain polymers are given.

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INTRODUCTION

Since the discovery of the existence of macromolecules, the molecular-weight dependence of the viscosity of chain polymers has been an important subject in polymer physics. Therefore, numerous articles have been published on the subject[1]. Nevertheless, it is worth trying to clarify interesting physics behind the molecular-weight dependence.

Among many problems concerning the molecular-weight dependence of the viscosity of chain polymers, we shall discuss here only the two extreme cases: the intrinsic viscosity in the dilute limit and the melt viscosity in the opposite limit.

For our purpose, we shall ignore polydispersity, chain stiffness, branching and other complicating factors. These factors affect the molecular-weight dependence, but we shall consider only flexible chains based on a pearl-necklace model. In this model, each chain consists of N segments, and each segment is a sphere of diameter a and has a bond length b. With this model, we shall show that the two limiting cases can be treated in an equally simple way. Our consideration will be in the limiting case of zero shear rate. In this limit, the deformation of chains may be ignored.

INTRINSIC VISCOSITY

As is well known[1], the molecular-weight dependence of the intrinsic viscosity of chain polymers is expressed by:

$$[\eta] = KN^{\alpha} \tag{1}$$

where K is a constant, and the exponent α is around 0.7. This variation has been attributed to the excluded-volume effect by Flory[2], who utilized Einstein's viscosity formula for a spherical solute:

$$[\eta] = 2.5N_0v_s/M \tag{2}$$

where N_0 is Avogadro's number, M is the molecular weight and v_s is the volume of the solute. For a flexible chain:

$$v_s \sim R^3 \sim N^{3\nu} \tag{3}$$

where $\nu = 0.598$ in the presence of the excluded-volume effect. Hence:

$$[\eta] \sim N^{0.794} \tag{4}$$

The excluded-volume effect is expected to vary with the flexibility of the chain. However, when the chain is stiff, the molecular shape may deviate from the spherical shape that is expected from a random-walk model, and can even be rod-like. In such a case, both microscopic and macroscopic calculations show that the intrinsic viscosity varies strongly with the rod length[3]. Therefore, there can be cases in which the viscosity exponent exceeds the above value of 0.794. We shall not discuss cases in which such deviations from Flory's limit appear, as it has already been reviewed[4]. Instead, we shall be concerned only with a randomly coiled shape.

As discussed[5] by Kirkwood and Riseman (KR) and by Debye and Bueche, the hydrodynamic interactions between the segments can cause a molecular-weight dependence because outer segments of a polymer shield inner segments from the fluid flow. This effect has been considered independently of the excluded-volume effect, but we note that both effects originate from the finite size of the segments. In fact, in the absence of this finite size, there will be no hydrodynamic effect. Hence, it is appropriate to take both effects into consideration simultaneously.

In order to take both effects into consideration, it is convenient to introduce a force field in space represented by $\boldsymbol{F}(\boldsymbol{r})$ with reference to the centre of a polymer[4]. The KR integral equation can then be modified into a similar integral equation for this force defined in space. This equation depends on the pair segment distribution function referred to the centre of gravity of a reference polymer. Such a distribution function can be evaluated in the presence of the excluded-volume effect[6].

Instead of pursuing this integral equation approach, it is advantageous to adopt an intuitive method for interpreting the intrinsic viscosity behaviour. Let us consider a representative segment of a polymer in a laminar flow with a velocity gradient q. This segment is located at position R with reference to the centre of gravity. R is expected to be of the order of the radius of gyration. As such, we expect:

$$R = N^{\nu}b \tag{5}$$

where $\nu = 3/5$ in good approximation.

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The laminar flow at the position R has a speed qR in an approximate order of magnitude. Under the influence of this flow, the segment will rotate about the centre of the given polymer. The order of magnitude of this rotational velocity is $v^0(R) = qR$ if there is no hydrodynamic interaction. In its presence, the velocity will be reduced by a factor $1/(1 + AN/R)$ because velocity $\mathbf{v}$ is given by[5]:

$$\mathbf{v}(\mathbf{R}) = \mathbf{v}^0(\mathbf{R}) - \frac{\zeta N}{4\pi\eta_0} \int \frac{\mathbf{v}(\mathbf{r})w(\mathbf{r})}{|\mathbf{R} - \mathbf{r}|} \mathrm{d}\mathbf{r} - \frac{1}{2\eta_0} \nabla_{\mathbf{R}} p$$

in which the last term is small. Here $w(\mathbf{r})$ is a segment distribution function and p is the Oseen pressure. The energy loss that is carried by the fluid per unit time per unit volume is then $(qR)^2/(1 + ANb/R)$.

On the other hand, a uniform fluid with viscosity η in a laminar flow of velocity gradient q dissipates energy at a rate ηq^2 per unit time per unit volume. In the present case in which the dissipation due to the polymer is being investigated, the rate is $(\eta - \eta_0)q^2$, where η_0 is the solvent viscosity.

Hence, equating the two energy-loss expressions, we arrive at:

$$[\eta] = KN^{2\nu}/(1 + AN/R) \qquad (6)$$

Thus, with equation (5) we obtain:

$$[\eta] = KN^{6/5}/(1 + AN^{2/5}) \qquad (7)$$

We remark that in effect equation (6) represents only a modification of the free-draining result of Debye in terms of an effective hydrodynamic effect, which varies as $1/R$, where R is an average end-to-end distance. The exponent $\nu = 3/5$ corresponds to Flory's approximation to the volume effect, and for $N \to \infty$, equation (7) agrees with Flory's expression. However, for relatively small N, a stronger N variation can be expected. The intrinsic viscosity formula can be tested experimentally by plotting $N^{2\nu}/[\eta]$ against $N^{1-\nu}$. We remark that equation (6) is consistent with the form obtained by Peterlin[7], according to which a plot of $N/[\eta]$ against $N^{1/2}$ should be linear.

MELT VISCOSITY

Another interesting molecular-weight dependence has been observed in melt viscosity. For a wide range of chain polymers, it has been found that[8]:

$$\eta = KN^{\kappa} \qquad (8)$$

where

$$\kappa = \begin{cases} 1.0, & N < N_c \\ 3.4, & N > N_c \end{cases}$$

Melt viscosity is a complex quantity, and in fact there are cases in which deviations from the above simple power law are observed[9]. Moreover, the transition may not occur at a point at N_c but rather for a certain interval of molecular weight. In such cases, the 'critical' number N_c must be determined by extrapolation from both sides of the region. In spite of these details, it is remarkable that such a simple power law holds for a wide range of chain polymers.

The above empirical power law has been considered by several authors[10]. In particular, Bueche attributed the dependence to molecular entanglements, with a slippage effect. He considered a hierarchy of molecular entanglements, a portion of which has a slippage motion in addition to the usual type of motion. Therefore, his final result was expressed in terms of an infinite series. Although he obtained a power 3.5 in the long-chain limit, it is somewhat difficult to interpret this particular power in relation to the experimental value 3.4. Therefore, it seems worth giving a simple and direct interpretation of this power.

We picture a polymer melt as a uniform fluid. If this fluid has viscosity η and is subject to a laminar flow with a velocity gradient q, the energy loss per unit time and unit volume is equal to ηq^2 as before. In this fluid, the segments are distributed more or less uniformly. For our pearl-necklace model, the segmental density is of the order of $1/(a^2b)$. The energy loss of this fluid originates from the motion of effective moving units.

For small molecular weights, molecular entanglements may not be strong. In this case, each polymer moves independently of other polymers, and each segment constitutes the effective unit for energy dissipation. The laminar flow at position R of a representative segment of a polymer will have a speed qR. The segment will rotate about the centre at a speed that is effectively equal in magnitude to qR. We assume that it encounters a resistance ζqR. Hence, the energy loss per unit time per unit volume is $\zeta(qR)^2/(a^2b)$. Equating this with ηq^2, we find:

$$\eta = \zeta R^2/(a^2b) \sim N^{1.0} \qquad (9)$$

if $R \sim N^{1/2}$ is assumed.

For long chains with molecular entanglements, clusters of polymers have to be considered in place of the previous case with single polymers. Hence, an effective unit for energy dissipation is enlarged by a factor of order N so that its friction coefficient becomes $N\zeta$. In contrast to the previous case, the average distance of this unit from the centre of a molecular cluster is enlarged to $R(R/b)$ with a scaling factor R/b. Hence, equation (9) is modified to:

$$\eta = \zeta NR^4/(a^2b^3) \sim N^{3.4} \qquad (10)$$

since equation (5) can be used for large N. It appears that on average the above scaling with a factor N is valid even though deviations can take place. On the other hand, there is evidence that ν equals $1/2$ in concentrated solutions. Hence, in this case:

$$\eta \sim N^3 \qquad (11)$$

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