Relaxation Times of Flexible Polymer Chains in Solution from Non-Conventional Viscosity Measurements

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Abstract: This work is devoted to the study of the viscosity and relaxation of flexible polymer chains in dilute solutions. Our aim was to determine the relation between the intrinsic viscosity and the relaxation times of the polymer internal normal modes within the bead-spring approach. In the theoretical part we generalize the Zimm theory of the polymer dynamics by taking into account the permeability of the solvent into the polymer coil interior and the hydrodynamic interactions between different coils. For theta solvents the polymer relaxation is described as depending on the draining parameter and the concentration of the coils. Using the calculated relaxation times, the intrinsic viscosity has been obtained. The free-draining (Rouse) and non-draining (Zimm) expressions for this quantity follow from the theory as special cases of infinite and zero permeability, respectively. In the experimental part we studied the viscosity of high-molecular poly(N-vinyl-2-pyrrolidone) water solutions at different temperatures down to such low concentrations when conventional capillary viscosimetry fails to probe the viscosity without a complicated additional treatment of the data. Using a new Couette-type viscosimeter with a magnetically suspended rotor allowed us to directly determine the intrinsic viscosity. It notably differs from the previous values reported in the literature. By comparison of the data to the theory, the quantities used in the description of the universal polymer behavior in solution have been estimated.

Keywords: Flexible polymers, extremely dilute solution, viscosity, relaxation times.

INTRODUCTION

For the study on dynamics and conformations of polymer chains in solution, precise knowledge of polymer relaxation times, corresponding to different modes of motion of the chain, is required. Among the methods used in the determination of the polymer longest relaxation time, which corresponds to the motion of the chain as a whole [1, 2], various viscosimetry techniques are widely used. However, the interpretation of these experiments encounters serious difficulties. This is due both to problems with the treatment of experimental data [3, 4] and to the fundamental problems with the theory of viscosity of polymer solutions [5, 6]. The present contribution deals with the experimental and theoretical study of dilute polymer solutions. Although commercially used polymer solutions are usually nondilute (an important exception being the solutions used in turbulent drag-reducing flows), there are several reasons for the interest in dilute solutions: they are important for the characterization of a polymer’s molecular weight, stiffness, branching, interaction with solvent, and for understanding hydrodynamic forces in the solution, free from the complications of intermolecular entanglements [5]. Note that there are several criterions in the literature concerning the term “dilute”. We shall consider as dilute such solutions in which the polymer coils are well separated so that the effects of overlapping of different coils can be neglected. The volume fraction of the coils in solution will be small (often the criterion \( c < 1 / [\eta] \) is used, where \( c \) is the mass or number concentration of the polymers and \( [\eta] \) is the corresponding intrinsic viscosity of the solution) but different chains still interact hydrodynamically with each other. It is commonly accepted that the reduced viscosity of dilute solutions, \( \eta_{\text{red}} = (\eta(c) - \eta) / (\eta c) \), should linearly depend on \( c \): \( \eta_{\text{red}} = [\eta](1 + k_H[\eta]c +...) \), where \( \eta \) and \( \eta(c) \) are the viscosities of the solvent and solution, respectively, and \( k_H \) is the Huggins coefficient. Alternatively, the Kraemer expression for the viscosity is \( (1/c)\ln\eta_{\text{red}} = [\eta](1 + k_K[\eta]c +...) \), where \( k_K \) is Kraemer’s constant. At low \( c \) the latter quantity should obey the equation \( k_K = 1/2 - k_H \). However, in practice an anomalous, strongly nonlinear, behavior of \( \eta_{\text{red}} \) is observed at very low \( c \) where the linearity is most of all expected [3, 4], which is one of the mentioned problems with the data treatment in the conventional capillary viscosimetry. In our work we have avoided these problems using a distinct way of measurements that allowed us to directly observe the linear dependence of \( \eta_{\text{red}} \) on \( c \). This is one of the main achievements of the work. Other our efforts concerned the theoretical description of the results. The main idea comes from the known but often neglected fact that the phenomenological parameters used in the description of polymer behavior should be determined from experiments coming from a model, which includes the hydrodynamic interaction (HI) between the beads and does not a priori assume the impermeability of the coil with respect to the solvent. This means that, contrary to the usual approach to the interpretation of experimental data, we do not consider the polymer dynamics in its non-draining limit, which is the opposite case to the free-draining (or fully permeable) model [1, 2]. In the latter
(Rouse) model [7] the solvent is nonmoving; in the Zimm generalization [8] the motion of beads leads to the flow of the solvent which, in its turn, influences the bead movement. Only for infinitely strong HI the coil behaves as an impermeable body. A correct theory must describe both the cases and contain these models as limits of infinitely small (Rouse) and large (Zimm) HI. The strength of HI is connected with the draining parameter $h$ that appeared already in the famous Kirkwood and Riseman (KR) work [9]. There has been much debate concerning the necessity to take into account these effects (i.e., to join the Rouse and Zimm description of polymer dynamics) is seen from the following consideration. The basic equation within the bead-spring models of polymer dynamics is the equation of motion for the position vector of the bead [1, 2],

$$\frac{d\mathbf{x}_n}{dt} = \frac{1}{\xi} \left( \mathbf{f}^{\text{ch}}_n + \mathbf{f}_n \right) + \mathbf{v}(\mathbf{x}_n).$$

(1)

Here, $f^{\text{ch}}_n$ is the force on the $n$th bead from the neighboring beads, $f_n$ is the random force due to the motion of the molecules of solvent, $v(\mathbf{x}_n)$ is the velocity of the solvent, and $\xi$ is the friction coefficient (for a spherical particle $\xi = 6\pi \eta b$, where $\eta$ is the solvent viscosity and $b$ is the bead radius. As distinct from the theory by Rouse [7], where the solvent is nonmoving ($\nu = 0$), Eq. (1) takes into account the HI [8]. Within the Zimm theory the velocity field $\mathbf{v}(\mathbf{x}_n)$ is expressed through the Oseen tensor $\mathbf{H}$,

$$\frac{d\mathbf{x}_n}{dt} = \frac{1}{\xi} \left( \mathbf{f}^{\text{ch}}_n + \mathbf{f}_n \right) + \sum_{m \neq n} \mathbf{H}(\mathbf{x}_n - \mathbf{x}_m) \left( \mathbf{f}^{\text{ch}}_m + \mathbf{f}_m \right)$$

(2)

In the sum $m \neq n$ since $\mathbf{v}(\mathbf{x}_n)$ in the point $n$ is created by all other $N - 1$ beads in the chain except the $n$th one. If one, following [2], formally defines the Oseen tensor for $n = m$ as $H_{nm} = \delta_{nm} / \xi$, the summation in (2) can be extended to all $n\, m$ to include the first term on the right. Usually the continuum approximation with respect to $n$ is used $(\mathbf{x}_n(t) \rightarrow \mathbf{v}(t, n))$. After this step, however, the term $-\xi^2$ disappears. One should require that the Zimm model generalizes the simpler Rouse model. If we act as described above, this is not the case: the two models are independent. Moreover, imagine that in the Rouse model (with $\nu = 0$) we lose in the continuum approximation the term $-\xi^2$ in (1); the model would become meaningless. Thus, to generalize the Rouse model, we have in the continuum approximation to keep the $-\xi^2$ term in (2). The $m = n$ term in the sum can be defined arbitrarily since it will not influence the integration. As a result, the Rouse-Zimm equation in the continuum limit should be

$$\frac{d\mathbf{x}_n(t, n)}{dt} = \frac{1}{\xi} \left[ \mathbf{f}^{\text{ch}}_n (t, n) + \mathbf{f}_n (t, n) \right]$$

$$+ \sum_{m \neq n} dm \mathbf{H}(n, m) \left[ \mathbf{f}^{\text{ch}}_m (t, m) + \mathbf{f}_m (t, m) \right]$$

(3)

Depending on the polymer parameters, the model gives the description of the polymer behavior more close to the Rouse or Zimm dynamics. In general, however, both terms on the right side of Eq. (3) should be kept in consideration. After this correction of the method described in the monograph [2], one can follow the standard way and obtain, in particular, the spectrum of polymer internal modes in theta solutions, the relaxation rates of these modes will have a particularly simple form $1 / \tau_{\text{ch}} = 1 / \tau_{\text{ch}} + 1 / \tau_{\text{pZ}}$, where the limiting relaxation times are given by the known formulas [1] ($a$ is the mean-square distance between the beads long the chain)

$$\tau_{\text{ch}} = \frac{2N^2 a^3 \eta}{\pi^{\frac{1}{2}} \gamma^{\frac{1}{2}} \rho}, \quad \tau_{\text{pZ}} = \frac{\left( N^{\frac{1}{2}} a \right)^3 \eta}{\left( 3 \pi^{\frac{1}{2}} \rho \right)^{\frac{1}{2}} k_B T}.$$
or Rouse ($h \ll 1$) type. The Oseen tensor for the case when the flow is affected by other polymers in solution (with the concentration $c$) has been calculated in [15]. In this case the Rouse relaxation time remains the same as in (4), but the Zimm time $\tau_{Z}$ depends on $c$, so that at small $c$

$$\tau_{Z}(c) = \tau_{Z} \left( 1 + \frac{N_{A}^{1/2} a^{3} c}{6 \pi \eta N_{A}} - \ldots \right).$$

(5)

The friction coefficient of the coil is connected with its diffusion constant by the Einstein relation $D = k_{B} T / \eta$ with $D = D_{h} + D_{z}$, where $D_{h} = k_{B} T / (6 \pi N_{A} \eta)$ and $D_{z} / D_{h} = 4 \sqrt{2} h / 3$, which corresponds to the KR result [9] (but disagrees with the Flory version [14] according to which the ratio between $R_{G}$ and the hydrodynamic radius determined from $D$ is a universal constant). Having the relaxation times, the steady-state viscosity can be calculated according to the known formula [5]

$$\eta(c) = \eta_{\text{ref}} + \frac{1}{2} k_{B} T c \sum_{p=1}^{\infty} \tau_{p}(c).$$

(6)

Using this expression and (5), the intrinsic viscosity and Huggins coefficient can be calculated as the zero and first order coefficients in the $c$-expansion of $\eta_{\text{ref}}$. Let us first consider the Zimm limit of (6). If $h \to \infty$, $[\eta]_{Z} = \lim_{c \to 0} [\eta(c) - \eta]/[\eta(c)]$ in the volume/mass units will have the form

$$[\eta]_{Z} = \frac{N_{A}^{1/2} a^{3}}{(12 \pi)^{2/3}} \sum_{p=1}^{\infty} p^{-2/3} = \Phi_{0} \frac{N_{A}^{1/2} a^{3}}{M},$$

(7)

where $N_{A}$ is Avogadro’s number, $M$ is the polymer molar mass, and $\Phi_{0} = 2.56 \times 10^{23}$ is the Flory-Fox factor. Note that this value results from several approximations. The Oseen tensor has been preaveraged over the equilibrium (Gaussian) distribution of beads and the nondiagonal elements in the resulting matrix have been neglected [2]. More exact numerical calculations give slightly different values of $\Phi_{0}$ [6]. When the preaveraging procedure is avoided, the second-order perturbation theory gives $\Phi_{0} = 2.66 \times 10^{23}$. It is seen from (4) and (7) that the relaxation times can be directly obtained from the viscosity measurements: the longest relaxation time of the Zimm polymer of mass $m$ is $\tau_{Z} - \tau_{Z}(c) m / T$ with the proportionality constant $N_{A} / (\sqrt{3 \pi} \Phi_{0} k_{B})$. In theta solvents $[\eta]_{Z}$ and $\tau_{Z}$ are proportional to $(h^{1/2} a)^{3}$. In good solvents the dependence on $N$ changes to $N^{3/2}$, $\nu = 0.6$ [1]. For arbitrary strength of HI $[\eta]$ should be a function of $h$. Obtaining the dependence of $[\eta]$ on $h$ for good solvents needs further investigations; for theta solvents it can be written as in Eq. (7) but with $\Phi_{0}$ replaced by the following function of $h$ [15]

$$\Phi_{0}(h) = \Phi_{0} \left( \sum_{p=1}^{\infty} p^{-3/2} \right)^{-1} \sum_{p=1}^{\infty} \frac{p^{-3/2}}{1 + p^{-3/2}} h.$$

(8)

This result for $[\eta]$ is similar to that of KR but with a significant difference due to a different $h$.

When the polymer shrinks to the globule as it is observed in poor solutions, and is completely impenetrable to solvent, it can be regarded as a solid sphere of the volume $V$. Then the familiar Einstein theory of the viscosity of suspensions can be used. In this approach the intrinsic viscosity and the hydrodynamic radius are readily expressed as

$$[\eta] = 2.5 \frac{V N_{A}^{1/2}}{M}, \quad R_{G} = \left( \frac{3[\eta] M}{10 \pi N_{A}} \right)^{1/3}.$$ 

(9)

Thus, having measured the viscosity of a polymer solution, the above formulas (7) – (9) can be used to determine the intrinsic viscosity and then the polymer size. In theta solution the polymer relaxation times, as well as the combination $N^{3/2} a$ or the gyration radius $R_{G} = \sqrt{N / 6} a$ can be found, assuming the Flory-Fox factor is known. Alternatively, if $R_{G}$ is known, the function $\Phi(h)$ can be determined from $[\eta]$ and from Eq. (8) the draining parameter $h$ can be extracted. Based on the KR formula for $D$ (see the text after Eq. (5)) also the hydrodynamic radius of the chain can be evaluated from the relation $\sqrt{\pi} R_{G} / R_{G} = 8 / 3 \pi \sqrt{2} / h$. The polymer radii are measured also in light scattering experiments. Such independent data then could serve for testing the proposed theory, in particular, the importance of draining in the polymer dynamics.

EXPERIMENTAL

In our experiment, the Couette-type viscosity and density meter with a magnetically suspended rotor was used. The device was constructed especially for measurements of macromolecular solutions while scanning temperature as well as at constant temperature. Its detailed description is given in [13]. Here we only note that in this rotational viscosimeter the whole inner cylinder is immersed into the sample and works without mechanical contact with the outer parts of device. The requirement of constant shear rate (it can vary in the range from 20 to about 130 s$^{-1}$, when Taylor vortices appear in the volume of the sample thus disturbing the Couette flow around the rotor) is fulfilled in the device and the elimination of the influence of surface forces on the bulk phase is guaranteed. Before our measurements the independence of the results on the value of the shear rate has been verified. Then the device was calibrated at the shear rate 80 s$^{-1}$, which was then used throughout the experiment. The rotor and sample chamber are removable and made of glass for simple cleaning and preparation of samples. For our experiments it was important that no influence of the polymer film eventually adsorbed on the surface of the cylinder on the measured viscosity has been detected. This effect reveals itself mainly at the lowest measured concentrations $c$ and, as in the works [3, 4], would lead to qualitatively different dependences of the measured viscosity on $c$ if compared to the moderately diluted solutions. Since this effect has not been observed in our experiment, we suppose that the measured viscosity depends only on the known polymer concentration in the solution. The accuracy of both the viscosity (if changed in the range 0.3 - 300 mPAs) and density (0.7 - 1.4 g/ml) measurements is ~ 0.1% and the temperature can be
scanned with the accuracy 0.02 °C from 5 to 85 °C [13]. We probed the viscosity of aqueous poly(N-vinyl-2-pyrrolidone) (PVP) solutions within the 0.1 - 4 mg/ml range of c at different temperatures. Our attempts to study lower concentrations led to unreliable results weighted with too large experimental errors. PVP was a commercial product from Sigma Chemical Co. with molecular weight 3.6·10^5. The volume of the studied samples was 1.6 ml. The samples were always cooled to 15 °C and then heated up to 40 °C. The scan rate was 15 °C per hour.

Fig. (1). Viscosity dependence on the polymer concentration at three different temperatures. The lines represent quadratic polynomial fits. In all the cases η(0)/η = 1, with errors less than 0.2%.

A fit of the measured viscosity η_{rel} = η(c)/η to a quadratic polynomial (see Fig. 1) was used to determine the viscosity functions η_{rel} and (ln η_{rel})/c. Examples of the results are shown in Fig. (2). Both these quantities have been fitted by linear functions. These straight lines (Huggins and Kraemer plots) have common intercepts (the difference being less than 1%) that coincide with the intrinsic viscosities [η] at given temperatures T. By this way the T dependence of [η] has been determined.

Fig. (2). Huggins and Kraemer viscosity functions from dilute to extremely dilute PVP solutions.

In Ref. [4], the range of concentrations from approximately 0.15 to 4 mg/ml has been studied at the temperatures T = 20, 25, and 35 °C. The deduced η_{rel} at these temperatures changes roughly in the following intervals: 0.125-0.150, 0.120-0.145, and 0.110-0.135 (ml/mg). These changes correspond to those in our experiments, however, the absolute values of our results notably, by a factor of 1.3-1.4, exceed the results [4]. Due to this, not only [η] but also k_H are different. So, the values of k_H found by us are from about 1.5 to 1.9 times smaller than k_H as we have estimated them from the data [4]. The obtained intrinsic viscosities [η] (in ml/mg) at different temperatures are as follows: 20°C: 0.166, 25°C: 0.163, 30°C: 0.157, 35°C: 0.151, 40°C: 0.145. Correspondingly, the Huggins (Kraemer) coefficients at these temperatures are 0.246 (0.212), 0.251 (0.209), 0.289 (0.188), 0.347 (0.154), and 0.399 (0.121). The absolute errors of [η] decrease with increasing temperature from 0.020 ml/mg at 20°C to 0.010 ml/mg at 40°C. These errors come mainly from the quadratic fit to the data on η_{rel} (in comparison with the fits to η_{rel}, the errors from the linear fits to η_{rel} are negligible). As distinct from the works [3, 4], no additional treatment of the data was necessary. Note that while the additional procedure of the data handling in [3, 4] seems to be meaningful, a possible reason for the discrepancy with the numerical values from these works could originate in the change of the constants K and t_k, supplied by the manufacturer and used for the determination of viscosity via the equation η = Kρ(t - t_k), where r is the measured time of the flow of the sample through the capillary (note that the equation (1.1) for η in [4] is too simple to be directly used for the precise determination of the viscosity). These constants depend on the viscosimeter geometry and when the inner radius of the capillary changes due to the adsorption or solution, K and t_k also change thus altering the determined viscosity. In particular, when the inner radius of the capillary changes due to the adsorption or solution, K and t_k also change thus altering the determined viscosity.

The theta temperature T_θ of PVP in pure water has been determined in studies of PVP in water containing salts. By extrapolation to the zero concentration the theta temperatures of such systems, T_θ was found to be 413±5 K in Ref. [16] and 420±7 K in [17]. Our systems at these temperatures cannot be studied experimentally. However, assuming universal character of the theory presented for theta solutions, one can till determine the polymer parameters. This can be done as follows. It has been experimentally verified (see, e.g., [18] and refs. therein) that the viscosity of long polymer solutions depends on the temperature as η = Aexp(B/T), where B = B_0 + α(M)c and ln(A/A_0) = β(M)c, with A_0 and B_0 being the values for the solvent. By comparison of this formula with the representation of viscosity at c → 0, η(c) = η(1+[η]c+...), one finds [η] = β + α/T. For the given M, we have then determined from our experiment the constants α = 90.334/T K ml/mg and β = -0.142 ml/mg. Thus, [η]_θ = 0.077 and 0.073 ml/mg for T_θ = 413 and 420 K, respectively. The problem in these estimations is in the fact that from the beginning we cannot judge on the degree of draining of the studied polymers, i.e., we have no information on the value of h in Eq. (8). Assuming a complete impermeability of the PVP polymers [19], we have deter-
mined from Eq. (7) $\sqrt{Na} = 46.65$ nm using the value $[\eta]_0 = 0.075$ ml/mg as $[\eta]_z$ and the polymer mass per mole $M = 360$ kg. The gyration radius $R_G = 19.04$ nm and the corresponding hydrodynamic radius for Zimm polymers is $R_H = 3\sqrt{\pi} R_G / 8 = 12.66$ nm. The longest relaxation time from the formula given after Eq. (7) is of order of $\mu$s, for example, at $T = 413$ K it is estimated as $\tau_z = 1.17 \mu$s.

Since the experimental temperatures are well below the theta point, it is reasonable to estimate the polymer radius using Eqs. (9). So, we obtain $R_H = 20$ nm for the hydrodynamic radius. This is close to the value 18.95 nm found in [19] for the same PVP mass at the same temperature, although the measured viscosity in that work leads to $[\eta] = 0.118$ ml/mg, which is a value notably lower than $[\eta] = 0.163$ ml/mg at 25°C from our experiment. In any case, both values of $R_H$ are larger than the above estimated value at theta temperature. This result needs a special consideration.

CONCLUSIONS

One would expect that from a variety of polymeric systems the dilute solutions of flexible polymers are particularly suitable for theoretical description and interpretation of experimental data. However, a number of long-standing problems shows that these systems are in fact very complicated. For instance, it is not clear why some solutions in the region of time and space scales much exceeding the atomic ones behave universally as predicted by the Zimm theory, and the other do not. It concerns various observed characteristics of polymer solutions, in particular their viscosity, which was the subject of the present work. Being motivated by the viscosimetry experiments that demonstrated an anomalous behavior of the viscosity at low concentrations of polymers, we have realized experiments, which, as distinct from the traditional capillary viscosimetry, yielded the expected linear dependence of the reduced viscosity on polymer concentration. In addition, the obtained solution characteristics, such as the intrinsic viscosity, notably differ from their values in other experiments. At the same time, some of our results are rather surprising and cannot be explained within the known theories. This relates, e.g., to the temperature dependence of the intrinsic viscosity or an unexpectedly small value of the hydrodynamic radius of polymer coils in theta conditions. The model developed by us for the viscosity of polymer solutions does not solve these problems. Partially this is due to the lack of independent (not viscosimetric) information on the studied systems and the absence of the model development for good and poor solutions. However, we believe that the starting point of the used approach, which consists in the necessity to take into account a nonzero permeability of the polymer with respect to the solvent, is inclusive. The permeability (or draining) breaks the universality conception since it leads to an additional parameter which is different for distinct polymers even in the “universal” region of their behavior. This phenomenological parameter then should appear in various polymer characteristics, such as the polymer radii or relaxation times. The idea goes back to the classical work by Kirkwood and Riseman [9] but is mostly ignored by experimentalists. Taking into account the hydrodynamic interactions between different polymer coils in theta solutions, we have obtained formulas for the individual polymer relaxation times and the solution viscosity at low concentrations. In particular, the KR result for the intrinsic viscosity has been corrected. At present, no theory of the viscosity of polymer solutions can be considered as commonly accepted. We thus believe that the used experimental method and the obtained results could be of importance for a further development of the polymer solution rheology.

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