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Investigation of local viscosity in polymer solutions by means of electrolytic conductivity

Hans Vink
Institute of Physical Chemistry, University of Uppsala, P.O. Box 532, 751 21 *Uppsala, Sweden*
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The local viscosity in aqueous solutions of polymers (dextran and hydroxyethyl cellulose) and low-molecular weight viscogenic compounds (glycerol and d-glucose) has been studied by measuring the electrolytic conductivity of probe electrolytes. For low-molecular weight viscogenic compounds the local viscosities determined were close to the macroscopic viscosities of the solutions, whereas pronounced differences exist for polymer solutions. Of particular interest was the finding that the local viscosity for dextran was only marginally higher than the local viscosity for the corresponding monomer, d-glucose. The local viscosity for hydroxyethyl cellulose was somewhat higher than the local viscosity for dextran, indicating greater flexibility of the dextran chain.

Keywords Polymer solutions; viscosity; conductance;dextran; glucose; hydroxyethyl cellulose; glycerol

Introduction

The local viscosity, or microviscosity, of a polymer solution can be studied by various diffusion methods, either by directly determining the diffusion coefficient of a probe molecule[1-4], or indirectly by fluorescence depolarization[5-7], diffusion determined reaction kinetics[8,9] and polarography[10,11]. In the present investigation an alternative method, based on the determination of the electrolytic conductivity of a probe electrolyte in polymer solutions, is used. This method is best suited to aqueous solutions and has certain advantages over the diffusion method. As the probes are subjected to a steady external force the method is directly related to Stokes' law, and does not involve Einstein's equation for the diffusion coefficient. The method also takes advantage of the simplicity and high inherent accuracy of conductivity measurements.

Theory

The limiting equivalent conductivity of a binary 1:1 electrolyte may be related to the frictional properties of the constituent ions by the equation

$$\Lambda^0 = \lambda_+^0 + \lambda_-^0 = \frac{F^2}{f_+} + \frac{F^2}{f_-} \tag{1}$$

where Λ^0, λ_+^0 and λ_-^0 are the limiting equivalent conductivities of the electrolyte and the cation and anion, respectively, f_+ and f_- are the corresponding molar friction coefficients and F is the Faraday constant.

Using Stokes' law we may express the friction coefficients in the form

$$f_i = N_A 6\pi r_i \eta, \quad i = +, - \tag{2}$$

where N_A is the Avogardro constant, r_i the ionic radius and η the local viscosity. It should be noted that in conjunction with the macroscopic viscosity, the constant factor 6π in equation (2) should be replaced by a smaller number (4π or smaller[12]) when applied to bodies of molecular dimensions. As the value of this factor is unknown, it is appropriate to retain the value 6π and define the (apparent) local viscosity by equation (2).

Combining equations (1) and (2) we obtain

$$\Lambda^0 = \frac{F^2}{N_A 6\pi\eta}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{3}$$

Thus, provided the ionic radii are constant, Λ^0 is a direct measure of the local solution viscosity. Denoting by Λ_0^0 and η_0 the values of the respective quantities in pure solvent (water) we have

0032 3861/82/010006 04$03.00

$$\frac{\Lambda^0}{\Lambda_0^0} = \frac{\eta_0}{\eta} \tag{4}$$

The determination of the limiting equivalent conductivity is tedious and it is therefore desirable to extend equation (4) into the range of finite concentrations of the probe electrolyte. At low electrolyte concentrations ($c < 0.01$ mol dm^{-3}) the concentration dependence of the equivalent conductivity is adequately represented by the Onsager limiting law[13]

$$\Lambda(c) = \Lambda^0 - \left(\alpha\Lambda^0 + \frac{\beta}{\eta}\right)\sqrt{c} \tag{5}$$

where the parameters α and β depend on temperature and the dielectric constant of the solution. Neglecting this dependency, we have at a fixed concentration c

$$\frac{\Lambda(c)}{\Lambda_0(c)} = \frac{\Lambda^0}{\Lambda_0^0} \frac{1 - \left(\alpha + \frac{\beta}{\eta\Lambda^0}\right)\sqrt{c}}{1 - \left(\alpha + \frac{\beta}{\eta_0\Lambda_0^0}\right)\sqrt{c}} \tag{6}$$

Because of equation (4) the parameters in brackets in the right hand side of equation (6) are equal, and we obtain

$$\frac{\Lambda(c)}{\Lambda_0(c)} = \frac{\Lambda^0}{\Lambda_0^0} = \frac{\eta_0}{\eta} \tag{7}$$

It is thus possible to determine the local viscosity from single point measurements, provided the concentration of the probe electrolyte is sufficiently low and the dielectric constant of the solutions is not changed appreciably by the viscogenic compound. The validity of equation (7) may be easily verified by determing η_0/η at different concentrations. Here measurements performed in the concentration range 0.0008–0.015 mol dm^{-3} of the probe electrolyte were in agreement within experimental error.

Experimental

A Leeds and Northrup conductivity bridge, described by Dike[14], was used. The measurements were carried out with an immersion-type conductivity cell, having black-platinized electrodes, and a cell constant of 170.6 m^{-1}. The conductivity water had an electrolytic conductivity $K < 10^{-4} \Omega^{-1}$m^{-1}. The conductivity measurements were carried out at 1 kHz, at the temperature 25°C. As a.c. conductivity represents a non-stationary process a few d.c. conductivity measurements (with KCl in dextran and glucose solutions) were carried out, using a modification of the Ives–Swaroopa techniques[15]. In all cases the a.c. and d.c. conductivities were in agreement within experimental error ($\pm 0.2\%$), which demonstrates the stationary character of the determined local viscosities.

Materials

The electrolytes were KCl (Merck), LiCl (Mallinckrodt) and tetrabutylammonium pivalat, TBP. This salt was prepared from tetrabutylammonium bromide (Eastman) and pivalic acid (trimethylacetic acid, Fluka). This was done by first preparing tetrabutylammonium hydroxide from the corresponding bromide, with the aid of freshly prepared silver oxide, and subsequently neutralizing the hydroxide with an equivalent amount of pivalic acid.

The viscogenic substances were glycerol (doubly distilled), d-glucose (Fisher), dextran (Pharmacia, $[\eta] = 0.31$ dl g^{-1}, $M_w = 110\,000$) and hydroxyethyl cellulose, HEC (Union Carbide, $DS = 0.88$, $MS = 1.67$, $[\eta] = 1.65$ dl g^{-1}, $M_v = 68\,000$).

In order to keep the solvent correction for conductivity low, the viscogenic substances had to be specially purified. The purity of glycerol was found to be adequate and it was used without further purification. Glucose was repeatedly extracted with a 95% ethanol–water mixture, and subsequently dried in a vacuum. The polymers were subjected to prolonged dialysis against distilled water in bags of cellophane dialysis tubing (Union Carbide) and subsequently freeze dried. From the viscogenic substances concentrated stock solutions were prepared, which had an electrolytic condictivity K in the range 10^{-3}–3.10^{-3} Ω^{-1} m^{-1}. The solutions used in the measurements were prepared by mixing weighed amounts of these stock solutions and standardized solutions of the electrolytes.

Macroscopic viscosities were determined with an Ostwald viscometer, calibrated with aqueous glycerol solutions.

Results and Discussion

Different probe electrolytes were used in order to study the effects of ionic size and ionic hydration on the determined local viscosity. As small ions are extensively hydrated the possibility was considered that the hydration of the ions is affected by the viscogenic compounds, and hence the radii in equation (3) are not constant. To check this measurements were performed with the salts KCl and LiCl, which have cations differing appreciably with respect to hydration numbers.

The salt TBP was chosen because it consists of two large nearly spherical ions, which are essentially unhydrated. The limiting equivalent conductivity of TBP in water was determined to be $\Lambda^0 = 49.10^{-4} \Omega^{-1}$m^{2}mol^{-1}. With the help of Stokes' law its ionic radii were estimated to be 2–3 times greater than those of KCl and LiCl.

As viscogenic compounds both low-molecular weight and polymeric substances were used. The former were included for comparison purposes and it was considered of special interest to study the viscogenic effects of a polymer (dextran) and the corresponding monomer (d-glucose).

The results of the measurements are shown in *Figures 1* and *2*. In *Figure 1* measurements on the low-molecular weight viscogenic compounds are shown. In this case a close correspondance between the local and macroscopic viscosities is expected. We find that this is true for the TBP probe, whereas for the smaller KCl and LiCl probes deviations occur. This discrepancy is a manifestation of the before mentioned inadequacy of the Stokes' equation when applied to bodies of the size of solvent molecules. To make this explicit we rewrite equation (2) in the form

$$f_i = N_A 6\pi\varphi_i r_i \eta' \qquad i = +, - \tag{8}$$

where η' is the macroscopic viscosity and $\varphi_i \leqslant 1$ represents the deviation from Stokes' law. The value of φ_i decreases

Table 1 Viscosity data for solutions of the viscogenic compounds

Viscogenic compound	Probe	k	Macroscopic viscosity w	 η'/η_0'	 $k' = \lim_{w=0} \frac{1-\eta_0'/\eta'}{w}$
Glycerol	KCl, LiCl TBP	1.79 ± 0.02 2.14 ± 0.02	0.1	1.288	2.24 ± 0.02
d-Glucose	KCl, LiCl TBP	1.92 ± 0.02 2.28 ± 0.02	0.1	1.327	2.46 ± 0.02
Dextran	KCl, LiCl TBP	2.22 ± 0.03 3.19 ± 0.04	0.107	13.2	31* ± 0.5
HEC	KCl, LiCl TBP	2.64 ± 0.06 4.24 ± 0.06	0.1	138	165* ± 1

* Computed from the intrinsic viscosity according to $k' = 100[\eta]$

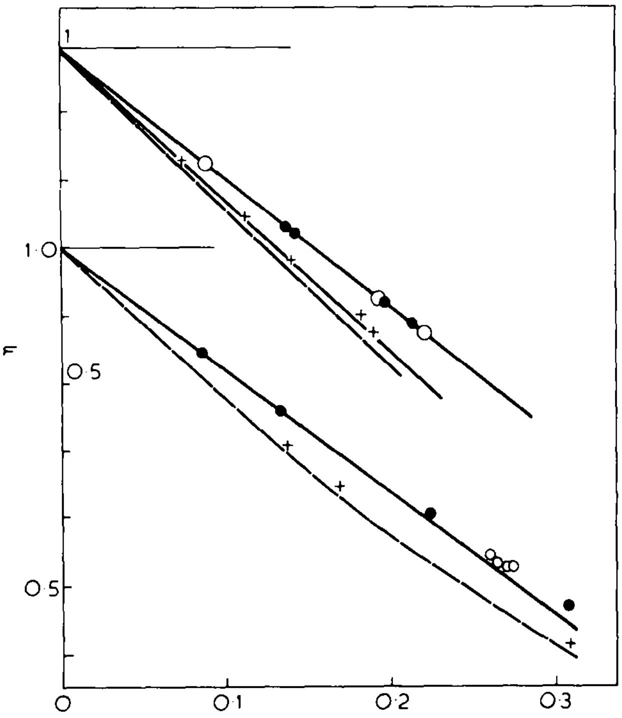

Figure 1 Relative local viscosity *versus* weight fraction of d-glucose (upper curves) and glycerol (lower curves): ●, KCl; ○, LiCl and +, TBP. Broken line represents the macroscopic viscosity

when the size of the probe molecule decreases in relation to solvent molecules. Inserting equation (8) into equation (7) we obtain

$$\frac{\Lambda(c)}{\Lambda_0(c)} = \frac{\eta_0}{\eta} = \frac{\varphi_0\eta_0'}{\bar{\varphi}\eta'} \qquad (9)$$

where $\bar{\varphi} = \left(\frac{1}{r_+}+\frac{1}{r_-}\right)\Big/\left(\frac{1}{r_+\varphi_+}+\frac{1}{r_-\varphi_-}\right)$ is the value of φ averaged over the two ions of the salt.

The addition of large viscogenic molecules to water increases the average size of the molecules in the composite solvent and hence $\bar{\varphi} < \varphi_0$. The displacement of the curves in *Figure 1* is therefore well understood. We also find that the results for the KCl and LiCl probes are identical, which indicates that ionic hydration is unaffected by the viscogenic compounds in the range of concentrations studied.

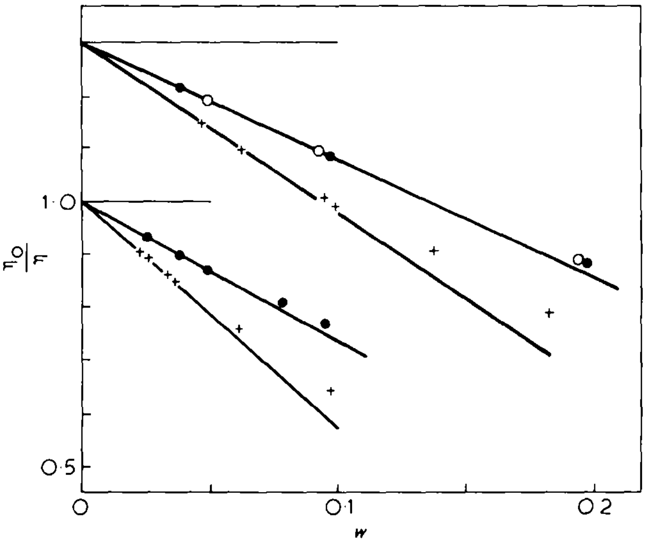

Figure 2 Relative local viscosity *versus* weight fraction of dextran (upper curves) and HEC (lower curves): ●, KCl; ○, LiCl and +, TBP

In *Figure 2* measurements on dextran and HEC are represented. The local viscosity in HEC solutions is appreciably higher than in dextran solutions, which probably is due to the higher rigidity of the cellulosic chain. The local viscosity curves are perfectly linear at low concentrations and there is no indication of a critical overlap concentration, as reported in earlier investigations[1,11]. From the linear parts of the curves, represented by the equation

$$\frac{\eta_0}{\eta} = 1 - kw \qquad (10)$$

where w is the weight fraction of the viscogenic compound, the initial slopes k were evaluated and are listed in *Table 1*, together with macroscopic viscosity data for the solutions.

An inspection of the data reveals that the local viscosities for small probes (KCl, LiCl) are nearly the same for dextran and its monomer d-glucose. This indicates that dexgran is a very flexible polymer and that the local mobility of the monomer units is only marginally impeded by the bonding of the units into long chains. It is also seen that for polymer solutions the macroscopic and microscopic viscosities are unrelated and differ by orders of magnitude with respect to their numerical values.

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Raman spectroscopy of flowing poly(ethylene terephthalate) melts

P. J. Hendra, D. B. Morris and R. D. Sang
Chemistry Department, Southampton University, Southampton SO9 5NH, UK

and H. A. Willis
ICI Plastics Division, Welwyn Garden City, Hertfordshire, UK
(*Received* 17 *September* 1981)

Studies have been made of the Raman spectrum of a poly(ethylene terephthalate) melt being extruded through a glass die. The effects observed in the spectrum are interpreted in terms of changes in molecular shape which vary with shear rate and melt temperature.

Keywords Spectroscopy; Raman; poly(ethylene terephthalate); melts; extrusion; shear; temperature

Introduction

The study of flow phenomena in polymers has attracted much interest because the major forming processes for polymers depend on flow under controlled conditions. Many of these rheological studies have aimed at an understanding of macroscopic flow effects such as die swell, melt fracture and frozen-in orientation. Of equal importance is the characterization of mass flow in the injection moulding and extrusion processes. The results of these studies have frequently been discussed in terms of molecular level behaviour, particularly entanglement and orientation. However, such interpretations have normally been essentially empirical since direct observation at the molecular level has proved extremely difficult.

In the absence of specific techniques for study at the molecular level, resort has been made to indirect observation. An example of one such method is the measurement of birefringence in polymer solutions undergoing shearing flow. A good understanding of such systems has been achieved through the work of Frank and Mackley[1,2]. A further approach has been made through morphological studies of solidified material produced under specified flow conditions. A 'shish kebab' morphology has been observed by Keller *et al.*[3,4] in polymers crystallized from solutions being rapidly stirred. Extrusion of highly oriented polyolefin fibres from the solid state has been demonstrated by Southern and Porter[5]. Experiments on flow-induced crystallization are of more direct relevance to the subject at present under discussion. The formation of oriented crystallized material, under quenched cooling conditions, at the die entry region has been observed in poly(ethylene terephthalate) (PET) by Griswold and Cuculo[6] and in polyolefins by Collier *et al.*[7]. None of these experiments involved *in-situ* molecular level investigation.

The molecular property constantly invoked in the interpretation of flow phenomena is orientation. We have therefore addressed ourselves to the direct observation of this property in a flowing poly(ethylene terephthalate) melt. Probably the most versatile, molecular-level structural tool available is Raman spectroscopy.* We report here on the use of this technique for making *in-situ* measurements of flowing poly(ethylene terephthalate) both above the crystalline melting point and at high degrees of supercooling.

The use of laser Raman spectroscopy in the investigation of oriented polymers was first described by Cornell and Koenig[8]. They measured a depolarization ratio (p) in polystyrene where

$$p=\frac{\text{scattered light intensity observed through } \perp \text{ analyzer}}{\text{scattered light intensity observed through } \parallel \text{ analyzer}}$$

Depolarization of bands in the Raman spectrum may be the consequence of internal molecular symmetry; in order to apply its measurement to the determination of molecular orientation, the bands selected are ideally those which are depolarized in an isotropic sample. Simple measurement of the depolarization ratio as defined above is not of itself capable of giving quantitative information on the orientation in a polymer specimen. Extensive work by Bower *et al.*[9-11] has shown that application of the appropriate mathematical treatment to measurements of intensities of the band at $\Delta\bar{\nu}=1615\ \mathrm{cm}^{-1}$ in PET can provide measurements of P_2 and P_4 orientation functions. Fortunately, it can be experimentally shown as in *Figure 1* that changes in the depolarization ratio indeed

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* Raman spectroscopy is an inelastic light scattering process. If laser radiation of frequency ν_0 illuminates a sample whose molecules vibrate at frequency ν_{vib}, the scattered light will contain weak radiation at $\nu_0 - \nu_{\mathrm{vib}}$. Since $\nu_{\mathrm{vib}} \ll \nu_0$, the illuminating and scattered light is normally in the visible. See Raman spectra of synthetic polymers. Chapter in Developments in Polymer Chatacterization Vol II, Ed. J. V. Dawkins, Applied Science, 1980

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