Letters

Individual bead contribution to intrinsic viscosity of polymers

The most used necklace model of isolated randomly coiled linear macromolecule concentrates the frictional resistance in the $Z + 1$ identical beads each with a hydrodynamic radius a_h. The translational resistance of each bead equals $6\pi a_h \eta_s \vec{v}_{\mathrm{rel}}$. Here η_s is the viscosity of the solvent and $\vec{v}_{\mathrm{rel}}$ is the difference between the velocity of the bead $\vec{v}^*$ and the unperturbed solvent flow $\vec{v}$ at the location of the bead. The increase of shear stress caused by the presence of the macromolecule is the consequence of finite average friction forces on all the beads of the model. The beads are held together by ideally elastic forces of the massless and frictionless links of r.m.s. length b_0 connecting subsequent beads. The average relative velocity and hence the force on each bead increases as its average distance from the centre of mass, or more exactly, from the centre of hydrodynamic resistance which moves with the same velocity as the unperturbed solvent.

According to Zimm[1] the contribution of the model to intrinsic viscosity turns out to be:

$$[\eta]_Z = \frac{N}{M\eta_s\dot{\gamma}} \sum_{j=0}^{Z} \langle y_j F_{jx} \rangle = \frac{2\mu_0 NkT}{M\eta_s\dot{\gamma}} \langle \mathbf{yAx} \rangle = \frac{RT}{M\eta_s} \sum_{p=1}^{Z} \frac{\tau_p}{1 + i\omega\tau_p} \qquad (1)$$

$$\tau_p = 1/2\mu_0 D_0 \lambda_p$$

$$\mu_0 = 3/2b_0^2$$

$$D_0 = kT/6\,\pi a_h \eta_s$$

where N is the Avogradro number, M is molecular weight, $\dot{\gamma}$ is the velocity gradient, the index j applies to the jth bead, $\mathbf{A}$ is the link force tensor, λ_p is the pth eigen value of $\mathbf{HA}$, $\mathbf{H}$ is the hydrodynamic interaction tensor, τ_p is the pth relaxation time. The formulation of $[\eta]_Z$ as a function of coordinates is based on a flow field $\vec{v} = (\dot{\gamma}y, 0, 0)$.

Such a model represents fairly well the molecular weight dependence of intrinsic viscosity of linear polymers in theta solvent in the limit of zero gradient, and the frequency dependence of it. But it yields a vanishing intrinsic viscosity for a single bead at any frequency, and for any molecular weight at very high frequency. Both results are in disagreement with observations.

The second defect was removed by introduction of internal viscosity which measures the resistance of the coil against shape change[2]. The mathematically very handy formulation[3] in terms of normal modes of the model is not only not yet generally accepted but heavily opposed[4–6]. Hence one is tempted to look after any effect which may make unnecessary the introduction of internal viscosity. A great many efforts in this direction were made on the basis of correlation function[7,8] or of additional forces between second and still farther apart neighbours[9]. It turns out that in all cases a result at least superficially compatible with experimental data is only obtainable if one introduces some kind of model rigidity. This makes the original formulation by Cerf[3] still more acceptable because it makes the mathematical handling so much easier and the results calculated seem to agree better with experimental data than those of all later suggestions. As will be shown in this paper, a finite volume of the beads also introduces an intrinsic viscosity term which does not vanish in the limit of very high frequency.

Very few attempts were made for removing of the first defect[10–12]. They were based on the fact that a rigid sphere by itself yields an intrinsic viscosity $2.5/\rho$ (ρ is density of the sphere)[13]. This value is independent of gradient and frequency. In contrast to that, equation (1) yields a finite contribution of the sphere to intrinsic viscosity only in the case that it is located outside the xz plane going through the centre of hydrodynamic resistance of the system because only in such a case the contributing product of coordinate of the centre of the sphere with the x component of the relative velocity does not vanish. Since for a single sphere this centre coincides with the centre of the sphere the contribution according to equation (1) is zero.

As a consequence of the linearity of Stokes equation and the spherical shape[16] the intrinsic contribution of the sphere to viscosity can be in first approximation simply superimposed on that of hydrodynamic frictional forces, i.e. on $\langle y_j F_{jx} \rangle$. The total contribution of the model with $Z + 1$ beads is $2.5(Z + 1)/\rho$. Since the molecular weight of the model is $(Z + 1)$ times that of the bead the factor $Z + 1$ just cancels out. Hence one can rewrite equation (1) as:

$$[\eta] = 2.5/\rho + [\eta]_Z \qquad (2)$$

The intrinsic viscosity of the necklace model is the sum of intrinsic viscosity of the single beads (Einstein term) and the conventional contribution of the necklace (Zimm term).

Two important features follow from this formulation. Firstly the additional term $2.5/\rho$ is independent of molecular weight and hydrodynamic interaction. Secondly the term is independent of frequency so that one obtains a finite intrinsic viscosity even in the limit of high frequency where $[\eta]_Z$ vanishes. The socalled second Newtonian viscosity at ω going to ∞ would read:

$$[\eta]_\infty = 2.5/\rho \qquad (3)$$

It was hoped for a while that this result could eventually explain the experimentally observed finite values of the second Newtonian intrinsic viscosity without the introduction of internal viscosity or at least reduce its role. It turns out, however, that the experimentally observed $[\eta]_\infty$ values of polystyrene in aroclor are about 10 times too large, between 24 and 17 cm^3/g if one goes in molecular weight from 20 000 to 860 000 [14]. Since the value of $[\eta]_\infty$ caused by the beads alone is only about 2.5 it cannot explain the observed data although it reduces by about 10% the contribution which has to be supplied by internal viscosity. Hence the concept of internal viscosity needs to be retained.

A few words are needed about the dependence of the term $2.5/\rho$ on hydrodynamic interaction. According to Burgers[15] the distortion of the linear flow $\vec{v}$ by the presence of the sphere which contributes to the shear stress and hence to intrinsic viscosity can be described by two force doublets. The first doublet consists of a positive and a negative force in the direction of x-axis at the points $(0, -\epsilon, 0)$ and $(0, +\epsilon, 0)$, respectively. The second doublet has a positive and a negative force in the direction of y-axis at the points $(-\epsilon, 0, 0)$ and $(+\epsilon, 0, 0)$, respectively. The strength of the doublet, measured by the product ϵF, yields a flow modification proportional to $A = 5\dot{\gamma}a_h^3/12$. Both doublets hence produce a change in shear stress:

$$(\eta - \eta_s)\dot{\gamma} = 8\pi A\eta_s = (10a^3/3)\dot{\gamma}\eta_s = 2.5 \times (4\pi a_h^3/3)\dot{\gamma}\eta_s \quad (4)$$

yielding the Einstein value $[\eta] = 2.5/\rho$.

If one applies this method to any bead of the necklace model one has to take into account the actual gradient $\dot{\gamma}^*(\vec{r}_j)$ at the position $\vec{r}_j$ of the bead as it is modified by partial shielding of the flow inside the coil. By introducing vectors and tensors in the $3(Z + 1)$ dimensional space of $Z + 1$ beads one has for the velocity:

$$\vec{v}^* = \vec{v} - 2\mu_0 D_0 \mathbf{HA}\vec{r} - D_0\mathbf{H}\,\mathrm{Grad}\ln\phi \quad (5)$$

and from it for the gradient:

$$\dot{\gamma}^* = \partial v_x^*/\partial y = \dot{\gamma} - D\mathbf{H}\frac{\partial^2 \ln\phi}{\partial x \partial y} \quad (6)$$

if one accepts that the shear component of the motion of beads as described by $\vec{v}^*$ is practically identical with the shear component of the shielded flow field of the liquid inside the coil. The space average of the gradient is the integral over the whole space of this equation multiplied by the distribution function ϕ:

$$\langle\dot{\gamma}^*\rangle = \dot{\gamma} - D\mathbf{H}\int \frac{\partial^2\phi}{\partial x \partial y}\,\mathrm{d}V = \dot{\gamma} \quad (7)$$

since the volume integral of the second derivatives of ϕ can be transformed into a surface integral of the first derivatives of ϕ. The derivatives vanish faster than $1/r^2$ with increasing radius of the surface thus yielding a zero value for the integral. The average true velocity gradient at each bead equals the gradient of the unperturbed flow so that each bead yields the same Einstein type contribution $2.5/\rho$ to intrinsic viscosity.

Equation (2) may need an additional correction. The contribution $2.5/\rho$ corresponds to a sphere which rotates with the same angular velocity as the volume element of the unperturbed liquid, $\vec{\omega} = (0, 0, -\dot{\gamma}/2)$. In the polymer molecule each segment is so rigidly connected with its neighbours that such a rotation cannot take place if the molecule itself does not rotate with the volume element. In such a case one has to assume that also the beads representing the segments cannot rotate freely as assumed in Einstein's derivation. In the extreme case of fully blocked rotation the torque exerted on such a fixed sphere turns out to be[16]:

$$\vec{T} = 8\pi\eta a_h^3 \,\mathrm{rot}\,\vec{v}/2 \ \mathrm{g} = 4\pi a_h^3\eta_s\,(0, 0, -\dot{\gamma}) \quad (8)$$

It is proportional to the true local gradient $\dot{\gamma}^*$ which according to equation (7), has $\dot{\gamma}$ as its average value. The dissipated effect is the scalar product of the torque with the angular velocity $\vec{\omega}$ of the unperturbed flow:

$$\mathrm{d}W/\mathrm{d}t = (\eta - \eta_s)\dot{\gamma}^2 = 2\pi a_h^3\eta_s\dot{\gamma}^2 = \frac{4\pi a_h^3}{3}\,\frac{3}{2}\,\eta_s\dot{\gamma}^2 \quad (9)$$

yielding to intrinsic viscosity the additional term $1.5/\rho$. Together with Einstein's term $2.5/\rho$ one has for the intrinsic viscosity of the incompressible sphere which cannot rotate with the liquid[11]:

$$[\eta] = 4.0/\rho \quad (10)$$

which has to replace the value of $2.5/\rho$ in equations (2) and (3) if the molecule does not rotate at all. Since a perfectly soft molecule rotates uniformly with the volume element such a correction is not needed. Any deviation of coil from spherical shape and any coil rigidity however, introduces a nonuniform rotation which yields some addition to the value above 2.5 although less than 1.5 which corresponds to a complete fixation of the coil. In that which follows this excess contribution will be completely neglected.

All these deviations were performed as if the radius of the beads is so much larger than that of solvent molecules that one can treat the hydrodynamic problem as that of a sphere in a continuous medium without any slip of solvent on the surface of the sphere. In a conventional polymer solution the solvent molecules as a rule are not substantially smaller than the chain elements of the polymer. Surface slip may occur. The chain elements may even make so much easier the shear displacement of solvent molecules that their intrinsic contribution to viscosity becomes negative.

Hence the values $2.5/\rho$ has to be considered as ideal upper limit which may differ quite appreciably from the actual values. This means that although for polymer solutions one has to introduce a constant additive term in intrinsic viscosity as shown in equations (2) and (11) its value is not a universal constant, i.e. $2.5/\rho$. Its maximum value is $2.5/\rho$. But it may be smaller and even negative if the solvent molecules are large as compared to polymer chain groups and if their adhesion to the macromolecule is so weak that interface slip is facilitated.

Low molecular weight solutions indeed show even negative values of steady state intrinsic viscosity[17]. The same applies to low molecular weight normal paraffins in benzene or CCl_4 (negative values for 10 or less C atoms in the chain) and in bromobenzene (negative values up to C_{12})[18]. Poly(oxyethylene glycols) in many solvents yield an intrinsic viscosity[18]:

$$[\eta] = A + bM^a \quad (11)$$

with $A = 2\ \mathrm{cm^3/g}$ in water and methanol, 0.75 in dioxane, 0.5 in cyclohexane, and 0 in benzene and CCl_4. One has a large A, although smaller than 2.5, in solvents with small molecules which also possess enough affinity to the polymer so that the surface slip seems to be less likely to occur. With larger solvent molecules and less interaction between them and the solute A decreases and even vanishes. In paraffins such constant additive term must be negative in order to yield the observed negative intrinsic viscosity in spite of the fact that the conventional coil contribution $[\eta]_Z$ is always positive.

The addition of such a constant additive term does not affect appreciably the intrinsic viscosity values at high molecular weight and zero frequency. But the situation becomes more critical at very high frequency where $[\eta]_Z$ completely vanishes. A positive value of the observed second Newtonian viscosity in this region can be at least partially explained by the constant additive term if the term is positive. If it is negative it even increases the demand for some other explanation, for instance by the nonvanishing term resulting from partial coil rigidity as described by internal coil viscosity. Hence this analysis seems to corroborate the need fcr the introduction of internal viscosity in order to explain the finite limiting value of intrinsic viscosity at high frequency shear flow field.

Anton Peterlin
Polymers Division,
National Bureau of Standards,
Washington DC 20234, USA
(Received 23 December 1976)

References

1 Zimm, B. H. *J. Chem. Phys.* 1956, **24**, 269
2 Peterlin, A. *J. Polym. Sci. (C)* 1973, **43**, 187
3 Cerf, R. *J. Polym. Sci.* 1957, **23**, 125; *J. Phys. Rad.* 1958, **19**, 122
4 Booij, H. C. and van Wiechen, P. H. *J. Chem. Phys.* 1970, **52**, 5056
5 Fixman, M. and Stockmayer, W. H. *Ann. Rev. Phys. Chem.* 1970, **21**, 407
6 Osaki, K. *Adv. Polym. Sci.* 1973, **12**, 1
7 Edwards, S. F. and Freed, K. F. *J. Chem. Phys.* 1974, **61**, 1189
8 Felderhof, B. V., Deutch, J. M. and Titulaer, U. M. *J. Chem. Phys.* 1975, **63**, 740
9 Doi, M., Nakajima, N. and Wada, Y. *Colloid Polym. Sci* 1975, **253**, 905; 1976, **254**, 559
10 Bianchi, U. and Peterlin, A. *J. Polym. Sci. (A-2)* 1968, **6**, 1759
11 Peterlin, A. *Polym. Prepr.* 1968, **9**, 323
12 Prager, S. *J. Phys. Chem.* 1971, **75**, 72
13 Einstein, A. *Ann. Phys.* 1906, **19**, 289; 1911, **34**, 591
14 Massa, D. J., Schrag, L. J. and Ferry, J. D. *Macromolecules* 1971, **4**, 210
15 Burgers, J. M. *Verh. K. Ned. Akad. Wet. Afd. Natuurk. Reeks 1* 1938, **16**, 113
16 Happel, J. and Brenner, H. 'Low Reynolds Number Hydrodynamics', Prentice Hall, Englewood Cliffs, N.J., 1965
17 Kuss, E. and Stuart, H. A. *Z. Naturforsch. (A)* 1948, **3**, 204
18 Sadron, C. and Rempp, P. *J. Polym. Sci.* 1958, **29**, 127

Effect of pressure upon the dissociation of the benzoyloxy radical

The rate of dissociation of benzoyl peroxide into radicals is decreased by application of high pressures[1,2]. The benzoyloxy radicals first formed in the dissociation can dissociate further:

$$C_6H_5.CO.O. \rightarrow C_6H_5. + CO_2 \quad (1)$$

but there appears to have been no study of the effect of pressure upon this reaction.

The initiation processes in a radical polymerization initiated by benzoyl peroxide are:

$$C_6H_5.CO.O. + M \rightarrow$$
$$\rightarrow C_6H_5.CO.O.M. \quad (2)$$
$$C_6H_5. + M \rightarrow C_6H_5.M. \quad (3)$$

where M represents a molecule of the monomer. Ordinarily, the phenyl radicals produced in reaction (1) are subsequently consumed in reaction (3)[3]. The rate at which phenyl radicals enter polymer to form end-groups is therefore the rate of reaction (1); reaction (2) can be followed directly by measurement of the rate at which benzoyloxy end-groups are formed. The necessary end-group analyses can be performed by using suitably labelled benzoyl peroxide. Comparisons of the numbers of benzoyloxy and phenyl end-groups in polymers produced from solutions of a monomer in a diluent allow evaluation of k_1/k_2, the magnitude of which depends markedly upon the nature of the monomer[4].

If $\Delta V_1^{\ddagger}$ and $\Delta V_2^{\ddagger}$ are the volumes of activation for reactions (1) and (2), $(\Delta V_1^{\ddagger} - \Delta V_2^{\ddagger})$ could be evaluated from end-group analyses on polymers produced at various pressures. It is expected that $\Delta V_1^{\ddagger}$ would be positive and $\Delta V_2^{\ddagger}$ negative since reaction (1) is a dissociation and reaction (2) an association. $\Delta V_1^{\ddagger}$ might be comparable with $\Delta V^{\ddagger}$ for the dissociation of a molecule into radicals, and $\Delta V_2^{\ddagger}$ with $\Delta V^{\ddagger}$ for the growth reaction in a radical polymerization. These views have been tested for the polymerizations of styrene and methyl methacrylate at 60°C with toluene as diluent.

Benzoyl peroxide was labelled in its rings with tritium and in its carboxyl groups with ^{14}C; materials were assayed by scintillation counting in solution[5]. Low conversion polymerizations were performed in tubes of stainless steel[6,7] at pressures up to 4×10^8 N/m^2 (4000 bar) for styrene and up to 2×10^8 N/m^2 for methyl methacrylate; corrections were made for the compressibilities of monomers and diluents.[8] There were no systematic differences between results for polymerizations at atmospheric pressure in steel and glass vessels, or between those with toluene and those with benzene (the diluent used in most of the previous studies).

Pressure had a pronounced effect upon the balance between benzoyloxy and phenyl end-groups, as indicated by the typical results displayed in *Figure 1*; from the slopes of such plots, values of k_1/k_2 were found. Plots of $\ln(k_1/k_2)$ vs. pressure (see *Figures 2* and *3*) show that $(\Delta V_1^{\ddagger} - \Delta V_2^{\ddagger})$ varies with pressure for both monomers but, from the initial slopes of these curves, the values are 21 ± 3 and 15 ± 2 cm^3/mol for styrene and methyl methacrylate respectively as the monomers.

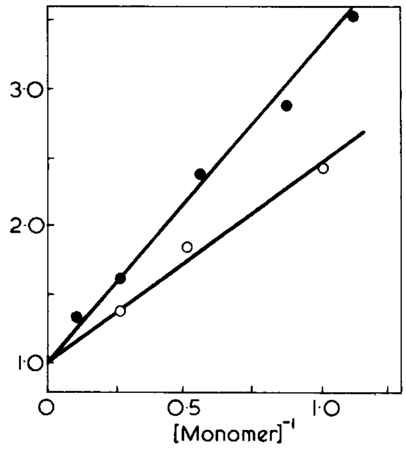

Figure 1 Variation of *x*, (number of benzoyloxy end-groups)/sum of numbers of benzoyloxy and phenyl end-groups), with molar concentration of monomeric methyl methacrylate for polymerizations at 60°C with toluene as diluent. ●, pressure = 0.3×10^8 N/m^2; ○, pressure = 1.5×10^8 N/m^2