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Comment on "On the Correlation between the Negative Intrinsic Viscosity and the Rotatory Relaxation Time of Solvent Molecules in Dilute Polymer Solutions"

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In a recent paper, Yoshizaki, Takaeda, and Yamakawa (YTY) presented an interesting series of measurements of solvent rotational relaxation in solutions containing polyisobutylene (PIB) dimer, poly(dimethylsiloxane) (PDMS) dimer, and a moderate molecular weight PDMS polymer.[1] The measurements were performed by depolarized Rayleigh scattering (DRS), and the solute concentrations ranged up to 0.5 g/mL. The solvents selected were benzene, for PIB, and bromocyclohexane, for PDMS. These choices were made because for these particular systems the observed intrinsic viscosity, $[\eta]_{\mathrm{obs}}$, is negative. They interpret these results as demonstrating "...that Lodge's view of the negative intrinsic viscosity is not always valid", as stated in YTY's abstract. However, what YTY assert as "Lodge's view" is not precisely, in fact, a view that Lodge has expressed, and therefore we feel it is important to clarify this point.

It has been established for numerous polymer–solvent systems that the observed high-frequency limiting viscosity, η'_∞, can lie below the neat solvent viscosity, η_s, and that the steady shear (or low-frequency limiting) intrinsic viscosity, $[\eta]_{\mathrm{obs}}$, can be negative.[2] In the following, we assume that these two phenomena have a common origin. These effects are clearly beyond basic hydrodynamic theories for polymer solutions, in which the solvent is modeled as a continuum with viscosity η_s. Birnboim and Schrag were among the first to suggest that the properties of the solvent in the solution could be largely responsible, and both the Yamakawa group[1,3] and we[2,4-6] have adopted this position.

Our perspective has recently been summarized in a review,[2] in which Lodge states "...a substantial fraction of the difference between η'_∞ and η_s can be attributed to polymer-induced changes in the solvent dynamics...". The observation that the *mean* solvent rotational relaxation time, τ_s, varied with polymer concentration, c, was used to define an "effective solvent viscosity", η_e[2,4]

$$\eta_e(c) \equiv \eta_s \frac{\tau_s(c)}{\tau_s(0)} \qquad (1)$$

We emphasized that η_e, although operationally well-defined, was not really a viscosity, *per se*, but could be viewed as representing a "microviscosity", or effective local friction. Similarly, an intrinsic $[\eta_e]$ was defined by analogy to $[\eta]$, in which $[\eta_e]$ quantified the initial rate at which the *mean* τ_s varied with polymer concentration; thus, in systems for which $[\eta_e] < 0$, the addition of polymer accelerates the *mean* τ_s. (We emphasize the word *mean* here, because the measurements of solvent dynamics inherently integrate over the entire solvent population. This should be contrasted with the expectation that the influence of the polymer on any property of the solvent should diminish as a function of distance from the chain.) Then, we compared the values of $[\eta_e]$ obtained for Aroclor 1248 (A1248) in solutions containing polystyrene (PS), 1,4-polyisoprene (PI), or 1,4-polybutadiene (PB), and at various temperatures, with values of $[\eta'_\infty]$ determined by high-frequency viscoelastic measurements on similar solutions. The results were shown in Figure 2 of ref 2. For example, near 0 °C, $[\eta_e]$ was 13 ± 1, -4 ± 1, and -10 ± 1 mL/g, for PS, PI, and PB, respectively; recall that all hydrodynamic theories for polymer solutions tacitly *assume* $[\eta_e] = 0$. For the same polymers and at the same temperature, $[\eta'_\infty] = 17 \pm 1$, -1 ± 1, and -16 ± 1 mL/g, respectively. The general correlation between $[\eta_e]$ and $[\eta'_\infty]$, in terms of sign and relative magnitude, was advanced as *prima facie* evidence that polymer-induced changes in the solvent dynamics were a substantial contribution to $[\eta'_\infty]$; recall that $[\eta_e]$ and $[\eta'_\infty]$ are determined from two completely different experiments. However, we did not assert that $[\eta'_\infty] = [\eta_e]$; in fact, the differences between the two are clearly substantial, being on the order of 4 mL/g. (The uncertainties of ±1 assigned to $[\eta_e]$ and $[\eta'_\infty]$ are felt to be reasonable estimates, based on measurements on different molecular weight samples, *etc.*; they are not derived by formal statistical analysis.)

Encouraged by this interesting result, we extended the analysis to $[\eta]$, as follows. If changes in solvent dynamics contribute in a frequency-independent (and molecular weight-independent) manner to η'_∞, they should also influence $[\eta]_{\mathrm{obs}}$. To estimate the magnitude of the effect, we proposed that the dilute solution viscosity, generally expressed as

$$\eta = \eta_s(1 + c[\eta]_{\mathrm{obs}} + ...) \qquad (2)$$

could rather be written

$$\eta \approx \eta_e(c)\{1 + c[\eta]_p + ...\} = \eta_s\{1 + c[\eta_e] + ...\}\{1 + c[\eta]_p + ...\} \qquad (3)$$

where $\eta_e(c)$ reflects the changing solvent contribution. We noted that relation 3 has no rigorous basis and emphasized that this was only an *estimate* of the magnitude of the effect, by using ≈ rather than = (see eq 21 of ref 2). Applying the standard definition of $[\eta]$ leads to

$$[\eta]_{\mathrm{obs}} = [\eta]_p + [\eta_e] \qquad (4)$$

which suggests that $[\eta_e]$ contributes additively to $[\eta]_{\mathrm{obs}}$. The other term in eq 4, which we called $[\eta]_p$, contains all the other polymer contributions to $[\eta]_{\mathrm{obs}}$, including, but not limited to, the standard chain dynamics (Kirkwood–Riseman) term. In particular, we pointed out that effects of local chain stiffness, chain ends, and the volume of the polymer segments (*e.g.*, the "Einstein viscosity of the beads") would also be subsumed in $[\eta]_p$. The conclusions which we drew from eq 4 were that the polymer-induced changes in the solvent dynamics could exert an influence on $[\eta]_{\mathrm{obs}}$, that the effect could be large or small, positive or negative, and that this contribution would grow in importance as molecular weight (and $[\eta]_p$) decreased. It was not advanced as a quantitative recipe for correcting $[\eta]_{\mathrm{obs}}$ for the solvent contribution. It clearly should not be so used, for a variety of reasons, including that (i) it has no basis in theory; (ii) it tacitly assumes that the effect of polymer on solvent dynamics is spatially-uniform, so that η_e, defined *via* the mean τ_s, is appropriate; (iii) η_e can adopt slightly different values (within a few mL/g) for a given

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polymer–solvent system, depending on the experimental technique and on whether τ_s corresponds to rotational or translational motion.[2,4,5,7–9]

Having summarized our own work, we can address the relevant comments in YTY. In their eqs 1 through 5, they nominally reproduce the above argument to arrive at an expression equivalent to our eq 4, with the notational differences k for $[\eta_e]$, $[\eta]$ for $[\eta]_p$, $\eta_0(c)$ for $\eta_e(c)$, and $\tau_{r,0}$ for τ_s. They then state that "Since the addition of hydrodynamic resisters to a viscous fluid necessarily gives rise to excess nonnegative energy dissipation, $[\eta]_p$ must be nonnegative at any frequency" and that therefore if $[\eta]_{obs} < 0$, $[\eta_e]$ must be negative. It is this latter conclusion, that $[\eta]_{obs}$ being negative requires that $[\eta_e]$ be negative, that they term "Lodge's view". Their experimental result, which deviates from this "view", is that $[\eta_e] = 0$ for the PIB dimer in benzene,[1] even though $[\eta]_{obs} = -0.72$ mL/g.[3] However, the proposition that $[\eta]_{obs} < 0$ requires $[\eta_e] < 0$ differs from our approach, in the following ways:

(1) We do not require that all contributions to $[\eta]_p$ be positive; for example, chain ends might well influence the behavior of the solution, in a manner distinct from the effect that the segments in the middle of a chain have on the solvent dynamics. Thus, $[\eta]_{obs} < 0$ does not necessarily imply $[\eta_e] < 0$.

(2) YTY's result is based on $[\eta_e]$ determined by DRS. However, as noted above, different measures of solvent dynamics can lead to values of $[\eta_e]$ that differ by several mg/L. Therefore, just because one particular set of experiments gives $[\eta_e] = 0$ does not mean that another measurement technique might not give $[\eta_e] = -1$ or $+1$ mg/L. To restate the point, at the level we have considered the problem, 0 and −0.72 mL/g are not significantly different. Note that this is *not* an argument about experimental precision.

(3) The results for $[\eta_e]$ and $[\eta'_\infty]$ for PB/A1248 cited above indicate that $[\eta'_\infty]$ is less than $[\eta_e]$ by about 6 mg/L, which indicates that there *must* be another contribution to $[\eta]_p$ which is negative in sign.

(4) Our work in this area has been concerned with solvent dynamics in polymer solutions, not solvent dynamics in mixtures of small molecules. Although we recognize that the two are related, it is also possible that there are important differences. For example, end effects could well be dominant for a dimer of PIB. Consequently, it is not clear that results obtained on dimers are quantitatively applicable to solutions of higher molecular weight chains.

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