Comments on "Viscoelastic Relaxation in Semidilute and Concentrated Polymer Solution"

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Brown and Štěpánek[1] recently published their photon correlation spectroscopic (PCS) results on polystyrene (PS) in semidilute poor solvent systems. They compared their results with Wang's theory, finding that the group of viscoelastic modes (referred hereafter as the slow component) in semidilute poor solvent solutions is unrelated to the density–concentration coupling parameter β. The β parameter, introduced in Wang's theory, is proportional to the difference in partial specific volumes of the polymer and solvent and is responsible for the coupling of density to concentration fluctuations. We have examined the condition of their experiments and found problems associated with this work. We now state our findings below:

Brown and Štěpánek (BS) stated that, although the β values of PS/cyclohexane and PS/diethyl oxalate solutions varied greatly, the proportion of the slow and fast components remained nearly constant. Thus, they have concluded that the existence of the slow component in the correlation function associated with quasielastic light (QEL) scattering is unrelated to the value of the density increment parameter β. However, according to Wang's theory,[2,3] the amplitude of the slow component relative to the fast component is given by the expression:

$$B = \beta M_0/(\beta M_0 + M_\pi) = 1/(1 + M_\pi/\beta M_0) \quad (1)$$

The amplitude of the slow component is determined not by β alone but by the quantity $M_\pi/\beta M_0$. Here M_π and M_0 are the osmotic modulus and longitudinal modulus, respectively. The β values differ in PS/cyclohexane and PS/diethyl oxalate solutions, but the M_π and M_0 values also differ in these systems. Without the values of M_π and M_0, it is premature to conclude that the amplitude of the slow component is unrelated to the β of these systems.

However, the β values for the systems that BS reported are suspect. According to the definition, β is given by:[2]

$$\beta = (\rho_2/\rho)(\partial\rho/\partial\rho_2)_{T,P} \quad (2)$$

where ρ is the equilibrium solution density and ρ_2 is the polymer concentration. From our experiments on PS/diethyl phthalate[4] as well as Brown's experiments on the PS/cyclohexane system,[5] it has been found that, for ρ_2 increasing from 0 up to several times the overlapped concentration, β is proportional to ρ_2:

$$\beta = k\rho_2 \quad (3)$$

where k is a constant at a given temperature, but it changes as the temperature changes. From this expression, a simple calculation would show that the change of β with ρ_2 is given by

$$\beta = (\rho_2/\rho^\circ_2)\ln(\rho^\circ_2/\rho^\circ) \quad (4)$$

where ρ°_2 is the density of the polymer and ρ° is the density of the solvent. The validity of eq 4 has been checked in our laboratory by comparing the predicted values with directly measured values of several polymer solutions. We have found that the predicted and measured values agree to within 5%. Using eq 4, it is thus rather easy to check the validity of the β values reported by BS. In their experiments, except for the solutions with PS prepared by polymerizing styrene directly in diethyl malonate (DEM), which have concentrations of 0.7, 0.8, and 0.9 g/mL, all of the other systems have a concentration of 0.07 g/mL. The k constants for these systems are less than 1. Using eq 4, we expect these systems to have a β value much less than 0.07, in contrast to what they have reported. The β value of 0.36 quoted for the PS/cyclohexane system is far too large.[6] In addition, it is not clear how the β value is defined in the mixed-solvent system concerning PS/(diethyl phthalate/dioctyl phthalate). They obtained $\beta = 0$ at a temperature of 25.5 °C for PS in the diethyl phthalate/dioctyl phthalate mixed solvent. The result of a zero β value for the mixed-solvent system is difficult to interpret. Due to selective absorption involved in solution with mixed solvents, diffusion currents of the polymer with respect to each individual solvent are different. The concentration fluctuations of the polymer in one solvent will induce concentration fluctuations of the polymer in the other, but the two concentration fluctuations decay with different rates. As a result, the mixed solvent system may take a long time to achieve equilibrium. Our recent experiments have shown that the solution with mixed solvents exists initially in an unstable state; considerable time must be spent for the sample to reach a stable condition in order to obtain reliable QEL data.[7] Precaution is therefore needed to ascertain the state of thermodynamic equilibrium in mixed-solvent systems. It is not certain whether or not BS have taken this complex situation into account in interpreting their data.

Brown and Štěpánek used the equation

$$M_0 = K + (4/3)G \quad (5)$$

to analyze the data of M_0 obtained from eq 1. They calculated the M_0 value using eq 1 and found it to be about 10^6 Pa. However, they argued that, because K is about 10^{11} Pa, there was a discrepancy of several orders of magnitude between the value calculated from eq 1 and the accepted K value. From our experiments on PS/diethyl phthalate[4] and PS/benzene[7] systems, we found M_0 is in the range of 10^5–10^7 Pa, depending on the concentration and molecular weight of PS. The 10^6 Pa value for M_0 obtained by them is not off by much. However, it should be noted that the compressional (bulk) modulus K of the polymer solution associated with QEL is not on the order of 10^{11} Pa. Since the shortest delay time in the present state of the art electronic correlator used in PCS is about 10^{-6} s or longer, the M_0 value involved in QEL is associated with the difference between the value at 10^6 Hz and that at thermodynamic equilibrium, due to the fact that QEL scattering arises from fluctuations from equilibrium. The adiabatic longitudinal modulus as determined by Brillouin scattering is about 10^{11} Pa in the gigahertz frequency range.[8] On the other hand, the PVT data of polymer liquids give the value of the compression modulus on the order of 10^9 Pa.[9,10] Thus, the contribution of the compressional modulus K to the relaxation strength associated with QEL scattering is about 10^2 Pa and not 10^{11} Pa. This point has been elaborated on extensively in the literature.[11,12]

Another major difficulty in the BS paper is concerned with the solution of PS/diethyl malonate (DEM). For this system they prepared two types of solution: One has

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a concentration of 0.07 g/mL with nearly monodisperse PS having $M_w = 4.9 \times 10^6$; the others are concentrated solutions having concentrations of 0.7, 0.8, and 0.9 g/mL but with very polydisperse PS. As mentioned above, in the concentrated solutions PS was synthesized in DEM and used without fractionation. The molecular weight distribution of PS in this system was not known. There is also unpolymerized styrene left in the solution. The presence of monomer and oligomer is expected to significantly affect the β value due to the fact that the density of PS is different from that of styrene and PS oligomer. By extrapolation, they arrived at $\beta = 0$ for the PS/DEM solution at $T = -13.4$ °C. BS then assumed this result for all PS/DEM solutions in their study.

According to eq 4, to have $\beta = 0$, one needs $\rho^\circ_2 = \rho^\circ$; i.e., the polymer density equals the solvent density. Hence, at $\beta = 0$ the solution density is equal to the density of PS. Zoller and Hoehn have studied the change of PS density ρ°_{PS} with temperature below T_g.[13] They have shown that for PS with $M_w = 1.2 \times 10^5$ (close to the monodisperse PS used by BS, which has $M_w = 1.67 \times 10^5$) ρ°_{PS} varies with temperature according to $1.0517 \exp[-2.86 \times 10^{-4}(T\ (\mathrm{K}) - 273)]$. Gruner and Greer[14] have also studied the solution density ρ_{sol} of PS/DEM as a function of temperature. Using these results, we have obtained $\rho^\circ_{PS} = 1.0557$ g/mL and $\rho_{sol} = 1.0918$ g/mL at $T = -13.4$ °C, hence indicating that β is not zero at $T = -13.4$ °C for the PS/DEM solution. As mentioned above, the relative amplitude of the slow to fast component is determined by $M_\pi/\beta M_0$; even for β as small as 10^{-4}, if $M_0/M_\pi = 1000$, one would obtain $B = 0.09$, which can certainly be detected by PCS. More important is the fact that β is proportional to the polystyrene concentration (cf. eq 3). If β is not zero for the 0.07 g/mL semidilute solution, its effect on the amplitude of the slow component will become greater for the concentrated solution at the same temperature. This is due not only to an increase in β but also to a large increase in the M_0/M_π ratio at high concentration. When both β and M_0/M_π become large, the slow component is expected to dominate the PCS correlation function. This is indeed what BS have found in their QEL scattering experiment of the concentrated PS/DEM solution at −13.4 °C.

We are also concerned with the sample homogeneity of the concentrated PS/DEM solutions at −13.4 °C. If their osmotic modulus data of the PS/DEM solution were indeed correct as reported (Figure 3b of ref 1), one would obtain, by extrapolation, $M_\pi = 0$ at $T = 10$ °C. The temperature at which $M_\pi = 0$ is the temperature of spinodal decomposition. Therefore, at −13.4 °C, the solution is below the spinodal decomposition temperature and, as such, the solution is necessarily inhomogeneous. In this case, the PCS data obtained below this temperature are devoid of meaning, as the heterodyne contribution would make a significant contribution below this temperature. BS have, however, found in the 0.7 g/mL PS/DEM solution a different shape of the V_V correlation function in comparison from that of the V_H, hence indicating that this solution is probably not in the two-phase region. Gruner et al.[14] have shown that, in the PS/DEM system, the coexistence curve is strongly affected by impurity (especially water). For example, if the spectrograde DEM solvent was used without taking a step to remove absorbed humidity, the critical temperature could increase by more than 20 °C. Hamano et al.[15] have found an upper critical point at $T_c = 10.67$ °C and ϕ_c (volume fraction) = 0.083. Unfortunately, their coexistence curve covers only limited temperature and concentration ranges and does not include the region around 0.7 g/mL. However, due to significant polydispersity, the coexistence curve in the concentrated region is probably very different from the one expected from the monodisperse sample. To mix the results of the concentrated solution with that of the 0.07 g/mL solution does not provide a proper test to the theory, as the two types of solutions have different thermodynamic properties, not to mention that the concentrated solution used in their experiment also contains styrene monomer.

To conclude, we should point out that in addition to the theory for semidilute polymer solutions proposed by Brochard and de Gennes[16] based on the concept of transient gel and chain entanglements and that given by Wang,[2,3] who does not assume chain entanglements and gel dynamics, Akcasu, Klein, and Wang (AKW) have recently presented a microscopic theory to describe the coupling of concentration to density fluctuations and the effect of viscoelasticity in the binary polymer solution. The AKW theory yields the same equation as Wang's; however, the viscosity kernel for the equation of concentration fluctuations contains an extra term not present in Wang's theory. In AKW's formal theory, it is stated that, because of the presence of the extra term, the viscoelastic effect is still present in the binary solution even when $\beta = 0$. The AKW theory has, however, been examined recently by Wang,[17] who finds that the extra term vanishes if β is set equal to zero. Therefore, except for Brochard–de Gennes' phenomenological approach, all other theoretical results seem to indicate that, in order to observe the viscoelastic component in the binary polymer solution, the system must have a nonvanishing β.

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