Reply to Comments on "Viscoelastic Relaxation in Semidilute and Concentrated Polymer Solutions"

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Received March 14, 1994
Revised Manuscript Received June 10, 1994

We wish to draw attention to the Corrections[1] which deal with minor changes to ref 2. The necessity of the former has regrettably contributed to some misunderstanding between Sun and Wang (hereafter SW) and ourselves. Nevertheless, there are other aspects which require clarification, and in light of the paper from SW appearing in this issue,[3] we welcome this opportunity to extend the discussion and from our own point of view set the record straight.

We also wish to make it clear that, contrary to the assumption of SW, incorrect values of β ($=\beta' c$) were not used for the estimation of the longitudinal elastic modulus M_0 in the original paper.[2] The published Correction[1] simply refers to the labeling of Table 1 and the ordinate of Figure 5 of ref 2, although SW devote a significant part of their paper to this aspect. (The prime in β' was inadvertently missed in typesetting.) We note, however, that it is β' which is the most meaningful intensive physical quantity characterizing a particular polymer/solvent pair. Wang and co-workers were informed of the misprints in ref 2 and were given a copy of the Correction in mid-February before they submitted the revised version of their paper. They were thus aware that the absolute values of β' (denoted k by SW) we reported are in the same range as the value given by Wang and Zhang[6] and that this misprint has no effect on any experimental result, calculation, or conclusion drawn in our paper.

SW present a criticism of our experimental findings in their paper and maintain that Wang's theory[4-6] can quantitatively explain the nature of the slow modes characterizing semidilute polymer solutions. We find this criticism both surprising and unsubstantiated. It is surprising because the inadequacy of Wang's theory to describe existing experimental results has recently been acknowledged in a paper co-authored by Wang.[7] References 7 and 8 contain additional features that have not yet been tested against experiment.

1. SW claim without proof that the effect of the β-parameter (proportional to the differences in partial specific volumes of polymer and solvent) on the correlation function is exactly compensated by the combined effect of the osmotic modulus and the longitudinal modulus. This would be an incredible chance already for two different systems, and it is unimaginable that this would be the case for all four different polymer/solvent systems reported in our contribution,[2] examined moreover, at different temperatures. We also note that these four systems are exactly at the respective Θ temperatures, a feature which SW do not seem to consider important. We reiterate that, for a meaningful test of the theoretical expressions, it is essential to work in the Θ state where a significant amplitude of the viscoelastic modes is observed experimentally. In good solvents the amplitude of the viscoelastic modes is vanishingly small. We demonstrate in a forthcoming paper that the large amplitude of the "viscoelastic modes" reported by Wang in a polystyrene/benzene solution (good solvent)[9,10] is due to a transient effect which disappears when the solution is allowed to equilibrate for an extended period. We also note that in ref 7 co-authored by Wang it is acknowledged that the theory "does not explicitly display the effect of the solvent quality, the molecular weight and the entanglement of the chains on the viscoelastic modes".

The origin of the difficulties for Wang's theory to describe observed experimental behavior has been traced by Doi and Onuki[11] to the necessity of introducing separate velocities v_p and v_s for the polymer and solvent in the solution. These workers also explain why the viscoelastic contribution will be important in Θ solvents and small in good solvents.

2. We appreciate the postulated role of the various factors β, M_0, and M_π in eq 1 of the paper of SW,[3] and for this reason we were stimulated to perform the experiments described in ref 2. However, we considered the insensitivity of the relative amplitude of the sum of the viscoelastic modes in PCS experiments to the measured coupling parameter β to be worthy of comment in view of the postulated direct proportionality of the amplitude of the viscoelastic contribution to the parameter β as shown in eq 23b of ref 12. This equation was revised in ref 7 co-authored by Wang to include an extra term which *does not* vanish when $\beta = 0$. This statement has been revised anew in the paper of SW,[3] and ref 17 therein now says that this term *does* vanish for $\beta = 0$. While we appreciate the difficulty of establishing theoretically the exact role, if any, of β on dynamic light scattering results, the experimental observations are independent of these ongoing changes in Wang's theory.

3. We used a mixed-solvent system to obtain $\beta = 0$ since, in the absence of a single solvent in which the $\beta = 0$ condition is attainable, a mixture of diethyl phthalate and dioctyl phthalate was considered to be as close as possible to single-solvent conditions because the components are closely-related members of a homologous series. Our solutions were allowed to equilibrate for a considerable period (1 month) prior to measurements. Further PCS measurements have been made (at the time of writing this paper) after an interval of 1.5 years on the same solution, and the correlation functions were superimposable. We believe our finding of the same substantial relative amplitude of slow modes (≈ 0.35) under the condition $\beta = 0$ to be well-founded. Also, taken together with the other evidence, we consider our conclusions questioning the relevance of β to be justified.

We would agree with SW, however, that selective adsorption of one of the components on the PS probably occurs. Indeed, SW may have a problem themselves with this since they have recently[9,10] taken the same route as we had done earlier but have used a mixture of a good solvent (benzene) and a marginal solvent (diethyl phthalate), instead of taking a mixture of two poor solvents of similar structure. We note here that the magnitude of β' given by Wang and Zhang[6] for PS/diethyl phthalate is in the same range as the values we list in Table 1;[2] the reason we chose this solvent to combine with dioctyl phthalate to obtain a $\beta = 0$ system was its negative sign ($\beta' = -0.05545$).

4. In our paper[2] we discussed the quantities in $M_0 = K_0 + (4/3)G_0$. We initiated the discussion by considering the total bulk compressional modulus but subsequently proceeded to the stated view that in light scattering measurements in semidilute solutions the modulus K_0

0024-9297/94/2227-4842$04.50/0

governing the compressional mode is osmotic: it may be replaced by the osmotic compressional modulus.[13,14] SW thus misquote us in their assertion that we believe the compressional bulk modulus K associated with the QELS measurement to be on the order 10^{11} Pa. Since the effect of entanglements on the osmotic modulus is small in the gel, K is of the magnitude 10^2–10^3 Pa, as obtained from observations of the intensity of the light scattered by the concentration fluctuations. From the discussion in their paper,[3] it would appear that SW concur in this, since they also estimate the contribution of the compressional modulus to be about 10^2 Pa. They obtain the latter figure, however, by combining for the bulk polymer an adiabatic value for the longitudinal modulus in the gigahertz frequency range with the thermodynamic value at zero frequency to obtain a modulus in the megahertz frequency range, although the modulus is known to be strongly frequency dependent.[15] Moreover, it is not altogether obvious that data for the melt can be compared with those for a solution containing 93% of solvent and only 7% of polymer.

In new measurements on the system PS/DOP, we have determined both the osmotic compressional modulus ($\approx$67 Pa) from intensity light scattering and the shear modulus ($\approx$400 Pa),[2] giving $M_0 \approx 600$ Pa for a $C = 0.07$ g/mL semidilute Θ solution. Inserting the determined value of $\beta \approx 6 \times 10^{-3}$ with the above values into eq 1 of SW's paper yields $B \approx 0.05$. This means that the viscoelastic modes would only just be observable in the PCS experiment according to Wang's theory even under Θ conditions and clearly differs from the $\approx$35% contribution of the slow modes shown in Figure 1.[2]

As one moves away from Θ conditions, M_0 increases mainly owing to the increase in M_π since G_0 is virtually insensitive to changes in solvent quality. We show this by oscillatory shear measurements on the same solution as a function of temperature.[16] This leads to an even lower value for B in a good solvent. Thus, if under Θ conditions a maximum amplitude of the viscoelastic modes of 0.05 is predicted by eq 1 of SW's paper, then, at anything but Θ conditions, there would be little possibility of experimentally observing the slow modes according to Wang's theory.[4-6] We note here that SW find $M_0/M_\pi \approx 1000$ which differs greatly from our experimental finding of $M_0/M_\pi = 9$ under Θ conditions. However, their estimate rests only upon the presumed validity of their theoretical expressions. This means that Brochard's estimate of $M_\pi/M_0 \approx 1$ in a Θ solution[17] is closer to being correct, in contrast to the statement of Wang and Zhang[6] to the contrary.

5. We also considered the case of a concentrated solution (PS in diethyl malonate at 0.7 g/mL). To quote Wang:[4] "when the polymer concentration is increased to such an extent that a further increase does not significantly change the solution concentration, β becomes small". Wang then postulated that the power spectrum becomes identical to that for the bulk polymer since it was assumed that concentration fluctuations do not contribute significantly when β is small. This reasoning is clearly fallacious since it is widely known that, even for systems containing only a few percent of a plasticizing solvent, concentration fluctuations play an important role (see, for example, refs 15 and 18) and a solution of PS in diethyl malonate is in no way unusual in this regard. We sought the condition where $\beta = 0$ in order to test this proposition since we disagreed with Wang's presumption that β would become small at high C. We extrapolated to $\beta = 0$ and found this to be approximately valid at −13.4 °C. This conclusion was reached by making direct density measurements with a high precision densimeter and is not subject to the errors which may be introduced by using extrapolation procedures on different sets of ρ–T data as done by SW (who arrive in this way at a density difference of a mere 3.5%). (Note also that we have not "mixed the results of the concentrated solution with that of the 0.07 g/mL solution". No calculations using $\beta' = 0.0346$ were made by us for the concentrated solution in diethyl malonate as presumed by SW.)

SW also remark that (a solution)... "with very polydisperse PS" was used. This is probably incorrect. The conversion in the polymerization was about 96% at $C = 0.1$ g/mL and increased to about 99% in the bulk limit. The molecular weight at $C = 0.7$ g/mL was about 235 000. Thus their remark that the density parameter β will be significantly influenced by the presence of styrene monomer is unfounded. Furthermore, both the styrene and diethyl malonate were rigorously dried and distilled under vacuum into clean/dry scattering ampules and sealed under vacuum. SW do not need to have concern for the sample homogeneity in the PS/DEM system at −13.4 °C. The supposition of SW that $M_\pi = 0$ at 10 °C for both the semidilute solution (0.07 g/mL) and for the concentrated solution (0.7 g/mL) is, of course, completely wrong since the temperature of spinodal decomposition depends strongly on concentration. Due to the well-known shape of the spinodal curve, the temperature $T = -13.4$ °C certainly lies in the homogeneous region of the phase diagram for $C = 0.7$ g/mL. Using eq IV.12 of ref 19 leads to $T_s = -181$ °C for the spinodal with $C = 0.7$ g/mL. We have also measured M_π for the solution of 0.7 g/mL and have found $M_\pi = 2.5 \times 10^3$ kPa at −13.4 °C and 4.1×10^3 kPa at 25 °C showing that we are far from phase separation at $C = 0.7$ g/mL.

PCS measurements made at −13.4 °C showed that the scattering was ergodic and thus the solution homogeneous. No evidence for heterodyning was found contrary to the unsupported supposition of SW. Measurements of the polarized (V_V) correlation function for this same sample using our new monomodal fiber detection system show an almost theoretical intercept value of $g^2(t) - 1 = 0.95$.

We also note that SW write in one paragraph in consecutive sentences "...the solution is necessarily inhomogeneous..." and "...this solution is probably not in the two-phase region...". It is really difficult to assign any meaning to this combination of statements.

In summary, we feel that the arguments raised in the paper of SW[3] are unsubstantiated and do not cast doubt on the validity of either the experimental results or the conclusions presented in our paper.[2] We are convinced that the main result of our paper stands: i.e., the presumed relationship between the "coupling parameter" β and the amplitude of viscoelastic modes observed in the PCS experiment is not straightforward. We are continuing to examine the question and are making direct and independent measurements of the longitudinal modulus M_0.

References and Notes

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