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Does a Depletion Layer of a Polymer Solution Affect Surface Waves at the Air/Solution Interface?

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It is well known that polymer solutions exhibit non-Newtonian viscoelastic behavior. This effect produces a rich variety of phenomena. There has been much work done to understand their bulk properties.[1-4] Recently, the surface hydrodynamics of polymer solutions has attracted more attention.[5-8] At low polymer concentrations, polymer solutions are Newtonian fluids and the surface waves are standard capillary waves. However, at high polymer concentrations, polymer solutions are viscoelastic fluids and the surface waves may be strongly affected by the viscoelastic properties of the bulk. Furthermore, the surface waves of polymer solutions can cross over from capillary waves to elastic waves when the polymer concentration is increased sufficiently for the modulus to dominate.[5] Finally, the polymer concentration near the interface can be different from the bulk; that is, polymer solutions may have depletion layers or adsorption layers, which may further modify the surface waves.

We have chosen poly(bromostyrene) (PBrS)/toluene solutions with M_w = 90 kg/mol and M_w = 900 kg/mol as the system to study the surface waves by the technique of surface heterodyne light scattering.[6] This system has been studied by X-ray scattering[7] previously. It was found that the behavior of the static structure factor and height–height correlation function is capillary wave-like for solutions well into the semidilute regime in a typical X-ray scattering accessible experimental wavevector range ($\sim 10^3 - 10^8$ cm^{-1}). This finding indicates that PBrS in toluene exhibits a depletion layer near the air/solution interface. In this Note, we measured the power spectra of surface waves at several wavevectors, k (less than 10^3 cm^{-1}), and as a function of the bulk polymer concentration and the molecular weight in order to investigate their effects on the depletion layers.

Two theoretical models are used to analyze the experimental data. The first model uses capillary wave theory for a simple liquid interface.[9] This model treats the polymer solution as a Newtonian fluid with a surface tension, σ, and a viscosity, η. We expect this model to be inadequate to describe the behavior at high concentrations, where the solution becomes viscoelastic. Therefore for high concentrations, we employ a more sophisticated theory which accounts for the viscoelasticity of the bulk,[5] which is described by a Maxwell model involving three parameters: the surface tension, σ, the transient modulus, G_0, and the relaxation time, τ. Both theoretical models use the assumption that there are no gradients of polymer concentration near the interface. However, when these two theoretical models are applied to polymer solutions with depletion layers, the results can give a clear indication of the effect of a depletion layer on the surface waves. We compare the physical parameters obtained from the surface light scattering with those obtained from independent experimental measurements using a surface tensiometer and viscometry.

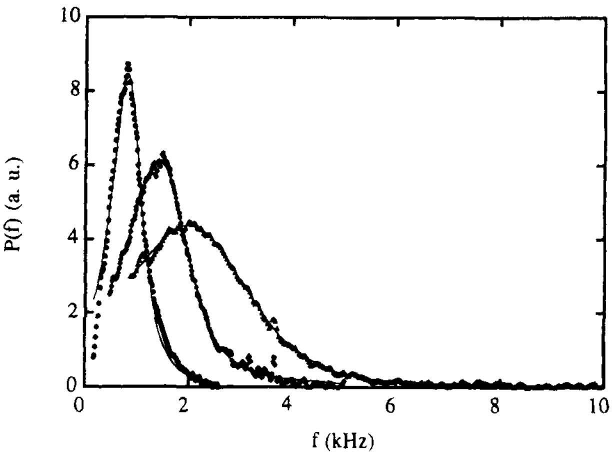

Figure 1. Power spectra of 4.0 g/dL concentration PBrS/toluene with M_w = 900 kg/mol at the diffraction orders 2–4, corresponding to k = 97.4, 146.1, and 194.5 cm^{-1}. They are rescaled to have the same baseline. The solid lines are the fits using the theory for polymer solutions. The symbols correspond to (●) n = 2, (♦) n = 3, and (▲) n = 4.

The bulk PBrS concentration ranges from 0.5 to 20.0 g/dL for 90 kg/mol and from 0.5 to 7.0 g/dL for 900 kg/mol. At very high concentration above the experimental range, we found that the surface waves are completely overdamped so that their power spectra have no well defined peaks. The surface tensions were obtained with the du Nouy ring method, giving $\sigma = 27.5 \pm 0.25$ dyn/cm. The shear viscosities were measured with a Couette viscometer. From the viscosity measurements, we found the chain overlap concentration is 3.4 g/dL for 90 kg/mol and 0.7 g/dL for 900 kg/mol.

Figure 1 shows the experimental power spectra for 4.0 g/dL and M_w = 900 kg/mol for diffraction orders n = 2–4. For comparison, we also plot the fits to the convoluted power spectrum for polymer solutions.[5,10] Both theories[5,9] give very similar fits to the power spectra of the polymer solutions within experimental error. However, the values of the physical parameters obtained from the spectral analysis using these two theories are different depending on the polymer concentration and the molecular weight.

We compare the parameters obtained from the light scattering with those obtained from the independent measurements. As shown in Figure 2, the values of σ and η obtained from the spectral fits using both theories[5,9] and the independent measurements agree over the entire concentration range for the 90 kg/mol solutions within experimental error. The values of the viscosities were calculated using $\eta = \eta_0 + G_0\tau$, where η_0 is the solvent viscosity and the relaxation time, τ, is about (1–3) × 10^{-5} s. Therefore, these surface waves are still in the capillary wave regime.

Figure 3 shows the results of σ and η obtained from the spectral analysis using both theories[5,9] and independent measurements for the 900 kg/mol solutions. The values of σ and η obtained from the spectral analysis using these theories[5,9] are in good agreement,

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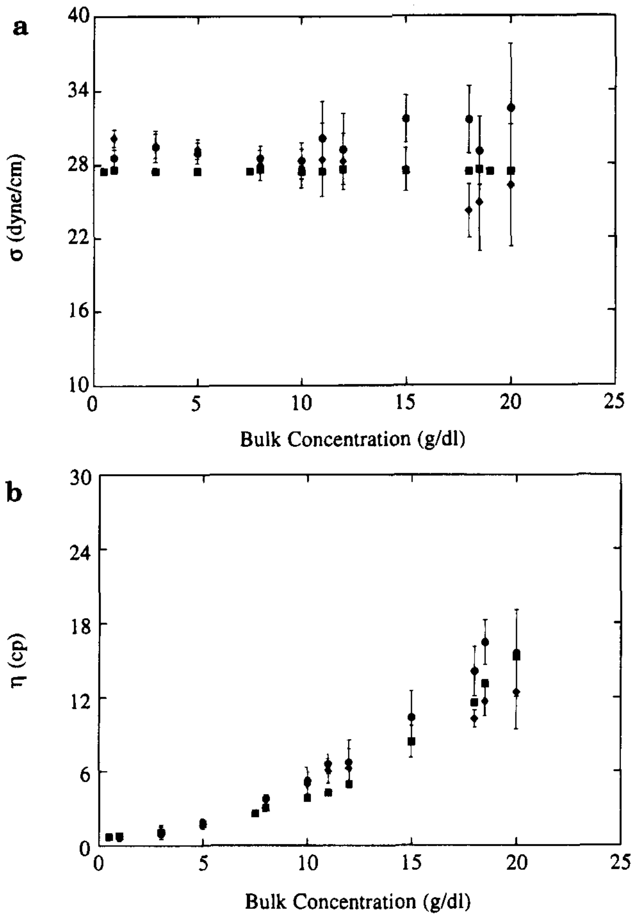

Figure 2. (a) Surface tension, σ, *vs* bulk concentration of PBrS/toluene with M_w = 90 kg/mol. The symbols correspond to (■) data obtained from the du Nouy ring method, (●) data obtained from the spectral fits using the capillary wave theory, and (♦) data obtained from the spectral fits using the theory for polymer solutions. (b) Viscosity, η, *vs* bulk concentration of PBrS/toluene with M_w = 90 kg/mol. The symbols correspond to (■) data obtained from a Couette viscometer, (●) data obtained from the spectral fits using the capillary wave theory, and (♦) data obtained from the spectral fits using the theory for polymer solutions.

but only at concentrations less than 3.0 g/dL. Interestingly, at higher concentrations, the surface tensions obtained from the fits using the capillary wave theory[9] show large deviations from those measured with the du Nouy ring method. Since the capillary wave theory is only appropriate for simple Newtonian fluids, we attribute this large deviation to the viscoelastic properties of the polymer solutions. By contrast, the theory for viscoelastic polymer solutions[5] yields surface tensions that are significantly improved, as shown in Figure 3a. This is direct evidence that the solutions are viscoelastic at the high concentrations, which strongly modifies their surface waves. Except for the two highest concentrations, the values of viscosities obtained from the fits using both theories are still in reasonable agreement with those measured with the Couette viscometer. The low viscosities obtained from the surface light scattering at high bulk concentrations are also seen for the polymer solutions with adsorption layers.[11] Therefore, the low viscosities may not be due to the depletion layer. A possible reason is that at high bulk concentrations, the relaxation time is long compared to the high frequency of surface light scattering, and we can not simply calculate the viscosity using $\eta = \eta_0 + G_0\tau$ for a shear-thinning case.

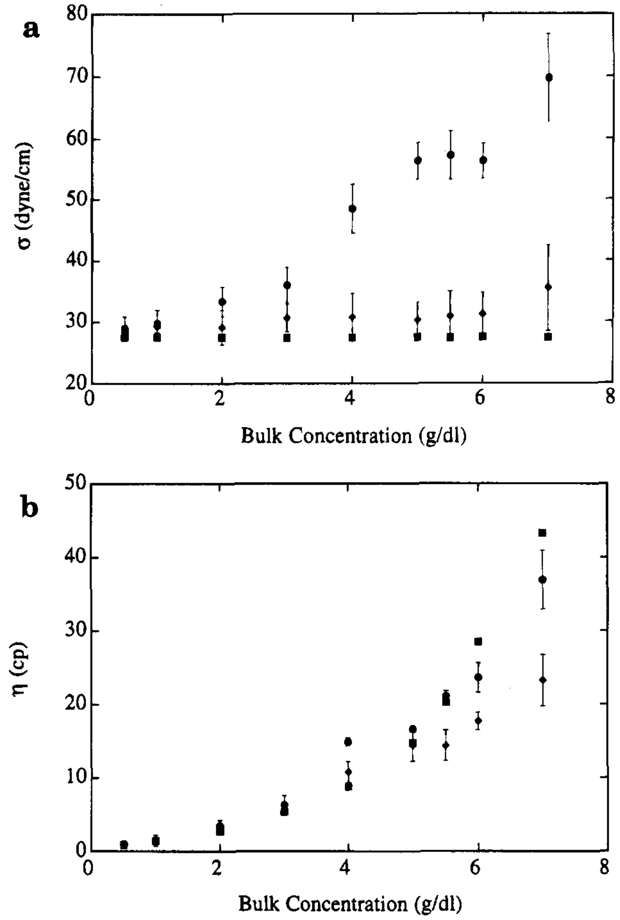

Figure 3. 3. (a) Surface tension, σ, *vs* bulk concentration of PBrS/toluene with M_w = 900 kg/mol. The symbols correspond to (■) data obtained from the du Nouy ring method, (●) data obtained from the spectral fits using the capillary wave theory, and (♦) data obtained from the spectral fits using the theory for polymer solutions. (b) Viscosity, η, *vs* bulk concentration for PBrS/toluene with M_w = 900 kg/mol. The symbols correspond to (■) data obtained from a Couette viscometer, (●) data obtained from the spectral fits using the capillary wave theory, and (♦) data obtained from the spectral fits using the theory for polymer solutions.

We should note that both theories[5,9] are derived for fluids with equal concentrations in the bulk and near the surface. Consistent with this assumption, the spectral results indicate that the depletion layers of the polymer solutions have no significant effect on the surface waves at the solution interface. The theory for polymer solutions[5] gives consistent results for both σ and η over the entire concentration range. By contrast, the capillary wave theory[9] describes the experimental data only at low molecular weight or low concentrations of high molecular weight polymer. This is understandable in terms of the thickness of the depletion layer.[4] We estimate the thicknesses of the depletion layers to be 20 Å for the 20.0 g/dL concentration solution with M_w = 90 kg/mol and 80 Å for the 7.0 g/dL concentration solution with M_w = 900 kg/mol, assuming the monomer size is 2 Å. Since the typical wavelength of the waves probed by surface light scattering is of the order of microns, these very small depletion layers are probably not large enough to affect the hydrodynamic behavior at the interface. Therefore, the bulk viscoelastic properties must play the dominant role in determining the properties of the surface waves.

To conclude, the surface waves of the 90 kg/mol solutions can be interpreted by both the capillary wave theory[9] and the theory for polymer solutions[5] over the entire concentration range. However, the surface waves of the 900 kg/mol solutions can be well described only by the theory for polymer solutions[5] over the entire concentration range. For the low concentrations, the surface waves are capillary waves. By contrast, for the high concentrations, the surface waves are strongly affected by the viscoelastic behavior of the bulk solutions. In all cases, the depletion layer at the interface of the PBrS/toluene solution has no detectable effect on the long wavelength surface waves. Compared with the previous X-ray scattering,[7] the surface wave power spectrum shows the viscoelastic behavior of the bulk solution at high polymer concentration range for a high molecular weight polymer (900 kg/mol).

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