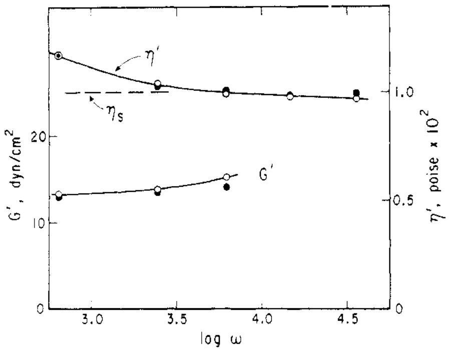

Figure 1. Plots of G' and η' (linear scales) against logarithm of frequency. Open circles, initial measurements (1–5 h after filling apparatus); black circles, after 2 days. Dashed line represents solvent viscosity.

Results and Discussion

The initial and final values of G' and η', differing almost negligibly, are plotted against log ω in Figure 1. There is very little frequency dependence in this range. In mechanical model terms, complete absence of frequency dependence would correspond to a Voigt element (spring and dashpot in parallel), which might represent a perfectly elastic structure with modulus G_e embedded in a viscous liquid with viscosity η_m. Actually, the combination of elastic and viscous stresses would depend on the coupling of the oscillating surface to both the ordered structure and the viscous medium, a feature discussed by Mitaku et al.[4] In our experiments, the latex particles appeared to adhere to the titanium surface and we assume that the coupling was good for both.

The slight change in G' and η' with frequency implies contributions from a relaxation spectrum H such that

$$G' = G_e + \int_{-\infty}^{\infty} [H\omega^2\tau^2/(1 + \omega^2\tau^2)] \, d \ln \tau \qquad (1)$$

$$\eta' = \int_{-\infty}^{\infty} [H\tau/(1 + \omega^2\tau^2)] \, d \ln \tau + \eta_m \qquad (2)$$

The internal consistency of the data can be tested by calculating H from the slopes of both G' and η' in Figure 1 with customary approximation relations.[16] The result at log ω = 3.39 gives H = 0.06 dyn/cm² from G' and 0.07 from η', in excellent agreement considering the very low slopes of these curves. The equilibrium static modulus G_e can be assigned an upper limit of 13 dyn/cm², but it is not clear whether there would be a further decrease at lower frequencies. The effective medium viscosity η_m is close to that of the solvent, η_s.

Comparisons with earlier measurements on polystyrene latices are not very useful because of the mostly much higher concentrations and lower per-particle charges in those studies. However, the data of Mitaku and collaborators on a latex with particle diameter 143 nm and 0.49 × 10⁴ charges per particle extend to our low concentration, and interpolation gives $G' \simeq 40$ dyn/cm² there at 40 kHz (log ω = 5.4). This is similar in magnitude to ours and suggests that G' may continue to increase at higher frequencies. In flow measurements, Mitaku et al. noted a yield stress of the order of 1 dyn/cm². In our experiments, the maximum stress is estimated to be well below this value.

In the investigations cited,[2–6] η' was found to be similar in magnitude to η_s, the solvent viscosity. In our measurements, η' appears to approach η_s at higher frequencies. If the integral in eq 2 makes a finite contribution at our highest frequency, this implies that η_m, the effective viscosity of the medium, is somewhat less than η_s. However, that depends again on the degree of coupling of the ordered structure to the surface. Additional measurements at both higher and lower frequencies are needed to determine the nature of this very unusual type of viscoelasticity. The origin of the relaxation process corresponding to the small changes in G' and η' with frequency is of particular interest. Nevertheless, the model of an elastic structure embedded in a viscous medium serves well as a first approximation.

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Interfacial Profile between Coexisting Phases of a Polymer Mixture

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The structure of polymer interfaces between coexisting phases in binary (A, B) polymer mixtures has previously been analyzed in two limiting cases: (i) the limit where the two polymer chains can be treated as completely immiscible, so that the volume fraction ϕ of component A changes throughout the profile from $\phi = 0$ to $\phi = 1$,[1,2] and (ii) the critical region where the volume fractions ϕ_1 and ϕ_2 of the two coexisting phases become (nearly) identical.[3] In the present note, we study this problem at general volume fractions intermediate between these two limits.

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For simplicity, we restrict our attention to a "symmetric" mixture where chain lengths satisfy $N_A = N_B = N$ and the effective Kuhn step lengths are equal, $\sigma_A = \sigma_B = \sigma$; however, our general conclusions should apply to the more general asymmetric cases as well.

Our approach is based on a generalized Flory–Huggins[4] free energy functional of the mixture, augmented by a gradient square term to account for volume fraction variations[3,5,6]

$$\frac{\Delta \mathcal{F}}{k_B T} = \int d\vec{r} \left\{ f[\phi(\vec{r})] + \frac{\sigma^2}{36\phi(1-\phi)}[\nabla\phi(\vec{r})]^2 \right\} \quad (1)$$

with

$$f(\phi) = \frac{\phi \ln \phi + (1-\phi)\ln(1-\phi)}{N} + \chi\phi(1-\phi) \quad (2)$$

χ being the standard Flory–Huggins interaction parameter.[4] Unmixing occurs if χ exceeds $\chi_{crit} = 2/N$; the volume fractions at phase coexistence are then found from[4,6]

$$\ln[\phi_1/(1-\phi_1)] + 2(\chi/\chi_{crit})(1-2\phi_1) = 0$$
$$\phi_2 = 1 - \phi_1 \quad (3)$$

Of course, eq 2 yields a correlation function of volume fraction fluctuations of Ornstein–Zernike form, and the associate correlation length at coexistence is[6]

$$\xi_{coex} = \frac{\sigma}{6}(2N)^{1/2}\left[1 - \frac{2\phi_1(1-\phi_1)}{1-2\phi_1}\ln\frac{1-\phi_1}{\phi_1}\right]^{-1/2} \quad (4)$$

This length diverges at the critical point $\phi_{crit} = {}^1/_2$ as $\xi_{coex} \approx (\sigma N^{1/2}/6)(\chi/\chi_{crit} - 1)^{-1/2}$, while for $\chi \gg \chi_{crit}$ where $\phi_1 \rightarrow 0$ it becomes of the order of the coil radius R_N. Here we are interested in relating ξ_{coex} to the characteristic lengths describing the concentration variation $\phi(x)$ in a direction x perpendicular to a flat interface between coexisting phases.

Following standard procedures, the interfacial profile is also found by minimizing eq 1 but looking for a solution with the boundary conditions $\phi(x \rightarrow -\infty) = \phi_1$ and $\phi(x \rightarrow +\infty) = \phi_2$. Hence the profile $\phi(x)$ must satisfy the Euler–Lagrange equation

$$\frac{\delta(\Delta\mathcal{F}/k_BT)}{\delta\phi(x)} = \frac{1}{N}\{\ln\phi - \ln(1-\phi)\} + \chi(1-2\phi) - \frac{\sigma^2}{18\phi(1-\phi)}\frac{d^2\phi}{dx^2} + \frac{\sigma^2}{36}[\phi^{-2} - (1-\phi)^{-2}]\left(\frac{d\phi}{dx}\right)^2 = 0 \quad (5)$$

Using the boundary conditions one can integrate eq 5 to find, using eq 3 and 4 after some algebra

$$\xi_{coex}^2\left(\frac{d\phi}{dx}\right)^2 = 2\phi(1-\phi)\left\{\phi\ln\phi - \phi_1\ln\phi_1 + (1-\phi)\ln(1-\phi) - (1-\phi_1)\ln(1-\phi_1) + \frac{2\chi}{\chi_{crit}}[\phi(1-\phi) - \phi_1(1-\phi_1)]\right\}\Big/\left[1 - \frac{2\phi_1(1-\phi_1)}{1-2\phi_1}\ln\frac{1-\phi_1}{\phi_1}\right] \quad (6)$$

For ϕ near ϕ_1 an expansion of eq 6 to second order yields

$$\xi_{coex}\frac{d\phi}{dx} = \phi - \phi_1,$$
$$\phi(x) - \phi_1 \approx \exp(x/\xi_{coex}), \qquad x \rightarrow -\infty \quad (7)$$

Thus it follows that far away from the center of the profile (fixed at $\phi = \phi_{crit} = {}^1/_2$ for $x = 0$) the deviation of ϕ from the bulk value is exponentially small, and the decay constant is always given by ξ_{coex}.

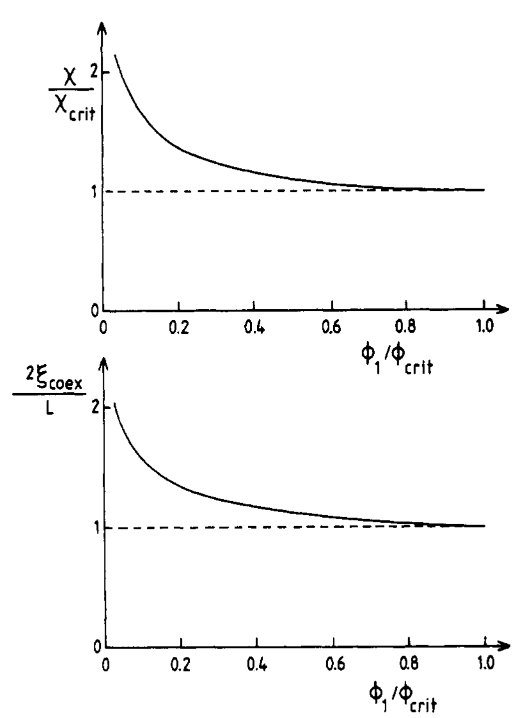

Figure 1. Ratio of characteristic lengths, $2\xi_{coex}/L$ (lower part) and ratio of Flory–Huggins parameters χ/χ_{crit} (upper part) plotted vs. volume fraction at phase coexistence. Only the regime $1 \leq \chi/\chi_{crit} \lesssim 2$ is shown, where the present treatment is quantitatively accurate.

On the other hand, inspection of eq 6 shows that a characteristic length L defined from the maximum slope of the profile as $L^{-1} \equiv 2(\phi_2 - \phi_1)^{-1}(d\phi/dx)$ for $x = 0$ agrees with ξ_{coex} only in the critical region but in general differs from ξ_{coex}. In particular, for $\chi/\chi_{crit} \gg 1$ this length becomes much smaller than ξ_{coex}. In this limit $\phi_1 \rightarrow 0$ and eq 6 simplifies to

$$\xi_{coex}^2\left(\frac{d\phi}{dx}\right)^2 = \frac{\chi}{\chi_{crit}}[2\phi(1-\phi)]^2 \quad (8)$$

by keeping only the leading terms. Equation 8 is solved by the familiar tanh profile

$$\phi(x) = \frac{1}{2}[1 + \tanh(x/L)]$$
$$L = \xi_{coex}(\chi_{crit}/\chi)^{1/2} = (\sigma/3)\chi^{-1/2} \quad (9)$$

Equation 9 reproduces Helfand's result[1,2] that the interface "thickness" $L \propto \chi^{-1/2}$, independently of chain length N; unfortunately the constant of proportionality in eq 9 is different. This discrepancy is due to a limitation of the gradient square theory, eq 1 and 2, discussed already in ref 6 in a different context: Equation 1 is quantitatively reasonable only for *slow* concentration variations, i.e., $R_N(d\phi/dx) \lesssim 1$, and hence it describes the much more rapid variation of volume fraction occurring in the center of the interfacial profile for $\chi \gg \chi_{crit}$ only qualitatively. However, our treatment is self-consistent in the *wings* of the interfacial profile, where eq 7 holds for all χ. This result, taken together with Helfand's treatment of the completely immiscible case,[1] proves the suggestion[6] that outside of the critical region (in which the profile is again of the tanh form,[6] $\phi(x) = {}^1/_2[1 + (1-2\phi_1)\tanh(x/2\xi_{coex})]$, consistent with eq 7), the interface profile is characterized by two different lengths.

In Figure 1 we plot the ratio of the two lengths ξ_{coex} and L (as given by eq 4 and 6 for $x = 0$, as discussed above) as a function of the volume fraction ϕ_1 at coexistence (the corresponding values of χ/χ_{crit} are related to ϕ_1 via eq 3 and are shown for comparison). Although for $\chi \gg \chi_{crit}$ our result for L is only qualitatively correct, we have not attempted to go beyond the "long-wavelength" theory for the following reasons: (i) real polymer mixtures are rather asymmetric, which gives rise to additional deviations from the simple result (eq 9) and (ii) in the derivation of eq 5 from eq 2 it is explicitly assumed that the Flory-Huggins parameter χ is independent of volume fraction (cf. also ref 6). However, it is well-known (see, e.g., ref 7) that there is a rather distinct dependence of χ on ϕ, which in the general case is not known explicitly and will also affect the detailed form and width of the profile. However, we hope that our treatment will be useful for understanding related other interfacial problems.[8] A more quantitative description of the profile should be possible in the framework of a formulation developed by Noolandi and Hong,[9] but this approach would require extensive numerical computations, which are outside the scope of the present work.

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Ruthenium Tetraoxide Staining of Polymers: New Preparative Methods for Electron Microscopy

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Recent introduction of ruthenium tetraoxide (RuO_4) as a new staining agent for electron microscopy (EM) of polymers and their blends[1,2] has opened the door to a new world of investigations. Osmium tetraoxide (OsO_4) (a routinely used staining agent) is mainly effective with polymers having some level of unsaturation.[3,4] Fortunately, RuO_4 is a far more vigorous oxidant than OsO_4, and this characteristic permits a greater number of polymers to be studied. Now scientists can examine the morphology and microstructure of saturated polymeric materials by EM. For example, our previous results have shown that RuO_4 stained polymers containing ether, alcohol, aromatic, amine, tertiary carbon, or unsaturated moieties in their unit structure.[2] The action of the stain improved image contrast considerably and stabilized the film against electron beam damage. In addition, the staining solution was easy to prepare and use. Nevertheless, some major disadvantages exist. The purpose of this note is to present two alternative preparative methods for RuO_4 staining solutions which may circumvent the problems addressed below.

Ruthenium tetraoxide (crystals sold in sealed ampules[5]) is very expensive and not always available. For example, both suppliers mentioned in ref 5 have temporarily discontinued sale of this material, due to the hazards and difficulties involved in isolating the pure metal oxide. We have recently found that it is no longer necessary to purchase RuO_4 in ampules or solution form. When difficult to obtain, RuO_4 can be easily prepared in the laboratory under a hood. Oxidation of hydrated ruthenium dioxide ($RuO_2{\cdot}xH_2O$) using sodium periodate ($NaIO_4$) to generate RuO_4 (see Experimental Section) has been investigated and the following equation reported:[6]

$$RuO_2{\cdot}2H_2O + 2NaIO_4 \rightarrow RuO_4 + 2NaIO_3 + 2H_2O$$

It was found that when synthesized, the cost of RuO_4 was reduced by a factor of 5. Also, the starting materials were more accessible[7] and aqueous staining solutions containing 0-1% RuO_4 (by weight) were simple to prepare. In order to stain samples in solution, an excess of hydrated ruthenium dioxide was used (synthesis I in Experimental Section) so that unreacted sodium periodate would not be present to oxidize the reduced polymer bound metal oxide.

When pure RuO_4 was dissolved in water, the golden yellow solutions obtained were stable for only a short time when left at room temperature. The tetraoxide slowly decomposed to lower oxide states in the dark but decomposed at a faster rate when exposed to light or heat. When an excess of sodium periodate (synthesis II in Experimental Section) was used, the solutions obtained were stable at room temperature for many days. Increased stability of the staining solutions was a result of unreacted $NaIO_4$ regenerating the reduced metal oxide. This process continued until the cooxidant was completely reduced. When RuO_4 solutions made from synthesis II were used, only vapor staining was possible.

Finally, RuO_4 is very toxic and little is known regarding health hazards. However, if RuO_4 is synthesized in the laboratory, only small amounts of the volatile material need be made, consequently reducing one's exposure.

Experimental Section

General Procedures. Hydrated ruthenium dioxide (Anal.: Ru, 59.27) and sodium periodate were purchased from Morton Thiokol, Inc. (Alfa Products). All aqueous sodium periodate solutions were cooled to 1 °C before hydrated ruthenium dioxide (black powder) was added. The glass bottles were lightly stoppered to prevent pressure buildup as RuO_4 was generated. Most of the tetraoxide remained in solution. Once the reactions were complete (approximately 3-4 h), the RuO_4 solutions were tightly stoppered and stored in the freezer for future use. Syntheses I and II produced aqueous solutions containing approximately 0.5% RuO_4 (by weight).

Synthesis I: Excess of $RuO_2{\cdot}xH_2O$. Sodium periodate (1.28 g) was dissolved in 100 mL of deionized water (25 °C) and cooled to 1 °C. Hydrated ruthenium dioxide (0.6 g) was then added to the chilled aqueous solution of $NaIO_4$. As $RuO_2{\cdot}xH_2O$ began to dissolve, golden yellow RuO_4 formed, and because $RuO_2{\cdot}xH_2O$ was in excess, the unreacted dioxide settled to the bottom of the bottle. Before use, each RuO_4 solution was filtered through glass

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