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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wool. Specimens were successfully stained in solution or by the RuO_4 vapors. Vapor staining methodology is given elsewhere.[8]

Synthesis II: Excess of $NaIO_4$. Sodium periodate (4 g) was dissolved in deionized water (25 °C) and chilled. $RuO_2\cdot xH_2O$ (0.6 g) was added to the aqueous $NaIO_4$ solution. All of the black ruthenium dioxide powder dissolved, producing a stable solution of RuO_4. Specimens immersed in this solution never darkened, and were eventually destroyed by RuO_4 oxidation.

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Concentration Dependence of the Mutual Translational Diffusion Coefficient of Polystyrene in Good Solvents

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The mutual translational diffusion coefficient D of a polymer chain in solution can be observed by the dynamic light scattering (DLS) technique, where the relaxation of concentration fluctuation of polymer is measured. Especially the concentration dependence of D in dilute solutions is sensitive to hydrodynamic and thermodynamic interactions of polymer chains. In this paper, we collected the data of the coefficient k_D of the concentration dependence of D obtained by DLS for dilute solutions of narrow molecular weight distribution polystyrenes in good solvents and compared them with the theoretical predictions proposed hitherto. It is shown that the relationship between k_D and weight-average molecular weight M_w is expressed by $k_D \propto M_w^{0.76}$ below $M_w = 4 \times 10^6$ but deviates downward in the higher molecular weight region and that the latter behavior is not predictable from any theory at present.

The irreversible thermodynamics gives the concentration dependence of D in the zero limit of the scattering vector q as[1]

$$D(q = 0)/D_0 = (f_0/f)(M/RT)(\partial\Pi/\partial c)_{T,\mu_1} \qquad (1)$$

where D and the collective friction factor f at concentration c are expressed in the volume-fixed frame of reference and the subscript zero denotes the values at infinite dilution. Π is the osmotic pressure of the solution, c the polymer weight concentration, μ_1 the chemical potential of the solvent, and M the molecular weight of the polymer. Thus, D depends on both hydrodynamic (f_0/f) and thermodynamic $[(\partial\Pi/\partial c)_{T,\mu_1}]$ interactions of polymers. Moreover, it should be noticed that[2] for the limit $q \rightarrow 0$ one observes relaxation of concentration fluctuation with wavelength larger than the polymer dimension.

In the dilute solution region, we may expand D and f as a series of c as

$$D/D_0 = 1 + k_D c + \ldots \qquad (2)$$

$$f/f_0 = s_0/s = 1 + k_s c + \ldots \qquad (3)$$

We can then obtain from eq 1 the relation[3]

$$k_D = 2A_2M - k_s \qquad (4)$$

where s is the sedimentation coefficient at concentration c and A_2 the second virial coefficient of the polymer. The coefficient k_s of the concentration dependence of f is expressed theoretically in the forms

$$k_s = BN_AV_H/M \qquad \text{(Ba, Fe, PF)} \qquad (5)$$

$$k_s = 1.2A_2M + N_AV_H/M \qquad \text{(Y)} \qquad (6)$$

$$k_s = (6/4^{2/3})(A_2M)^{2/3}(N_AV_H/M)^{1/3} \qquad \text{(AB)} \qquad (7)$$

where N_A is the Avogadro number and V_H the hydrodynamic volume of the polymer. B in eq 5 is a quantity which depends on the hydrodynamic interactions acting on the polymer segments. Only for hard-spherical interactions can B be treated rigorously: Batchelor[4] (Ba) and Felderhof[5] (Fe) gave $B = 6.55$ and 6.44, respectively, for hard spheres of radius R_a with the particle volume $V_e = V_H = (4\pi/3)R_a^3$. In the case of soft-spherical interactions, Pyun and Fixman[6] (PF) gave $B = 7.16 - K(A)$ for interpenetrable spheres of uniform density. $K(A)$ is a function of the thermodynamic parameter A and becomes zero, i.e., $B = 7.16$, for the good solvent limit (=hard sphere) at $A = \infty$. Equation 6 was proposed by Yamakawa[7] (Y) for Gaussian chains with the Flory–Krigbaum potential, and eq 7 was calculated by Akcasu and Benmouna[8,9] (AB) for Gaussian chains with an effective hard-spherical radius $\bar{S}$ related to A_2.

In the good solvent limit, the thermodynamic interaction term A_2M becomes

$$A_2M = 4N_AV_e/M = 4N_AV_H/M \qquad (8)$$

Then we obtain for the above-mentioned theories (eq 5–7) the same molecular weight dependence of k_D

$$k_D = (8 - B)N_AV_H/M = (2 - B/4)A_2M \qquad \text{(Ba, Fe, PF; hard spheres)} \qquad (9)$$

$$k_D = 2.2N_AV_H/M = 0.55A_2M \qquad \text{(Y; hard spheres)} \qquad (10)$$

$$k_D = 2.0N_AV_H/M = 0.50A_2M \qquad \text{(AB; hard spheres)} \qquad (11)$$

If we use the relation $V_H = (4\pi/3)R_H^3$, where R_H is the hydrodynamic radius of the polymer, the second equality of eq 8 leads an equivalence to setting a parameter $X = 1$, X being introduced by Akcasu and Benmouna[8,9] as a ratio $\bar{S}/R_H$; i.e., $X^3 = 3A_2M^2/16\pi N_AR_H^3$. A relation $R_H \propto M^{\nu'}$ or $A_2 \propto M^{\beta}$ then may give the M dependence of k_D as $k_D \propto M^{3\nu'-1}$ or $k_D \propto M^{1+\beta}$ at $X = 1$.

In Figure 1 we show the logarithmic plot of k_D data against M_w. The data were summarized from DLS measurements made so far for dilute solutions of narrow molecular weight distribution polystyrenes (PS) under the good solvent–temperature conditions[10–15] given in Table I. The k_D value for the highest molecular weight sample in Figure 1 was estimated at $qR_G = 0.713$, where the scattering angle was 10°. The data points exhibit a clear M dependence below the molecular weight $M_w \cong 4 \times 10^6$ as

$$k_D = 4.60 \times 10^{-3}M_w^{0.76\pm0.01} \quad (\text{cm}^3/\text{g}) \qquad (M_w < 4 \times 10^6) \qquad (12)$$