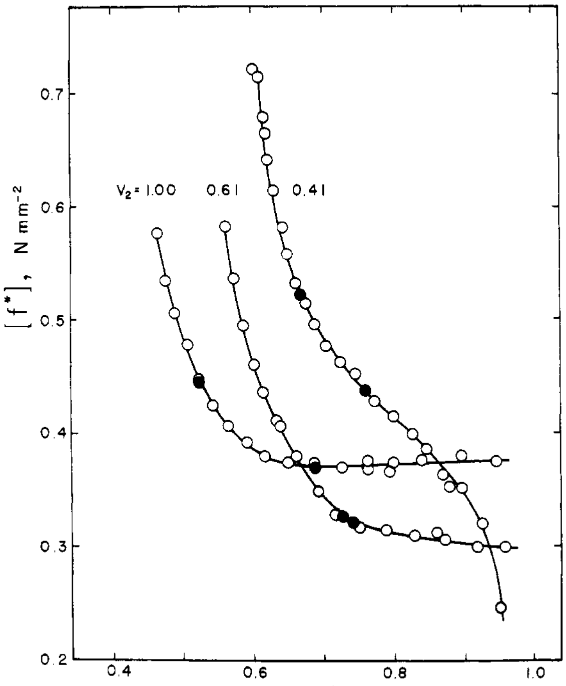

Figure 1. Stress-strain isotherms at 25 °C for the poly(dimethylsiloxane) bimodal networks containing 90 mol % of the short chains. Each curve is labeled with the volume fraction of polymer in the network. The open circles locate results obtained using a series of increasing values of the elongation α and the filled circles the results obtained out of sequence to test for reversibility.

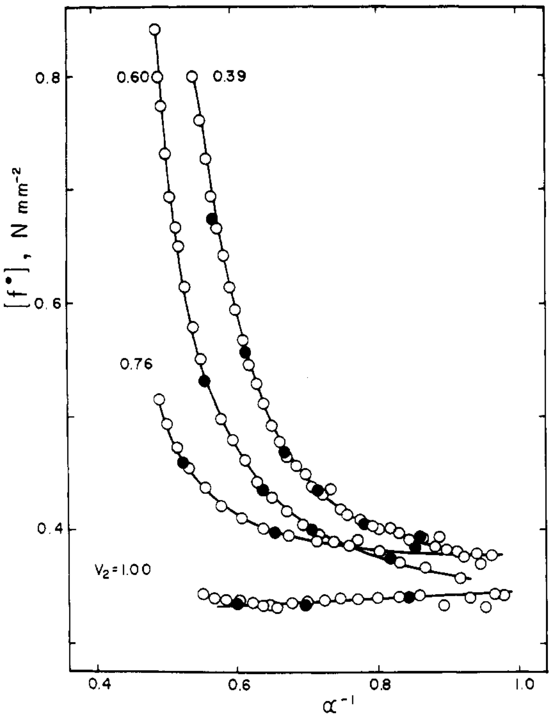

Figure 2. Stress-strain isotherms for the networks containing 85 mol % short chains; see legend to Figure 1.

from intermolecular effects seem to be unimportant.

The observation that swollen networks that are bimodal have much better properties than is typical for swollen materials could be of practical importance.[18] It suggests, for example, that oil extension could be used to give relatively inexpensive silicone elastomers having very good ultimate properties.

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Polymer Diffusion in Blends: Effects of Mutual Friction

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A number of experiments have been carried out in recent years on the mutual diffusion of polymer blends.

For A/B polymer blends, the free energy in the liquid state is relatively well described by the Flory-Huggins expression[1]

$$\frac{F}{kT} = \frac{\phi}{N_A} \log \phi + \frac{1-\phi}{N_B} \log (1-\phi) + \chi\phi(1-\phi) \quad (1)$$

where ϕ is the volume fraction, N_A and N_B are the indices of polymerization, and χ is the interaction parameter. The (few) pairs of compounds which are miscible at a microscopic scale have $\chi < 0$; i.e., the enthalpy of mixing is negative. This means that A/B monomers interact via interactions other than van der Waals, e.g., by hydrogen bondings.[2-4] It has been observed by Monnerie[8] that these interactions could also lead to *large A/B friction forces* and thus play an important role in the dynamical behavior of the mixtures.

In previous work[5] we have calculated the mutual diffusion coefficient for a miscible polymer mixture, *neglecting* the viscous coupling between the two polymer currents J_A and J_B. We had written

$$J_A = -\Lambda_A \nabla(\mu_A + U) \quad (2a)$$

$$J_B = -\Lambda_B \nabla(\mu_B + U) \quad (2b)$$

U is a potential ensuring incompressibility.[9] Λ_i (i = A, B) are the mobilities: for small chains ($N_i < N_e$), $\Lambda_i = \phi_i \zeta_{ii}$, where ζ_{ii} is a friction coefficient for species i; for entangled chains ($N_i > N_e$), the mobility is reduced: $\Lambda_i = \phi_i(N_e/N_i)$

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ζ_{ii}, where N_e is an average distance between entanglement points.

From eq 1 and 2, we derived the mutual diffusion coefficient D

$$J_A = -J_B = -D\nabla\phi$$

and found

$$D = D_0\phi(1 - \phi) \tag{3}$$

Assuming $\zeta_{AA} = \zeta_{BB}$ and $N_A = N_B$, the prefactor is $D_0 = D_1(2|\chi|)$ for $N < N_e$ and $D_0 = D_1(2|\chi|)(N_e/N)$ for $N > N_e$ (where D_1 is a monomer diffusion coefficient).

This strong dependence of D upon ϕ predicted by eq 3 can lead to unusual concentration profiles: for pure A and pure B blocks put into contact at time $t = 0$, we expect an anomalous diffusion zone where $\phi_t(x)$ is *linear* in the spatial coordinate x.[5]

What happens if we add a strong viscous coupling between A and B species? We shall see that the effect is very different in the nonentangled case (where it should be strong) and in the entangled case (where it should be minor).

Strong A/B Viscous Interactions

We modify eq 2 to include viscous A/B coupling. In fact, a monomer A is submitted to two forces: (a) $-\nabla(\mu_A + U)$, the osmotic force associated with a concentration gradient of A with the requirement $\phi_A + \phi_B = 1$; (b) a viscous force due to the motion of B monomers. We expect this force to be proportional to the relative velocity $(v_B - v_A)$ and to the density of B

$$F_v = \zeta_{AB}\phi_B(v_B - v_A) = \zeta_{AB}\left(J_B - \frac{\phi_B}{\phi_A}J_A\right) \tag{4}$$

where ζ_{AB} is a microscopic coefficient describing mutual friction. Equations 2a and 2b are modified into

$$J_A = \Lambda_A\left[-\nabla(\mu_A + U) + \zeta_{AB}J_B - \zeta_{AB}\frac{\phi_B}{\phi_A}J_A\right] \tag{5a}$$

$$J_B = \Lambda_B\left[-\nabla(\mu_B + U) + \zeta_{BA}J_A - \zeta_{BA}\frac{\phi_A}{\phi_B}J_B\right] \tag{5b}$$

The forces-flux coupling equations can be written as

$$-\nabla(\mu_A + U) = J_A\left(\frac{1}{\Lambda_A} + \zeta_{AB}\frac{\phi_B}{\phi_A}\right) - \zeta_{AB}J_B \tag{6a}$$

$$-\nabla(\mu_B + U) = -\zeta_{BA}J_A + J_B\left(\frac{1}{\Lambda_B} + \zeta_{AB}\frac{\phi_A}{\phi_B}\right) \tag{6b}$$

The cross-term viscous coefficient must be equal (according to the Onsager relations)

$$\zeta_{AB} = \zeta_{BA} \tag{7}$$

The determinant associated with eq 6 is always positive $(1/\Lambda_A\Lambda_B + \zeta_{AB}(\phi_B/\phi_A + \phi_A/\phi_B) > 0)$. Thus our assumptions are compatible with a positive entropy source.

For Fourier components ($q \neq 0$), incompressibility imposes $J_A + J_B = 0$. Subtracting eq 6a and 6b, we find

$$-\nabla(\mu_A - \mu_B) = \left(\frac{1}{\Lambda_A} + \frac{1}{\Lambda_B} + \frac{\zeta_{AB}}{\phi(1 - \phi)}\right)J_A \tag{8}$$

$\mu_A - \mu_B$ is the exchange chemical potential and is equal to $\partial F/\partial\phi$ For compatible pairs with $\chi < 0$, this leads to

$$J_A = -D\nabla\phi \tag{9a}$$

$$D = \frac{2|\chi|kT}{\dfrac{1}{\Lambda_A} + \dfrac{1}{\Lambda_B} + \dfrac{\zeta_{AB}}{\phi(1 - \phi)}} \tag{9b}$$

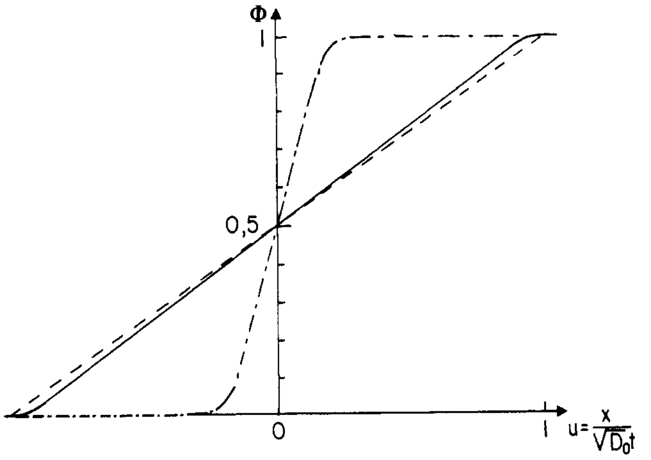

Figure 1. Concentration profiles for pure melts in contact for *unentangled* chains in three cases ($D_0 = 2|\chi|kT/\xi_{AA}$): (a) dotted line, $\xi_{AB} = 0$ (no viscous coupling) $[D = D_0\phi(1 - \phi)]$; (b) full line, $\xi_{AB} = \xi_{AA} = \xi_{BB}$ $[D = (D_0/2)\phi(1 - \phi)]$; (c) dash-dotted line, $\xi_{AB} \gg \xi_{AA}$ ($\xi_{AB}/\xi_{AA} = 100$), large A/B friction forces ("sticking effect") $[D = D_0/100)\phi(1 - \phi)]$. As shown in ref 5, the profiles are just straight lines if $D \sim \phi(1 - \phi)$.

Discussion

(a) Entangled Chains ($N_{A,B} > N_e$). Inserting in eq 9 the mobilities of entangled chains ($\Lambda_i = \phi_i(N_e/N_i)\zeta_{ii}$) leads to

$$D = \frac{2|\chi|kT}{\dfrac{N_A}{N_e}\dfrac{\zeta_{AA}}{\phi} + \dfrac{N_B}{N_e}\dfrac{\zeta_{BB}}{1 - \phi} + \dfrac{\zeta_{AB}}{\phi(1 - \phi)}} \tag{10}$$

The microscopic friction coefficients ζ_{ij} are expected to be independent of N_A and N_B and also (hopefully) independent of ϕ. Even if $\zeta_{AB} \gg \zeta_{AA}, \zeta_{BB}$, the effect of the coupling term is small if N/N_e is large as shown by eq 10. Returning to eq 4, we find that this means the viscous A/B force F_v is *small* compared to the osmotic driving force $F_{os} = -\nabla(\mu_A + U)$ in the entangled regime, because the contorted path of the chains leads to a reduction of AB velocities (illustrated by the expression of Λ_i).

(b) Small Chains ($N_{A,B} < N_e$). The mobilities of A and B are large ($\Lambda_i = \phi_i\zeta_{ii}$) and eq 9 leads to

$$D = \frac{2|\chi|kT}{\dfrac{\zeta_{AA}}{\phi} + \dfrac{\zeta_{BB}}{1 - \phi} + \dfrac{\zeta_{AB}}{\phi(1 - \phi)}} \tag{11}$$

Now F_{os} and F are comparable and the coupling term becomes important.

(1) Moderate Mutual Friction ($\zeta_{AB} \cong \zeta_{AA} \cong \zeta_{BB}$). The main conclusions of ref 2 are valid: D depends strongly upon ϕ ($D = 0$ for $\phi = 0$ and $\phi = 1$). For two blocks of A and B put into contact we still find a zone of mixing of finite width, as in ref 2, and the profile is strictly linear if $\zeta_{AB} = \zeta_{AA} = \zeta_{BB}$ (Figure 1) and almost linear if $\zeta_{AB} \simeq \zeta_{AA} \simeq \zeta_{BB}$ (ref 2). But the mutual friction plays an important role in the prefactor.

(2) Strong Mutual Friction ($\zeta_{AB} \gg \zeta_{AA}, \zeta_{BB}$). As soon as $\zeta_{AA}/\zeta_{AB} \gg 1$, the viscous coupling term is dominant

$$D = 2|\chi|\frac{kT}{\zeta_{AB}}\phi(1 - \phi) \tag{12}$$

D is *much smaller* than $D_A = kT/\zeta_{AA}$ or $D_B = kT/\zeta_{BB}$.

Mutual diffusion is reduced by a "sticking effect" between A and B.

If ζ_{AB} is independent of ϕ the composition profiles are linear, even if monomer A and B mobilities are different (Figure 1).

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Conclusion

Large A/B viscous interactions can induce a slowing down of dynamical process in A/B compatible mixtures. We predict a large effect for small chains (unentangled regime) and large mutual viscosity ($\zeta_{AB} \gg \zeta_{AA}, \zeta_{BB}$). For long chains, viscous coupling is negligible and the conclusions of ref 2 are not modified.

Acknowledgment. We thank Professor L. Monnerie, who mentioned to us the possible importance of mutual friction.

Appendix

The full free energy including compressibility is

$$F_{\mathrm{cm}^3} = \frac{kT}{a^3}\left[\frac{\phi_A}{N_A}\log\phi_A + \frac{\phi_B}{N_B}\log\phi_B + \chi\phi_A\phi_B\right] + \frac{1}{2}E(\theta-\theta_0)^2$$

with

$$\phi_A = \mathcal{N}_A/(\mathcal{N}_A + \mathcal{N}_B + \mathcal{N}_v)$$

$$\phi_B = \mathcal{N}_B/(\mathcal{N}_A + \mathcal{N}_B + \mathcal{N}_v)$$

$$\theta = \mathcal{N}_v/(\mathcal{N}_A + \mathcal{N}_B + \mathcal{N}_v)$$

E, the compressibility modulus, is often much larger than $\chi kT/a^3$. Assuming viscous motions (no sound waves), the motion equations are

$$\dot\phi_A = -\operatorname{div} J_A = \Lambda_A\Delta^2(\mu_A - \mu_v)$$

$$\dot\phi_B = -\operatorname{div} J_B = \Lambda_B\Delta^2(\mu_B - \mu_v)$$

with $\mu_v = E(\theta - \theta_0)$. They lead to two modes:

(a) A fast mode

$$\frac{\dot\phi_A}{\Lambda_A} = \frac{\dot\phi_B}{\Lambda_B} = -Eq^2(\delta\phi_A + \delta\phi_B)$$

controlled by the *fast* species and describing relaxation toward optimal density.

(b) A slow mode

$$J_A = -J_B$$

describing mutual diffusion, for which

$$\nabla\mu_v = -\frac{\Lambda_A\nabla\mu_A + \Lambda_B\nabla\mu_B}{\Lambda_A + \Lambda_B} = -\nabla U \neq 0$$

as assumed in ref 5.

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(9) This approach was criticized for ignoring vacancy flux by Kramer.[6] Kramer introduces a chemical potential μ_v for vacancies proportional to U. His working hypothesis is to set μ_v = constant; i.e., U = constant. We explain in the appendix that μ_v = constant is satisfied for fast compression modes, whereas for the slow mutual diffusion mode studied here, μ_v is not constant and $U = -(\Lambda_A\mu_A + \Lambda_B\mu_B)/\Lambda_A + \Lambda_B$ as set in ref 5.

Dynamic Viscoelastic Properties of Poly(styrenesulfonate) Latex

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Aqueous suspensions of monodisperse charged latex particles with very low concentrations of electrolyte form ordered structures, whose properties have been studied by many different methods.[1] Several investigations of polystyrene latices have revealed unusual viscoelastic properties with a finite yield stress and a substantial storage shear modulus in small oscillating deformations at frequencies both in the 50-kHz region[2-4] and from 0.05 to 350 Hz.[5,7] The storage of elastic energy in deformation is attributed to changes in electrostatic energy, and its dependence on particle volume fraction, salt concentration, and other variables has been calculated.[3,7-9] The frequency dependence of viscoelastic properties has been examined only for latices with quite high concentrations.[5,7]

We have now made measurements of storage shear modulus and dynamic viscosity (loss modulus divided by radian frequency) over a wide frequency range from 100 to 5700 Hz on a polystyrene–poly(styrenesulfonate) copolymer latex[10,11] which carries a considerably higher charge per particle and has a much lower concentration than investigated previously.

Materials and Methods

A latex of polystyrene copolymerized with poly(styrenesulfonate) was generously given us by Professor Norio Ise, Kyoto University. The concentration was 7.4% by volume; particle diameter was 100 nm and number of charges per particle was 2.7×10^4, determined as described previously by Ise et al.[10,11] To remove contaminating ions which would disturb the formation of the ordered structure, the suspension was treated with analytical grade mixed-bed ion-exchange resin (BioRad AG 501-X8, an equal mixture of Dowex 1-X8 and 50W-X8). Approximately 20 mL of the stock suspension was added to 50 mL of dry resin; the mixture was sealed and left to stand for several days. The resin was removed by filtering with an 8-μm Millipore filter and then three 5-mL aliquots of 15-MΩ deionized water were used to wash most of the latex from the resin. The resulting latex suspension was somewhat iridescent. A final deionization was accomplished by passing the suspension through an ion-exchange column (1-cm diameter, 40 cm long, AG501-X8 resin) with doubly deionized water. Central fractions, with high iridescence, for a total of 45 mL were pooled and used immediately for multiple-lumped resonator measurements. The latex concentration was 1.400 ± 0.004 w/w % (volume concentration 1.33%), determined gravimetrically. The conductance of water similarly treated was $1.1 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, corresponding to a KCl concentration of 8×10^{-6} M. At this very low electrolyte concentration, the ordered array of latex particles should be stable.

Measurements of storage (G') and loss (G'') shear moduli were made at 20.0 °C at frequencies ν of 102, 394, 986, 2380, and 5820 Hz by the Birnboim–Schrag multiple-lumped resonator[12] with a modified data acquisition and processing system described elsewhere.[13] This is a surface-loading instrument which measures the complex impedance per unit area at an oscillating surface.[14] Both the resonator and the housing were constructed of a titanium alloy.[15] They were washed for several days with deionized water until no increase in conductivity could be observed after water remained in the instrument overnight. The instrument was filled very slowly through a syringe with a needle diameter of 1.4 mm. Because of concern that the ordered latex structure might be disrupted by this procedure, measurements were made at intervals over a 2-day period to allow any disrupted structure to be reestablished. There was actually very little change with time. The results are reported as G' and the dynamic viscosity $\eta' = G''/\omega$, where ω is the radian frequency ($2\pi\nu$).

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