is formed. ϕ^* depends crucially on δ, the ratio of the length of block A and homopolymer chains. For high δ, for which micelles are expected to be fairly swollen, ϕ^* may be very small. For example, for systems considered in Figure 2 we find ϕ^* equal to 0.046 and 0.11 for shorter and longer homopolymer chains, respectively. It should be stressed that the transition concentration will depend weakly on temperature unless the system is close to the cmc.

A prediction of the macrolattice structure is a delicate problem. Strictly speaking, for hard-sphere systems a closely packed cubic structure is to be expected. However, for actual "softer" interaction potentials the body center cubic lattice may occur on the ordering curve as has been argued in general by symmetry considerations[9] and shown for pure copolymers.[10] In practice, due to very long diffusion times a true long-range order may not actually be observed and a glassy phase of micelles may obtain. In any case the rheological properties of the system will be strongly affected at the transition because the micelle motions will be strongly correlated. This will result at ϕ^* to a more or less sharp increase in relaxation times. Rheological effects of this type have been observed in block copolymer solutions in selective solvents and have been interpreted in terms of the ordering transition of micelles.[11]

Acknowledgment. We are indebted to S. Alexander and D. Lhose for interesting discussions and to W. Graessley for drawing our attention to rheological experiments on homopolymer–copolymer mixtures and many helpful remarks.

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(12) Strictly speaking, η is given by the minimization of the total free energy as discussed in detail in ref 3. However, for long copolymers for which the cmc is very small the difference between η obtained by the minimization of $F(r)$ with $r = R_A + R_B$ and the actual value is negligibly small.

Effect of Swelling on the Short-Chain Reinforcement Observed in Bimodal Elastomeric Networks

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Received April 2, 1984

Elastomers which contain a large mole fraction of very short chains as part of a bimodal distribution of network chain lengths have been shown to be unusually tough, even in the unfilled state.[1-5] The primary reason for the increased toughness is a marked upturn in the stress at high elongations, and this has been attributed to the limited extensibility of the very short chains.[1-3] This explanation, which is entirely intramolecular in nature, is supported by insensitivity of the strengthening upturns to temperature and the absence of any deviations from linearity in the force–temperature and birefringence–temperature relationships.[6] The most stringent test, however, for the possible importance of intermolecular effects (for example, strain-induced crystallization),[7] is the dependence of the stress–strain isotherms on degree of swelling. Should any strain-induced crystallization be present it would be greatly diminished by incorporation of diluent into the network, through the depression of the melting point.[8,9] Effects of limited chain extensibility, in contrast, would not be diminished by swelling and could in fact be enhanced because the swelling dilation causes some stretching of the chains prior to their additional deformation in the elongation experiments.

The present investigation thus focuses on determination of the effects of swelling on the stress–strain isotherms of bimodal elastomeric networks.

Experimental Details

The two bimodal elastomers investigated were portions of two poly(dimethylsiloxane) networks which had previously been studied in the undiluted state.[1] They had been prepared by end-linking very short chains having a number-average molecular weight of 220 with relatively long chains of 18.5×10^3. The first consisted of 90 mol % short chains and the second 85 mol %. Both had been extracted to remove the 5 wt % soluble matlerial they contained.[1]

The nonvolatile solvent chosen as swelling diluent was a mixture of linear dimethylsiloxane oligomers having 8–11 repeat units; it was generously provided by Dow Corning Corp. Two portions of the network containing 90 mol % short chains were swollen to give values of the volume fraction v_2 of polymer present of 0.61 and 0.41, respectively. Three portions of the other network were swollen to $v_2 = 0.76$, 0.60, and 0.39, respectively.

Stress–strain measurements in elongation were carried out on both the unswollen and swollen networks at 25 °C in the usual manner.[1,2,10,11] The elastomeric quantity of primary interest was the reduced stress or modulus defined by[8,11,12]

$$[f^*] \equiv f v_2^{1/3} / A^*(\alpha - \alpha^{-2}) \qquad (1)$$

where f is the elastic force, A^* is the cross-sectional area of the unstretched and unswollen sample, and $\alpha = L/L_i$ (where L and L_i are the stretched and unstretched lengths, respectively, in the swollen state). The measurements were carried out to the rupture points.

Results and Discussion

The representation of the stress–strain data was based on the Mooney–Rivlin equation[13,14]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (2)$$

where $2C_1$ and $2C_2$ are constants. These plots, of the reduced stress against reciprocal elongation, are shown in Figures 1 and 2. Only the curves for the unswollen networks ($v_2 = 1.00$) have any portions which show the usual decrease in $[f^*]$ with increasing α,[13,14] which is due to the increasingly nonaffine nature of the deformation.[15,16] The rest of the results all show very strong increases in $[f^*]$ at high elongations, with the upturns in some cases being very nearly vertical. Of greatest importance is the observation that swelling does not diminish this toughening effect; in fact, it generally seems to enhance it! These results thus give very strong support to the interpretation[1-3] of this interesting behavior in terms of the limited extensibility[17] of the short chains in the network structure. Contributions

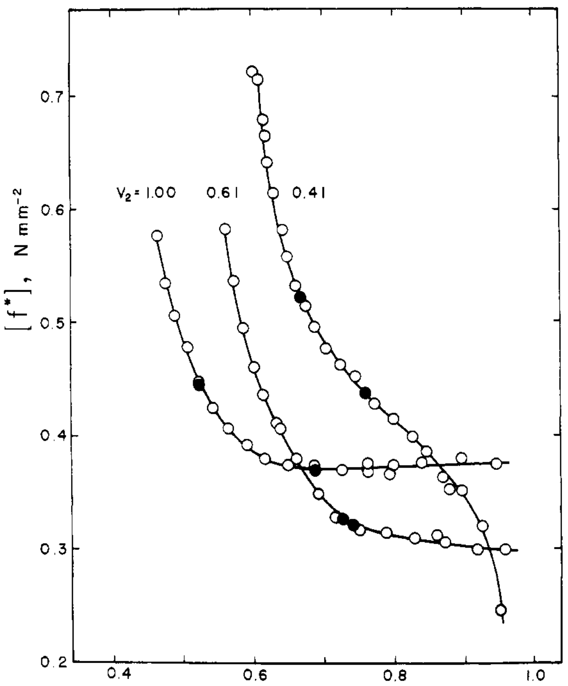

Figure 1. Stress–strain isotherms at 25 °C for the poly(dimethylsiloxane) bimodal networks containing 90 mol % of the short chains. Each curve is labeled with the volume fraction of polymer in the network. The open circles locate results obtained using a series of increasing values of the elongation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

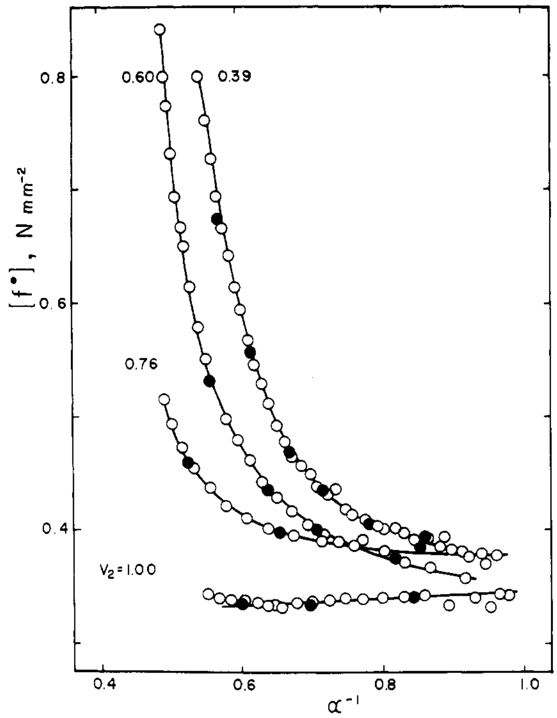

Figure 2. Stress–strain isotherms for the networks containing 85 mol % short chains; see legend to Figure 1.

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.

Acknowledgment. It is a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR 79-18903-03 (Polymers Program, Division of Materials Research) and the assistance of Dr. J. L. Thiele.

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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]

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

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

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

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

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: $\Lambda_i = \phi_i(N_e/N_i)$