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We now want to examine the various possibilities which could produce two separate bands when suspensions of OPS and FPS are mixed.

(a) The first possibility is that OPS and FPS have the same structure. The observed difference in density is due to microbubbles of air adhering to the FPS suspended particles. Such microbubbles could not exist for OPS because sonication would quite certainly destroy them. This possibility is remote. The pressure at the location of the FPS strip, the one nearest the meniscus, is about 60 atm. At such a pressure microbubbles should either float or dissolve in the surrounding medium.

(b) The difference in density is due to some cyclohexane remaining in the freeze-dried product. This is quite improbable. The freeze-drying lasted 20 h and after 13 h no more cyclohexane was sublimating, as shown by the constancy in weight of the freeze-drying flask. On the other hand, the product, about 50 mg, was left at -18 °C for several months in a sealed flask of about 1-L capacity. Finally, assuming that some cyclohexane still adhered to the FPS, it should for the most part have dissolved in the ethanol when the FPS was suspended in ethanol. For the same reason, the density cannot be ascribed to swelling of one of the samples by ethanol since, if OPS and FPS had the same structure, they should swell the same way in the identical nonsolvent mixtures. At any rate, the trace of remaining cyclohexane cannot account for the very significant density difference observed.

(c) The surface area may be considerably greater in the FPS suspended particles. If one of the components of the nonsolvent mixture is preferentially adsorbed, this may lead to a density difference with OPS particles. We cannot rule out such a possibility, but it seems likely that, if such a phenomenon occurred, we should have had a continuous distribution of densities (due to the polydispersity of the surface/volume ratio of the FPS suspended particles) or at least not two sharply defined bands.

(d) A more consistent interpretation would be that, due to their different thermal histories, the OPS and FPS samples are in permanent metastable states of different densities. It was shown long ago by dilatometric studies[16] that the density of a glassy polymer depends on its previous thermal history. More recently, it was shown that poly(vinyl chloride) and polystyrene samples having different thermal and solvent vapor exposures show differences in vapor sorption isotherms and, inferentially, have different densities.[17-19] Quite recently, it has been found that freeze-drying has a substantial effect on the differential scanning calorimetry curves of polystyrene and poly(methyl methacrylate).[20] For the above reasons, it is quite possible that the observed density difference merely reflects the different thermal histories of our OPS and FPS samples, both samples having the usual structure of entangled chains.

(e) There remains the possibility that the observed density difference is due to a different bulk structure of the OPS and FPS samples, in which case the FPS sample may have the structure schematically shown in Figure 1a. Such a possibility should not be discarded, particularly if one considers previously obtained electron microscopy results,[11-14] where, clearly, aggregation of macromolecules in a compact form has been observed. The freeze-drying process of the very dilute solution here used seems equivalent to the evaporation process of microbubbles of a poor solvent containing, on the average, a single macromolecule.[13]

Further progress to elucidate the reason for the density difference observed in this work will necessitate the use of various techniques, which may include differential scanning calorimetry (DSC), small-angle neutron scattering (SANS), and electron microscopy.

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Concentration Dependence of Viscoelastic Properties of Concentrated Solutions of Six-Branched Polystyrenes[†]

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The rheological properties of star polymers of styrene,[1-6] butadiene,[7,8] isoprene,[9] and α-methylstyrene[10] have been investigated by various authors. Among these investigations, experimental results obtained for three- and four-branched star polymers[5,8] indicate that the steady-state compliance (J_e°) is inversely proportional to the polymer concentration over a wide range of concentration. This behavior is quite different from those obtained for linear-polymer solutions. The concentration dependence of J_e° measured for four- and six-branched polyisoprenes[9] is very complicated. Recently, the viscoelastic properties of star polybutadienes having three and four branches and their concentrated solutions were measured by Marin et al.[8] However, no work on solutions of six-branched star polymers over such a wide range of concentration has been reported yet.

In the present study, the rheological properties of concentrated solutions of six-branched star polystyrene were measured, and the concentration dependences of the zero-shear viscosity (η_0), steady-state compliance (J_e°), and rubbery plateau compliance (J_{eN}°) were determined. The concentration dependence of these rheological parameters are discussed and compared with those for linear poly-

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[†] Rheological Properties of Anionic Polystyrenes. 8.

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Table I
Molecular Weights, Molecular-Weight Distribution, and Coupling Ratio P (Number of Branches in a Molecule) of the Star and Linear Polystyrenes

sample	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n	P
LS1	3.61	4.26	1.18	6.1
L50	2.76	2.98	1.08	

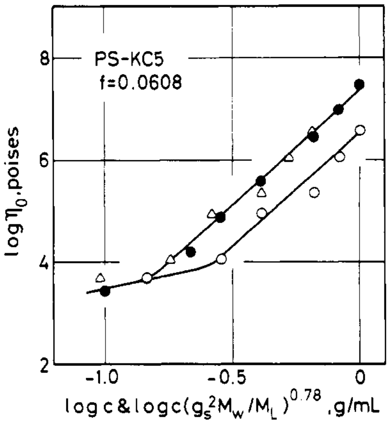

Figure 1. Concentration dependences of zero-shear viscosity, η_0, for solutions of six-branched star polystyrene (LS1; open circles) and linear polystyrene (L50; closed circles) in the iso-free-volume state. The plot of log η_0 against log $c(g_s{}^2M_w/M_L)^{0.78}$ is shown by triangles, where M_L is the molecular weight of L50, 2.98×10^5.

styrene as well as for three- and four-branched star polystyrenes.

Experimental Section

The star-shaped polystyrene sample used in this study is a six-branched star polystyrene (LS1) prepared by coupling narrow-distribution polystyryl anions with cyclic trimer of phosphonitrilic chloride. Details of the preparation, fractionation, and characterization of this sample were described in the preceding paper.[6] A linear polystyrene (L50) used for comparison was also prepared by anionic polymerization. The weight- and number-average molecular weights, the ratio M_w/M_n, and the coupling ratio P [the ratio of M_n for a star polymer to that for its branch (=number of branches in a molecule)] are given in Table I. Solutions of LS1 and L50 at various concentrations (0.147, 0.284, 0.412, 0.641, 0.832, and 0.987 g/mL at 50 °C) were prepared and used for viscoelastic measurements. As a solvent, partially chlorinated biphenyl, Kaneclor 500 (KC5), was used.

The real and imaginary parts (G' and G'') of the complex rigidity were measured by means of a concentric cylinder type rheometer.[1,11] Frequency dependence curves of G' and G'' at various temperatures were superposed into a master curve at temperature T_r', where the fractional free volume f is 0.0608.[11,12] No difference was found in shift factors for all solutions of the linear and star polymers. Rheological parameters, η_0, $J_e°$, and $J_{eN}°$, were evaluated from master curves of G' and G'' by the usual procedure.[12]

Results and Discussion

Zero-Shear Viscosity. The concentration dependence of η_0 in the iso-free-volume state ($f = 0.0608$) for solutions of the six-branched (open circles) and linear polystyrenes (closed circles) is shown in Figure 1. η_0 for the star and linear polystyrenes at high concentrations can be represented by a straight line with a slope of 4.5, which is somewhat larger than 4.0 obtained by Marin et al.[8] for linear and branched polybutadienes. Marin et al. plotted η_0 against the volume fraction ψ rather than against $c = \rho'\psi$, where ρ' is the density of polymer. A plot of η_0 against c makes the slope a little steeper because ρ' at higher concentrations is lower than at lower concentrations due to the difference in T_r' in the iso-free-volume state. In Figure 1, a line having a slope of unity[13] is also drawn in the low-concentration region. In a previous paper,[6] η_0 of the linear and six-branched polystyrenes was found to be proportional to $M_w{}^{3.5}$. η_0 could also be reduced satisfactorily by $g_s{}^2M_w$, where

$$g_s{}^2 = (3P - 2)/P^2 \tag{1}$$

These results suggest that η_0 of both the linear and star polystyrenes can be represented by a single straight line when it is plotted against $c(g_s{}^2M_w/M_L)^{0.78}$, where M_L is molecular weight of L50 (2.98×10^5) and $0.78 = 3.5/4.5$. This type of plot is shown by triangles in Figure 1. The triangles calculated for the six-branched star polystyrene agree very well with the closed circles for the linear polymer.

Although it appears difficult to determine the critical concentration c_c accurately from Figure 1, a concentration at the intersection of the two straight lines for L50 solutions, 0.15 g/mL was assumed to be c_c. Using this value, we evaluated c_cM_w and $c_c{}^{1.29}M_w$ ($1.29 = 4.5/3.5$) as 4.5×10^4 and 2.6×10^4, respectively. The literature value[13] for the critical molecular weight M_c for undiluted linear polystyrenes is 3.7×10^4, which is between the above values of c_cM_w and $c_c{}^{1.29}M_w$. The critical concentration for LS1 was estimated from the plot of η_0 against $c(g_s{}^2M_w/M_L)^{0.78}$ to be 0.21 g/mL.

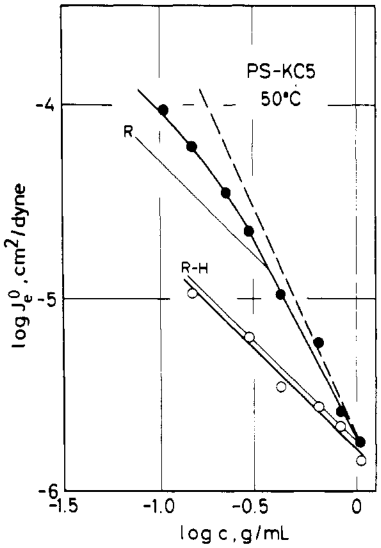

Figure 2. Concentration dependences of steady-state compliance, $J_e°$, for solutions of six-branched star polystyrene (LS1; open circles) and linear polystyrene (L50; closed circles) at 50 °C. R and R-H denote the lines from eq 2 and 3, respectively. The broken line indicates the de Gennes prediction.[18]

Steady-State Compliance. The concentration dependence of the steady-state compliance for L50 and LS1 solutions is shown in Figure 2. In this figure, $J_e°$ at 50 °C rather than in the iso-free-volume state is plotted against concentration c. $J_e°$ for L50 is proportional to c^{-2} at higher concentrations and to c^{-1} at lower concentrations. The critical concentration c_c', where $J_e°$ shows a break, is 0.20 g/mL, which is 1.3 times higher than c_c for η_0 shown in Figure 1. The Rouse equation[15]

$$J_e° = 0.4(M/cRT) \tag{2}$$

is also drawn with a thin line (R) in Figure 2. Experimental data at lower concentrations are somewhat higher than this line. The concentration at the intersection of the Rouse and experimental line (c^{-2}) is 0.37 g/mL $\approx 2.5c_c$.

$J_e°$ for LS1 solutions is proportional to c^{-1} at concentrations ranging from c = 0.147 g/mL to the undiluted

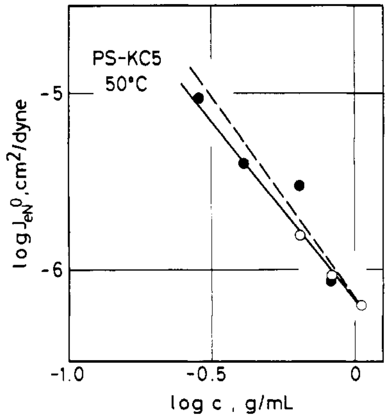

Figure 3. Concentration dependence of rubbery plateau compliance $J_{eN}°$ for solutions of six-branched polystyrene (LS1; open circles) and linear polystyrene (L50; closed circles) at 50 °C. The broken line indicates the de Gennes prediction.[18]

state. This behavior of $J_e°$ for the six-branched polystyrene is very similar to that reported for three- and four-branched star polybutadienes[6] but differs from those obtained by Graessley et al.[9] for solutions of four- and six-branched polyisoprenes as well as those by Kajiura et al.[10] for three-branched poly(α-methylstyrenes).

Recent experimental investigations[3,4,6,9] have shown that the molecular weight dependence of $J_e°$ for star polymers having P up to 4 can well be represented by the Rouse–Ham equation[15,16]

$$J_e° = 0.4(g_2M/cRT) \quad (3)$$

where

$$g_2 = (15P - 14)/(3P - 2)^2 \quad (4)$$

Equation 3 is plotted by a thin line (R-H) in Figure 2, which can represent well the concentration dependence of $J_e°$ of the six-branched star polystyrene. A similar dependence of $J_e°$ on M for star polymers has been reported by a theoretical consideration on a reptation of polymer chain.[17]

Rubbery Plateau Compliance. One of important parameters for characterizing the rubbery region is the rubbery plateau compliance $J_{eN}° = 1/G_{eN}°$, where $G_{eN}°$ is the rubbery plateau modulus. The concentration dependence of $J_{eN}°$ for the solutions at 50 °C is shown in Figure 3. As can be seen from this figure, $J_{eN}°$ for the linear (closed circles) and star (open circles) polystyrenes is proportional to c^{-2}. There is no difference in the concentration dependence of $J_{eN}°$ between the linear and branched polymers, in marked contrast to the case of $J_e°$.

de Gennes evaluated the molecular weight and concentration dependences of rheological parameters for moderately concentrated polymer solutions in a good solvent[18] by using a scaling concept.[19] This theory predicts that both of $J_e°$ and $J_{eN}°$ are proportional to $c^{-2.25}$. This prediction is shown by the dotted lines in Figures 2 and 3. The c^{-2} dependence appears better than $c^{-2.25}$, as can be seen from these figures.

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Excluded-Volume Effects in Dilute Polymer Solutions. 12. Remarks on François et al.'s Modified Blob Model

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The blob model[1-3] for a linear flexible polymer in a good solvent involves two assumptions:

(1) The mean-square distance $\langle r^2 \rangle$ between a pair of segments separated by t bonds of unit length depends only on t.

(2) The quantity ν, defined by $\langle r^2 \rangle/N_c = (t/N_c)^\nu$, is given, according to the scaling law, by

$$\begin{aligned} \nu &= 1 \qquad \text{for } 0 < t < N_c \\ \nu &= 1.2 \qquad \text{for } N_c < t \end{aligned} \quad (1)$$

where N_c defines the size of a blob in which Gaussian chain statistics is obeyed.

It is a very difficult task to remove the first assumption, but we may consider various strategies to improve the second assumption. In this paper, we concern ourselves with making some comments on the latter problem.

Theory of François et al.

Very recently, François et al.[4] approximated ν for $t > N_c$ by a continuous function which increases monotonically from 1 to 1.2 as t is increased. In actuality, they considered two forms for this function:

$$\begin{aligned} \nu &= 1 + 0.2[(t/N_c) - 1]/(k - 1) \qquad \text{for } N_c < t < kN_c \\ \nu &= 1.2 \qquad \text{for } kN_c < t \end{aligned} \quad (2)$$

and

$$\nu = 1.2 - 0.2 \exp\{-c[(t/N_c) - 1]^2\} \qquad \text{for } N_c < t \quad (3)$$

where k and c are adjustable parameters. With these ν functions, they calculated $\langle S^2 \rangle$ (the mean-square radius of gyration of the chain) as a function of N (the total number of bonds in the chain) for $k = 15$ and $c = 0.02$ and found for either function that the slope ν_G of the ln $\langle S^2 \rangle$ vs. ln N curve, i.e., $\nu_G \equiv \mathrm{d} \ln \langle S^2 \rangle/\mathrm{d} \ln N$, is unity for $N < N_c$, increases to a maximum higher than 1.2, and decreases asymptotically to the limiting value 1.2 as N is increased indefinitely. This behavior of $\nu_G(N)$ seems

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