data concerning the dipole moments were obtained by assuming that $\beta = 0$ and 10°. The absolute values of the temperature coefficient of D_∞ and C_∞ obtained from Tables III and IV are smaller than those corresponding to PVC due to, among other reasons, the small contribution of E_η in the case of PVB chains. The value of $10^3(\mathrm{d} \ln \langle\mu^2\rangle/\mathrm{d}T)$ for PVB chains with $p_i = 0$ is −0.2 and for those with $p_i = 1$ the value is −4.8. For chains with a tacticity similar to that of the chains used in the present study the value of $\mathrm{d} \ln \langle\mu^2\rangle/\mathrm{d}T$ is 0.6×10^{-3} K^{-1}. The temperature coefficient of the molecular dimensions of PVB chains is negative for all stereochemical compositions and has an unusually high value of -7.1×10^{-3} K^{-1} for isotactic chains. This is due to the fact that an increase in temperature also increases the disruptions of tgtg... conformations and, for the reasons explained above, drastically decreases the value of the molecular dimensions.

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Phenomenology of Self-Diffusion in Star-Branched Polyisoprenes in Solution

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ABSTRACT: We have measured polymer and solvent self-diffusion at 50 °C in equiarmed star-branched polyisoprenes of low molecular weights in solution with C_6F_5Cl and CCl_4, using pulsed-gradient spin-echo methods supplemented by NMR T_2 relaxation. In solutions and melts of stars with M(arm) $\simeq 10^4$ and $f \leq 18$, entanglements are less pronounced than in linear polymers of equal molecular weight. Polymer diffusion depends differently on M(arm) and f, the f dependence becoming weak at high f at all solvent concentrations. In dilute solution, diffusion behavior shows that these stars are relatively highly expanded; at high polymer concentrations, segmental diffusion mechanisms begin to contribute. Free volume theories explain solvent but not polymer diffusion.

Introduction

Star-branched polymers with arms of equal length are the simplest model systems that allow the effect of branching to be studied in the absence of the usual architectural randomness. This permits the most convenient testing of theories describing branched polymer behavior. Thus, star-branched polymers have attracted considerable experimental[2-4] and theoretical[5-12] attention, much of which has been directed toward their hydrodynamic and rheological properties. Of particular interest are their

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Table I
Molecular Characteristics of Linear and Star Polymer Materials

sample	$\bar{M}_n$(arm) × 10^{-3} [a]	$\bar{M}_n$(star) × 10^{-3} [a]	$\bar{M}_w$(star) × 10^{-3} [b]	$\bar{M}_z/\bar{M}_w$ [c]	$\bar{M}_w/\bar{M}_n$	f [d]	ref
			Polyisoprenes				
BNH-7 [e]	(5.05) [f]	10.1	11.0	1.05	1.09	(2)	33
3-IAA	8.0	23.3	24.3	1.08	1.04	2.9	this work
3-IIIAA	5.4	16.4	16.9	1.07	1.03	3.0	this work
8-VIIAA	14.0	104	110	1.01	1.06	7.4	4
8-VIIIA	5.1	39.0	41.0	1.08	1.05	7.6	4
18-VIIIAA	5.1	92.0	93.0	1.03	1.01	18.0	30
			Polystyrenes				
3PS-IA	11.6	34.3	35.1	1.05	1.02	3.0	this work
PS6-12AA	14.0	158	164	1.04	1.04	11.3	35

[a] Membrane osmometry. [b] Light scattering. [c] Via Chromatix KMX-6: Waters 150C GPC. [d] Degree of branching; $f = \bar{M}_n(\text{star})/\bar{M}_n(\text{arm})$. [e] Linear polyisoprene. [f] Calculated molecular weight.

viscosities in dilute solution,[2] in the melt,[13] and in solution with linear high polymers.[11] These measurements address themselves to the validity of the tube and reptation[14,15] models of polymer molecular motion. Thus the most useful star molecular weights (M) tend to be at or above M_c, the value at which entangled networks develop. Whereas the mobility of solvents and diluents is largely governed by free volume availability[16,17] and collision dynamics, in polymer molecules topological considerations tend to dominate the hydrodynamic behavior.[7,8,18-20]

Self-diffusion of several linear polymers in dilute[21-23] and concentrated solutions,[18,22-24] in the melt,[21,24-26] and in solution with other linear polymers[18,19,24] has been measured. The results are interpreted as consistent[22,23,27] with the reptation concept. The pulsed-gradient spin-echo method[28] of measuring self-diffusion is particularly convenient for studies of concentrated solutions. Since the method is very sensitive to polydispersity,[21,24] the most useful information is obtained from samples with the smallest molecular weight distributions. Nuclear magnetic resonance, mainly in the form of spin–spin and spin–lattice relaxation times, T_2 and T_1, respectively, has long been used in the study of polymer molecular motion[29,30] and can complement the information obtained from self-diffusion measurements.[25]

The purpose of this work is to study the molecular mobility of star-branched polymers of the smallest possible dispersity and low M across the full concentration ranges in solution in good solvents in order to observe the emergence of star-specific impediments to molecular motion. The three types of measurement performed were self-diffusion of the polymer, T_2 relaxation times of the polymer, and self-diffusion of the solvent. Particular effort was expended on studying the effect of the number of branches (arms) per star molecule at constant molecular weight per arm. To our knowledge, this is the first spin-echo self-diffusion study involving star-branched polymers. A preliminary account of this work has been given.[31]

Experimental Section

Samples. The preparation and characterization of most of the isoprene polymers used in this study have been described[4,32,33] in connection with earlier work. To complement the existing series, several new specimens were prepared and characterized in an identical manner. Since self-diffusion depends sensitively on molecular weight and size, its dependence on the arm number f of a star polymer is best displayed at constant M(span) = $2M$(arm); M(star) = fM(arm). Linear polymers are most appropriately fitted into this context by being regarded as two-armed stars, $f = 2$.

The anionic polymerization methods[4,32,34] resulted in near-monodisperse arms [$\bar{M}_w(\text{arm})/\bar{M}_n(\text{arm}) < 1.1$ in all cases]. After the linking reaction with chlorosilane was complete, fractionation was used to remove the remaining linear material. The resulting material thus also had low total dispersity: $\bar{M}_w(\text{star})/\bar{M}_n(\text{star}) < 1.1$. Table I summarizes the characteristics of the polyisoprenes. A molecular weight of about 10^4 is approximately the maximum for which bulk self-diffusion by the spin-echo methods can be reliably measured in linear polyisoprenes and for which entanglement effects are not yet evident. Also included in Table I are two polystyrene star specimens used for comparative purposes. Their preparation followed procedures described elsewhere.[4,32,35]

The characterization of the samples used in this work was done with a combination of gel permeation chromatography, membrane osmometry, and light scattering.[4,5,35] These results were supplemented by the use of the Chromatix KMX-6 low-angle laser light scattering instrument coupled with a Waters 150C GPC. The 150C GPC was equipped with a six-column μ-Styragel set having a porosity range of 10^6–10^2 Å. Tetrahydrofuran was the carrier solvent while a flow rate of 1 mL min^{-1} was used. The polyisoprene microstructure was examined by ^{1}H NMR. The cis, trans, and 3,4 contents of the BNH-7, 3-IAA, 3-IIIAA, and 18-VIIIAA samples were essentially identical with those found[4] for the two 8-armed polyisoprene stars.

Solvents used in the NMR and diffusion studies were CCl_4 (Matheson Coleman and Bell, 99.5% pure, less than 0.01% H_2O) and C_6F_5Cl (Aldrich, 95% pure). In neither liquid could any trace ^{1}H NMR be detected. C_6F_5Cl was used instead of C_6F_6 in spite of its less convenient NMR spectrum, because the solubility of the star polyisoprenes in C_6F_6 is limited to approximately 50 wt %. Above this concentration, phase separation was found to occur.

All polymer materials were kept under vacuum at temperatures between 50 and 80 °C until the NMR samples were prepared. These were sealed under N_2 within minutes of addition of the polymer and solvent. Postanalysis GPC evaluations showed that none of the samples had undergone any detectable chain branching or degradation.

NMR T_2. Proton spin–spin relaxation times in polymers were measured at 50 °C at 33 MHz as a function of solvent concentration. To eliminate the effects of self-diffusion on the T_2 measurements, the Meiboom–Gill variant[36] of the Carr–Purcell pulse sequence[37] was employed with various pulse spacings. In dilute solutions a single-exponential decay was found, whereas at high polymer concentration and melts for $f > 3$ two decay rates were present.

Self-Diffusion. The pulsed-gradient spin-echo method[28] of measuring diffusion was used. Our equipment and methods have been described in detail.[38-40] The time τ between the 90° and 180° radio-frequency pulses, and hence the effective diffusion time in a pulsed-gradient experiment, was 5–100 ms (typically 25 ms). The ^{1}H and ^{19}F spin echoes, mutually exclusive to polymer and C_6F_5Cl, were attenuated to determine the respective diffusion coefficients.

In order to characterize the expected multiple diffusion coefficients, the spin echoes were attenuated to less than $^1/_{10}$ their initial height at all concentrations and to about $^1/_{20}$ in solutions containing less than 25% polymer. In all cases the diffusion coefficients were independent of diffusion time, although the relative magnitude of the component exponentials did vary with diffusion time. A variation would be expected if, for example,

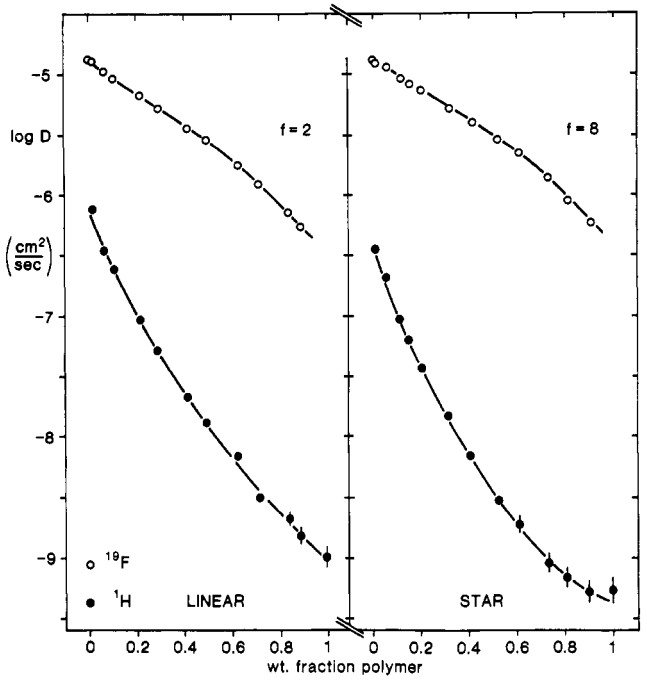

Figure 1. Self-diffusion at 50 °C of linear polyisoprene (left) and 8-armed star polyisoprene (right) of equal span molecular weights $\bar{M}_n$(span) $\simeq 1.0 \times 10^4$ dissolved in C_6F_5Cl. Solvent diffusion measurements are also shown.

the D components were to arise from distinct molecular species with different NMR T_2 relaxation times or from regions of a macromolecule with widely differing segmental mobilities in concentrated solution. In all cases exhibiting multiple diffusion coefficients, the slowest D component was unambiguously defined.

The fluorine diffusion was characterized by a single rate, while the proton diffusion, in linear as well as star-branched specimens at any solvent concentration, consisted of a narrow distribution of components ($1.2 \leq D_{max}/D_{min} \leq 2$). The origin of this distribution is not fully understood. However, since it occurs at all concentrations, i.e., over a wide range of diffusion rates and hence, diffusion distances, it is probably not an artifact of the experimental method or our techniques. The effect, though, may be related to the small polydispersities of the polymers. Our computer simulations of this effect confirm this interpretation.

The desired diffusivity is D_{min}. Our data reduction program[40] was modified to derive both D_{max} and D_{min}, the latter from the echo height data at the highest attenuations. At CCl_4 or C_6F_5Cl concentrations below 60 wt %, including pure star specimens, the very small spin echo at $\tau = 50$ ms had a component with a comparatively rapid $D \simeq 10^{-8}$ cm²/s. This diffusivity did not depend on concentration, but the relative magnitude of this component was largest in the melt. Above 40% polymer in solution, D_{max} is dominated by this contribution. This component was too small to be noticed during the T_2 measurements since its magnitude represents on the order of 0.2% of the ^{1}H NMR. We conclude that it arises from trace remnants of proton-containing chemicals used during polymer preparation, polymer fractionation, and/or residual amounts of antioxidant.

Because of the extreme sensitivity of spin-echo experiments to trace impurities, including trace oligomers, great care is necessary not only in preparing the specimens but also in preventing or eliminating contamination. While polyisoprenes are difficult to clean of solvents, polystyrenes[22,23] prepared by anionic methods tend to retain oligomers and volatile components[41-43] and, even after purification, absorb atmospheric water vapor.[43]

Results and Discussion

Linear and Star Polyisoprenes in C_6F_5Cl. Self-diffusion was measured at 50 °C for linear and 8-armed star polyisoprenes dissolved in C_6F_5Cl; solvent diffusion was also measured. The results are shown in Figure 1. The polymer specimens used (see Table I) were the linear BNH-7 (left graph in Figure 1) and 8-VIIIA (right graph in Figure 1); these have nearly the same span molecular weight. Several observations are in order.

First, the self-diffusion in solutions of polymers of identical M(arm) but different f decreases only slightly with increasing f. While the concentration dependences of the polymer as plotted in Figure 1 are similar, replotting as function of polymer molar concentration destroys this similarity.

Second, self-diffusion of the solvent under these conditions is, within experimental error, independent of f, again provided the abscissa represents weight (or volume) fraction. Solvent mobility is essentially unaffected by sparse branching while in rubbery polymers solvent diffusion decreases only slightly even at large cross-link densities.[44] The concentration dependence of solvent diffusion is consistent with the free volume theory, e.g., in the form proposed by Fujita.[16] This theory implies that the diffusion of a molecule in an amorphous melt is mainly determined by the availability of holes of a size sufficient to permit a thermally activated jump of that molecule, or one of its segments, from its present position. This hole free volume undergoes random redistribution, increases with increasing temperature, and is shared between solvent and solute in a solution. Thus the temperature and especially the concentration dependence of the diffusion constant of the solute (and solvent) molecules may be interpreted in terms of the free volume parameters of the constituent species. The free volume fraction, γ_s, of C_6F_5Cl is deduced to be 0.26 ± 0.01, given that for the linear polymer, $\gamma_p = 0.066 \pm 0.003$, determined earlier.[26] Because of the limited concentration range over which the Fujita–Doolittle equation[16] is valid, only data between 70 and 100% by weight of polymer were used to obtain this result. The identical result for γ_p in the 8-armed star simply attests to the fact that branching does not greatly affect free volume.[44]

Third, the concentration dependences of solvent and polymer diffusion are quite dissimilar for the linear as well as the star-branched polymer. These solutions are hydrodynamically nonideal in the sense that they do not obey the relation[45]

$$\log D_1(w,T) = \log D_2(w,T) + K_{12}(T) \qquad (1)$$

where K will depend on the properties of the two molecular species 1 and 2, as well as on temperature, but not on concentration, w. Moreover, for these data K does not even change linearly with w, so that these systems do not obey the most general free volume concentration dependence, derived by Vrentas and Duda,[17] which is capable of describing simple nonideality. On the basis of that theory, one would also expect[46] that the slopes $d \log D/dw$ of solvent and polymer at the same w would differ by a factor ξ that is independent of concentration and does not greatly exceed unity. Neither of these expectations is fulfilled; however, the worst disagreement ($\xi \cong 4$) occurs at dilute polymer concentrations, where free volume considerations are overshadowed by hydrodynamic effects. However, the inconsistencies in the nondilute regime ($w \gtrsim 0.2$) remain. They may arise in part from a failure of the free volume theory to describe the motion of long-chain molecules and/or from the failure of the spin-echo experiment to provide a definition of self-diffusion consistent with the customary theoretical framework. These possibilities will be considered below in more detail.

An upward concavity in log D(polymer) vs. concentration has been observed by other workers,[24] particularly at high polymer molecular weight. (This curvature persists if polymer concentration is expressed in terms of polymer weight fraction, as in Figure 1.) One possible explanation

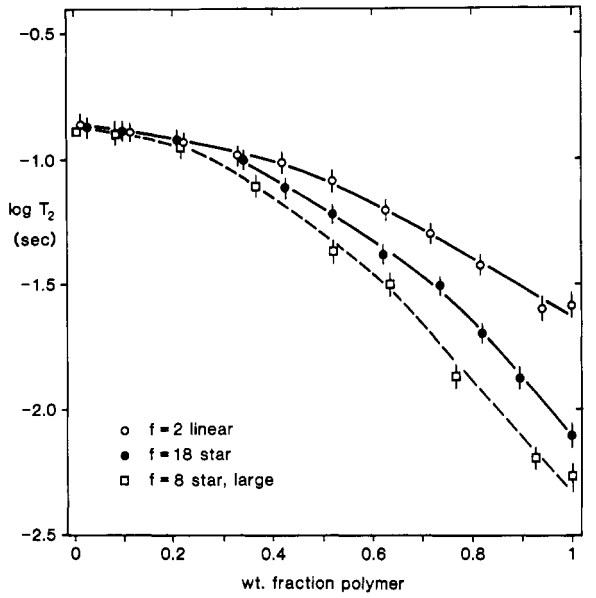

Figure 2. Spin–spin relaxation times T_2 at 50 °C of linear and star polyisoprenes dissolved in CCl_4. Linear polymer and 18-armed star have nearly identical $\bar{M}_n$(span) $\simeq 1.0 \times 10^4$ whereas the 8-armed star has $\bar{M}_n$(span) $= 2.8 \times 10^4$. For $f \geq 3$ and $w > 0.3$, data points represent T_2(short).

involves the well-known exaggerated sensitivity of any spin-echo experiment to even small fractions of the sample contributing a long T_2 component to the spin–spin relaxation rate spectrum.[21,22] In fact (see Experimental Section), diffusion of a trace reagent was observed at high polymer concentrations but could be easily separated from the diffusion of the polymer. The very narrow arm molecular weight distribution obtained from anionic polymerization, together with the repeated fractionation to separate low molecular weight components from the star polymers, eliminates the possibility that the upward concavities in Figure 1 are caused by polymer molecular weight irregularities. The presence of one single T_2 component (see below) in all our polymer solutions at low concentrations supports this conclusion.

The polymer diffusivities of Figure 1 may be replotted as a function of log c (mass of polymer per volume of solution). No obvious scaling region is apparent although a line with a power law slope of −1.75, suggestive of adherence to de Gennes' scaling law[47] for macroscopic self-diffusion,[22,23] meets the graph at $c \approx 200$ kg/m^3, which is near the concentration at which simple scaling ceases to be applicable. Similar results were obtained in CCl_4 solutions for all our polymers (see below). This indicates that the semidilute region is limited for these low molecular weight polyisoprenes.

Linear and Star Polymers in CCl_4. The spin–spin relaxation times T_2 of several polymers were measured at 50 °C over the full concentration range in CCl_4 solution. In all cases, a single relaxation rate was observed at w(polymer) ≤ 0.3. A second component began to emerge in more concentrated solutions and in the melts for $f > 3$ but became pronounced only for $f = 18$, M(arm) $= 5.1 \times 10^3$, and particularly $f = 8$, M(arm) $= 1.4 \times 10^4$. Even there, T_2(long) never exceeded twice the value of T_2(short), the relative intensities of the components being approximately equal. These observations pertain to 50 °C; the data [T_2(short)] are shown in Figure 2.

In the dilute regime T_2 is within experimental error independent of f for M(arm) $= 5.1 \times 10^3$ and decreases only by some 7% as M(arm) is raised to 1.4×10^4. Because the distances over which spin–spin relaxation mechanisms are effective are small, the semidilute T_2 behavior extends to polymer weight fractions as high as $w \simeq 0.2$, although the increasing proton concentration already enhances the dipolar relaxation rate. The Carr–Purcell technique minimizes the effects of diffusion on T_2 on the local, segmental scale.[36,37] The common value of T_2 at dilute concentrations shows that the details of segmental motion are largely independent of f or M(arm). Thus any differences in diffusion constant as measured by spin-echo methods at dilute polymer concentrations (cf. Figure 1) must be entirely due to motions on a scale much larger than the size of a polymer segment. In fact, with a measured diffusion constant of $D \simeq 10^{-7}$ cm^2/s or greater, the mean displacement produced over the experimental diffusion time of 25 ms is at least 7000 Å, far in excess of the radii of gyration of any polymers investigated here. It is only in concentrated solutions and in the melt, where $D < 10^{-9}$ cm^2/s, that the diffusion distance becomes small enough to approach the coiled dimension of a macromolecule of $M \gtrsim 10^4$.

In the concentrated region and in the polymer melt, T_2 [e.g., T_2(short)] depends on arm molecular weight as well as on f. The dependence of T_2 on log M for some linear polymers in concentrated solutions has two approximately linear segments;[25] the higher negative slope occurs below M_c, the critical molecular weight above which entanglements set in. The value of M_c for our stars is not known, but the approach to an entanglement network may be deduced from the onset of a two-component T_2 decay.[30] If M_c is sensitive to total molecular weight M(star), then evidence for dynamic network formation should be observed in melts of all our stars but not in the linear polymer. If, however, entanglements mainly form at sufficiently large M(span) $> M_c$, then only sample 8-VIIAA [M(span) $= 2.8 \times 10^4$] should be entangled.

The molecular weight dependence of T_2 in our star melts is consistent with

$$T_2(\text{short}) = \alpha - \beta \log [fM(\text{arm})] \qquad (2)$$

with $\alpha \approx 0.1$ s and β 0.02 s. Our limited range of M(arm) makes impossible a clear separation of the effects of M(arm) and f, although the f dependence appears to be slightly less pronounced. One might expect the M(arm) dependence to be somewhat stronger: near M_c, the segmental mobility decreases as fM(arm) is increased, but increasing M(arm) by itself also decreases the fractional free volume contributed by chain ends.

The gradual appearance of a two-component T_2 decay at high w(polymer), f, and M(arm) suggests the emergence of an entangled network. Since this occurs before M(span) exceeds the M_c value typical for linear high *cis*-polyisoprenes, entanglement in the stars apparently depends on M(star) rather than M(span). According to the previous paragraph our data do not permit a decision whether arm length or arm number is more effective in promoting entanglements. However, the difference in mobility between the entangled and unentangled regions is quite small, since at 50 °C T_2(long) differs by no more than a factor of 2 from T_2(short). There is some evidence that the fraction of protons in the more mobile regions decreases as M(arm) increases at constant f; for $f = 8$ this fraction decreases from 0.56 to 0.25 as M(arm) is raised from 5.1×10^3 to 1.4×10^4. Thus it appears that the approach to an entanglement network is more tentative in our star melts than in linear polyisoprene.[30]

Figure 3 shows the concentration dependence of self-diffusion of the polyisoprenes in CCl_4 solution for several f at M(arm) $= 5.1 \times 10^3$ and for $f = 8$ at M(arm) $= 1.4 \times 10^4$. Comparison with Figure 1 shows detailed agreement

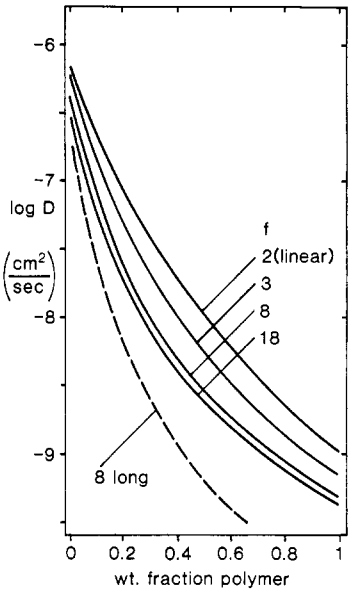

Figure 3. Concentration dependences of self-diffusion at 50 °C of linear and several star polyisoprenes in CCl_4. Data resemble those of Figure 1 but were omitted to avoid clutter. Data include polymers with $\bar{M}_n$(span) $\simeq 1.0 \times 10^4$ (solid lines) and $\bar{M}_n$(span) $= 2.8 \times 10^4$ (dashed line).

with the represented polymers in C_6F_5Cl solution. The diffusion at all concentrations w depends strongly on M(arm) but much more weakly on f, particularly at large f; a common dependence $D = D[fM(\text{arm})]$ is not consistent with the data. D never becomes independent of w, at least for the short-armed stars; the larger 8-armed star diffused too slowly to be measurable with our equipment above $w \approx 0.7$.

Of particular interest is the diffusivity in dilute solutions. Dilute solution behavior in stars requires that there be no significant overlap of arms of different stars. Calculation of the overlap concentration[12] gives values of w(overlap) $\simeq 0.02$. Hence an extrapolation to $w = 0$ from data over $0.01 \leq w \leq 0.08$ is not unreasonable. These extrapolated values are shown in Figure 4 (top) as function of f on a log–log plot.

Application of Flory's dilute solution theory[48] to self-diffusion[24] yields for good solvents

$$D(\text{trace}) \propto M^{-0.6}[M/\langle S^2\rangle_z]^{0.5} \tag{3}$$

The term in the square brackets is independent of M for a homologous series of samples of varying M. Equation 3 adequately accounts for the observed dependence of D(trace) on M for linear polymers[24] and for the M dependence of trace star diffusion at constant f ($f = 3$, $f = 8$ in Figure 4, top). In stars of varying f, one may identify $M = fM(\text{arm}) = fM(\text{span})/2$, and $\langle S^2\rangle_z = G\langle S^2\rangle_{z,L,M(\text{span})}$, where[2a] $G = g(f/2)$. The factors G and g are the ratios of the mean-square radii of gyration $\langle S^2\rangle$ of the f-armed to linear (L) polymers of the same span molecular weight and total molecular weight, respectively. Thus it is tempting to rewrite eq 3 as follows:

$$D(\text{trace},f) = A[fM(\text{arm})]^{-0.6}g(f)^{-0.5}\left[\frac{M(\text{span})}{\langle S^2\rangle_{z,L,M(\text{span})}}\right]^{0.5} \tag{4}$$

with the term in the square brackets independent of f and M(span) and with $g(f)$ having the form[8,49]

$$g(f) = (3f - 2)/f^2 + C \tag{5}$$

However, the derivation of eq 4 implies that the diffusion of stars is simply inversely proportional to their root-mean-square radii of gyration. This is not the case either according to random walk theory[50] or by inference from intrinsic viscosity experiments.[51] Therefore, eq 4 is at most a semiquantitative guide to the f dependence of D(trace) at constant M(span). Equation 4 does apply at $f = 2$ with $C = 0$; hence $g(2) = 1$. Figure 4 shows that for $f > 2$, eq 4 with $C = 0$ in eq 5 increasingly underestimates the f dependence of D(trace), just as eq 3 (i.e., eq 4 with $g(f) = 1$ for all f) overestimates it. Part of the disagreement of eq 4 with the data may arise from the fact[4,50] that stars with many short arms tend to be relatively more expanded than those with fewer arms. Figure 4 also includes two extrapolations for polystyrene stars ($f = 3$, 12) of somewhat higher M(arm), because they fortuitously share the f dependence of the polyisoprene stars.

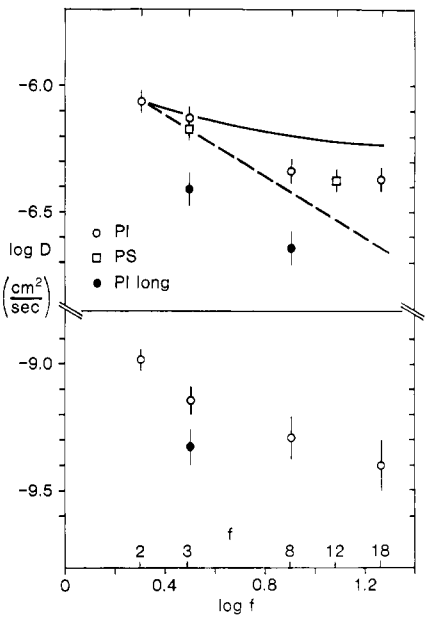

Figure 4. Diffusion of trace polyisoprenes and polystyrenes in CCl_4 (top) and self-diffusion in the melt (bottom). Symbols are extrapolations of D vs. w to $w = 0$ for data represented in Figure 3 and for two polystyrenes (3PS-1A and PS6-12 in Table I). Theory in upper graph is eq 4, with $C = 0$ in eq 5 (top) and with $g = 1$ (bottom) normalized to the measurement at $f = 2$.

At increasing polymer concentrations w (weight fraction), the diffusivity decreases from the trace limit at a rate that increases with f and with M(arm). This initial rate of decrease is shown in Figure 5 for the polyisoprene and polystyrene stars. For dilute solutions it has been shown that

$$D_i^{-1} = D_0'^{-1}(1 + k_f c + \ldots) \tag{6}$$

The least-squares extrapolations to infinite dilution shown in Figure 4 were made from plots of log D vs. w. The slopes obtained may be transformed to represent k_f in eq 6. The polyisoprene data of Figure 5 (six points) can be very well represented by a joint dependence on f and M(arm):

$$\left[\frac{\mathrm{d}\log D}{\mathrm{d}w}\right]_0 = a - b\log[fM(\text{arm})] \tag{7}$$

with $a = 10.0 \pm 0.8$ and $b = 3.84 \pm 0.10$. Equation 7 suggests that encounters among arms of different stars are the main source of polymer diffusivity decrease, although here, too, the effects of f and M(arm) cannot be separated. Adding arms increases intermolecular friction to the same extent as does lengthening the existing arms by the same total weight. These observations are not expected on the basis of a consideration of only the radii of gyration.

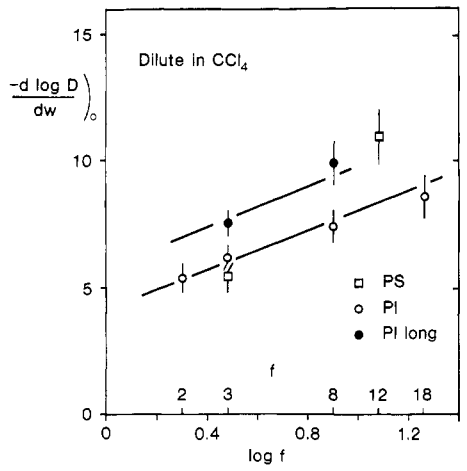

Figure 5. Rate of decrease of log D with w in the dilute limit for data in the polyisoprenes and polystyrenes of Table I in solution below $w \leq 0.08$. The intercepts of these extrapolations are shown in Figure 4 (top). Lines represent a common fit of eq 7 to polyisoprene data at both M(arm).

Equation 7 also contains a contribution from the decrease of free volume with increasing polymer concentration; this combination becomes nonnegligible below $M \approx 10^4$–10^5. We suspect that the reason for the disagreement below $M = 10^4$ between values of k_f deduced from experiment via eq 6 and theory (see ref 23) is the neglect of the free volume contribution. The leading term of the free volume concentration dependence may be derived from the Fujita–Doolittle equation.[16] While the latter cannot be directly applied in the dilute polymer regime because hydrodynamic effects dominate there, its parameters may be deduced from the concentrated solution data and continued into the dilute regime to effect a free volume correction to the hydrodynamics. Expanding the Fujita–Doolittle equation[16] about $c = 0$ yields

$$D_0' \approx D_0 \exp(\beta c) \approx D_0(1 + \beta c) \tag{8}$$

where

$$\beta = (\gamma_p - \gamma_s)/\gamma_s^2 \rho_p$$

The γ represent fractional free volumes, ρ_p being polymer density. The subscripts refer to polymer (p) and solvent (s), with c having dimensions of polymer mass per solution volume. Substituting into eq 7 yields to first order

$$D^{-1} \approx D_0^{-1}[1 + (k_f - \beta)c] \tag{9}$$

The (negative) quantity β may be estimated by equating it to the rate of decrease of solvent diffusion with concentration[17] (see Figure 1). In our case the correction for β deducts ~1.5 units from the ordinates of Figure 5. This correction is independent of f for constant M(arm) since adding arms does not change the fractional free volume of the polymer. In fact, this parameter only increases significantly for polyisoprene molecules[33] (other than rings) below $M \approx 10^4$. Above $M \approx 10^5$, the contribution to k_f directly proportional to M dominates the c dependence of eq 9, obviating the need for a free volume correction. Application of eq 9 to eq 7 over the domain of the data shows that k_f doubles from $k_f = 2.4 \times 10^{-3}$ to 4.8×10^{-3} m^3 kg^{-1} as fM(arm) is raised from 10^4 to 10^5. At the lower M, the correction from eq 8 amounts to a downward revision of k_f by some 30%. A detailed comparison of these results with theory over our limited molecular weight range would not be useful.

In concentrated solutions, polymer self-diffusion becomes less sensitive to w and to f, particularly at high M(star). The diffusion constants in the melts, where measurable, are shown in Figure 4 (bottom). For a diffusion constant $D \approx 5 \times 10^{-10}$ cm^2/s with a diffusion time of 50 ms, the distance traveled by the observed protons is some 700 Å. While this is in excess of the radii of gyration of our samples, various estimates for which[9,12,52,53] range between 60 and 200 Å, it is roughly commensurate with the stretched dimensions of the stars. Thus we cannot eliminate the possibility that our measurements at high concentrations or in the melt reflect motions of the outer segments ($r^2 > \langle r^2 \rangle$) of the arms about the stars' center of mass, in addition to the desired center-of-mass motion. This "arm waving" must be tightly coupled to the center-of-mass motion of neighboring stars, so that the two effects should be comparable and result in cooperative motion of the gel or melt. This explanation is consistent with the behavior of linear polymers of $M < M_c$, in which the M dependence of D can still be attributed entirely[26] to the center-of-mass motion. It is also consistent with the observation (Experimental Section) of a range of T_2 decays T_2(long)/T_2(short) ≤ 2 (since local mobility should depend on proximity to branch points and entanglements). Segmental diffusion mechanisms have been postulated[22,23,25] to explain D in linear polymers with $M > M_c$ and have been interpreted[54] as consistent with reptational backbone motion in polymers. Since branching severely suppresses reptation[11] only for $M > M_c$, this concept may apply to melts of short-armed stars as well, although the efficiency[11] of the reptation or tube renewal mechanism will be less than in linear polymers.

It has been suggested[22,55] that for certain types of polymer segmental motion the diffusion distance should not be proportional to the square root of the diffusion time τ, as is the case for long-range center-of-mass motion. In that case the measured diffusion constant would itself depend on τ and, naively interpreted, would give a distorted view of molecular mobility. These motions are expected to predominate in the absence of significant center-of-mass motion. In contrast to the situation in gels of high molecular weight polymers,[22] diffusion in our star melts is near the limit of the capability of the pulsed-gradient method. At these low values of D the spin-echo method, usually capable of direct measurements[22,28] of D as a function of τ, is confined to a very narrow range[24] of τ, virtually eliminating the possibility of quantifying this effect. Thus the possibility of a distortion of our results in concentrated solutions by time-dependent D components cannot be discounted.

Summary and Conclusions

This work has demonstrated that the molecular mobility in star-branched polyisoprenes of small molecular weight in solution depends strongly on weight fraction of polymer and more weakly on f and M(arm). An entanglement network forms as a function of weight fraction and M(star), but less efficiently than for linear polymers of equal molecular weight.

Self-diffusion in the dilute limit has a dependence on f intermediate between the Zimm–Stockmayer result and that expected on the basis of a radius of gyration of linear polymers of the same total molecular weight. The departure from the Zimm–Stockmayer expansion factor is several times larger here than for polyisoprene stars of higher molecular weight. The rate of decrease of the diffusion constant with concentration displays a common dependence on f and M(arm). The number of arms available to contact other stars is as important as their length in inhibiting center-of-mass motion.

At high polymer concentrations and in the melt, T_2 for both components of the narrow spectrum decreases

strongly with increasing polymer weight fraction and more weakly with increasing M(arm) or f—a common dependence on fM(arm) cannot be excluded on the basis of our data. Here, the diffusion coefficient begins to approach the value where motions other than center-of-mass diffusion may be included in the measured result. Such motions must be segmental in nature and must arise from cooperative motions of the concentrated gel or melt. These motions might include cooperative rotation or oscillation among neighboring stars, displacements that would generally result in non-Fickian contributions to D. It should be noted that a measured diffusion coefficient of $D \simeq 10^{-10}$ cm^2/s, a not unreasonable lower limit that might be approached (see Figure 3) at higher f or M(arm) or at lower temperatures, would correspond to segmental travel over distances comparable to the radius of gyration. Sample polydispersity or impurities are excluded as possible causes of the upward concavity of D vs. w for quantitative reasons and because of the observed single T_2 decay in dilute solutions.

Free volume based theories for the concentration dependence of polymer diffusion fail not merely at high concentrations, where the center-of-mass motion becomes comparable with segmental motions, but even just beyond the semidilute regime, where the topology of encounters among molecules overwhelms free volume considerations. Of course, the decrease of free volume is responsible for 20–30% of the decrease of D with increasing w, as may be seen by comparison with solvent diffusivity. As expected, solvent diffusion is essentially unaffected by the infrequent branches and entanglements in star-branched polymers.

The approach to a lower limit in D at increasing concentrations of a linear polymer in solution is compatible with reptation,[54] as is an M dependence of D in the melt[24] of the form $D \propto M^{-5/3}$ for M below as well as above M_c. Our limited data in concentrated solutions of stars are consistent with this exponent at constant f, although the f dependence at constant M(arm) is much weaker.

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Supplementary Material Available: Tabulations of the numerical data presented in Figures 1–5 (8 pages). Ordering information is given on any current masthead page.

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