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Self-Diffusion of Linear and 4- and 18-Armed Star Polyisoprenes in Tetrachloromethane Solution

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ABSTRACT: We have measured the diffusion of polyisoprene molecules, linear as well as 4- and 18-armed star branched, at 50 °C in dilute and semidilute CCl_4 solution over 4 orders of magnitude in molecular weight, using pulsed-gradient spin-echo NMR techniques. Flory's theory of dilute solutions (good solvent) and the Pyun–Fixman model account for the molecular weight and concentration dependences of the diffusivities for each architecture. Dilute diffusivity of the stars is significantly faster than that of linear molecules of equal molecular weight; the resulting hydrodynamic ratios h are independent of molecular weight and in good agreement with the Stockmayer–Fixman calculation. Certain predictions of scaling theory are confirmed.

I. Introduction

Regular star-branched polymer molecules permit convenient study of the influence of molecular architecture on molecular size and hydrodynamics, particularly in dilute solutions.[2] Given star molecules with f equal arms (linear molecules are described as $f = 2$), their ratio of translational friction coefficient F to that of linear molecules of equal molecular weight M in an identical solvent is defined as a hydrodynamic ratio[3]

$$h = F_0(f,M)/F_0(f = 2,M) \tag{1}$$

The subscript 0 denotes infinite dilution. The Einstein relation $F = kT/D$ permits h to be inferred from translational diffusion coefficients D:

$$h(f,M) = D_0(f = 2,M,T)/D_0(f,M,T) \tag{2}$$

Application of the Kirkwood–Riseman theory[4] to random-flight chain molecules of star architecture yielded,[3] for Θ solvents,

$$h(f) = f^{0.5}[2 - f + 2^{0.5}(f - 1)]^{-1} \tag{3}$$

Experimental results for h tend to exceed this value at Θ conditions, but results for good solvents are typically somewhat lower.[5] Another ratio[3] may be derived from measurements of intrinsic viscosity $[\eta]$:

$$g' = [\eta](f,M,T)/[\eta](f = 2,M,T) \tag{4}$$

For regular stars, a semiempirical result, also for Θ conditions, is[6,7]

$$g' = g^m, \qquad 0.5 \leq m \leq 0.6 \tag{5}$$

where[8]

$$g = (3f - 2)/f^2$$

Because of the greater ease of making precise intrinsic viscosity measurements and the greater sensitivity of g' to f, determination of h from diffusion measurements has until recently been comparatively neglected. Given the emergence of several techniques of precise self-diffusion measurement[9-12] as well as excellent control and characterization of molecular architecture,[2] the study of the ratio h (theoretically exactly calculable) is now becoming increasingly attractive.

An understanding of g' and h in regular stars with large f is of considerable current interest. Recent work[7] (intrinsic viscosity and sedimentation rate) has shown clear evidence that the deviations of g' and h from eq 5 and 3 increase with increasing f and decreasing M, pointing to a perturbation of Gaussian chain statistics by interference among arms, in qualitative agreement with current theoretical concepts.[13] The present work was undertaken principally to add an alternate experimental viewpoint to this subject.

We have used the pulsed-gradient spin-echo (PGSE) method[12] of measuring self-diffusion (proton NMR) of polyisoprenes (f = 2, 4, and 18) in a proton-free good solvent (CCl_4)[14,15] to determine $h(f)$ and its dependence on molecular weight. In two previous investigations[15,16] we had found that $h(f)$ could probably be distinguished from unity for large f (polyisoprenes) but not[16] for $f = 3$ (polybutadienes and polystyrenes). In the process, the M dependence of D_0 had been shown[16,17] to obey the Flory theory[18,19] of dilute solutions

$$D_0 = AM^s, \qquad -0.6 \leq s \leq -0.5 \tag{6}$$

while the concentration (c) dependence of D was in accord

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Table I
Molecular Characteristics of Linear Polyisoprenes

sample	$\bar{M}_n \times 10^{-3}$, dalton	$\bar{M}_z/\bar{M}_w$[a] ± 0.02	$\bar{M}_w/\bar{M}_n$[a] ± 0.02
PI-895	0.90	1.08	1.11
NH-1	1.67	1.07	1.08
NH-3	2.61	1.04	1.06
PI-3000	2.87	1.05	1.07
4A-5000	5.01	1.03	1.05
NH-2	6.44	1.04	1.05
8A-7500	7.56	1.02	1.02
6A-10000	10.0	1.03	1.04
NH-7	10.1	1.05	1.05
4A-15000	14.5	1.04	1.03
4A-30000	30.2	1.06	1.04
PI-3	41.7	1.03	1.03
PI-2	70.8	1.04	1.03
PI-1	251.2	1.02	1.05
PI-L-14	302.0	1.03	1.07

[a] Via size exclusion chromatography.

Table II
Molecular Characteristics of 4-Armed Polyisoprene Stars

sample	$\bar{M}_n \times 10^{-3}$, dalton	$\bar{M}_w \times 10^{-3}$, dalton	f[a]
PI-4A5	20.0	21.1	4.0
PI-SPI-4AA	35.2	37.8	3.9
PI-4A15	60.3	61.2	4.2
PI-SPI-7AA	66.9	67.1	4.2
PI-4A30	120.0	122.0	4.0

[a] $f = \bar{M}_n(\text{star})/\bar{M}_n(\text{arm})$.

with a dilute hydrodynamic behavior of the form appropriate[14] for self-diffusion:

$$D^{-1}(c) = D_0^{-1}(1 + k_F c + ...) \qquad (7)$$

Here[16] k_F obeyed the Pyun–Fixman theory[20,21] in its molecular-weight dependence:

$$k_F = PM^{-1}D_0^{-3} = BM^a \qquad (8)$$

so that the exponent a should be equal to

$$a = -1 - 3s \qquad (8a)$$

(see eq 6) and thus directly comparable[9,21] with the Mark–Houwink[22] molecular-weight exponent a_η of the corresponding intrinsic viscosities, establishing a proportionality between k_F and $[\eta]$ and thus an experimental connection between dilute and infinitely dilute solution behavior. The present work will confirm these findings; somewhat surprisingly, the ratio of diffusion rates for f = 2 and f = 18 will be seen to be essentially constant (at the value h) well into the semidilute concentration range. Again,[15,16] no multiple or non-Fickian diffusion components were observed, confirming our earlier impression (in contrast with other work[14]) that linear polymers display rather orthodox solution hydrodynamics as measured by PGSE methods and that star-branched molecules share this simple behavior. A preliminary report of this work has been given.[23]

II. Experimental Part

The preparation and characterization of the linear, 4-armed and 18-armed star-branched polyisoprenes followed the methods described elsewhere.[24-26] The anionic polymerization methods were able to produce linear molecules of very low dispersity ($\bar{M}_w/\bar{M}_n$ < 1.06 in most cases); these were examined directly (f = 2) or else linked, using chlorosilanes to produce star-branched molecules, thereby achieving even lower dispersity than that of the constituent arms. The star material was fractionated to remove incompletely linked molecules and unreacted arms. The molecular characteristics of the polymers used in this study are summarized in Tables I–III.

Table III
Molecular Characteristics of 18-Armed Polyisoprene Stars

sample	$\bar{M}_n \times 10^{-3}$, dalton	$\bar{M}_w \times 10^{-3}$, dalton	f
18-VIIA	61.0	61.7	17.9[a]
18-VIIIAA	92.0	93.0	18.0[a]
18-VIAA	193.0	197.0	18.0[a]
18-IIAA	216.0	218.0	18.0[a]
18-IAAA	340	344	18.1[a]
18-IIIAAA	*b*	800	17.4[c]
18-IXAAAA	*b*	6300	17.6[c]

[a] $f = \bar{M}_n(\text{star})/\bar{M}_n(\text{arm})$. [b] $\bar{M}_n$ too high for reliable determination. Our analysis assumes $\bar{M}_n = \bar{M}_w/1.05$. [c] $f = \bar{M}_w(\text{star})/\bar{M}_n(\text{arm})$.

To avoid observing the diffusion of trace impurities, no antioxidants or other additives were used. Polymer characterization was performed by using size exclusion chromatography (SEC), membrane osmometry, and light scattering. Instruments used were a Hewlett-Packard membrane osmometer, a Chromatix KMX-6 low-angle photometer, and a Waters 150C chromatograph with a six-column μ-Styragel set (porosities ranging from 10^2 to 10^6 Å; carrier solvent THF). High-resolution NMR was used to verify the microstructure of the polyisoprenes, with the expected results[27] for cis, trans, and 3,4 content.

CCl_4 (Matheson Coleman and Bell; less than 0.02% water) was the solvent for the PGSE diffusion measurements, conducted at 50 °C. No limits of polymer solubility were encountered. No trace proton NMR was detectable in the solvent; since polymer concentrations as low as 0.1 wt % were used, it was necessary to eliminate several sources of contamination by proton-containing mobile impurities.[15,16] This precaution included the polymer melts, which were kept initially sealed and refrigerated, later in vacuo at 40–60 °C for several weeks prior to preparation and sealing of the NMR samples.[15,16] Post-PGSE SEC spot checks failed to reveal any polymer degradation or unwanted branching. Because of the low viscosities of solutions below 0.5 wt % polymer, measures had to be taken there to suppress convection. A small positive vertical temperature gradient was created,[16] and decontaminated glass wool (<0.5 vol %) was inserted into the solutions before sealing.

Our methods of PGSE diffusion measurements are comprehensively described elsewhere.[15,16,28-30] Briefly, the experiment involves measurement of the amplitude A of the spin echo as function of a field gradient parameter X:

$$X = \delta^2 G^2(\tau - \delta/3) - \delta G G_0[(t_1{}^2 + t_2{}^2) + \delta(t_1 + t_2) + 2\delta^2/3 - 2\tau^2] \qquad (9)$$

which involves τ, the time between 90° and 180° radio-frequency pulses, the duration δ and magnitude G of each of a pair of magnetic field gradient pulses applied after a delay t_1 following the respective radio-frequency pulse, with $t_2 = \tau - t_1 - \delta$. A steady small magnetic field gradient G_0 was applied at all times.

A monodisperse diffusing species gives rise to a single-exponential echo attenuation[12]

$$A(X)/A(0) = \exp(-\gamma^2 DX) \qquad (10)$$

where γ is the magnetogyric ratio of the nucleus at resonance. Polydispersity results in a distribution of diffusivities, observable as an upward concavity in a plot of log A vs. X. This effect was modeled[31] given approximate knowledge of the molecular weight distribution function, permitting the extraction from the data of D at any point on the distribution. Since $D(\bar{M}_n)$ is most representative of PGSE data,[16,31] it is the quantity reported here. Accordingly, $\bar{M}_n$ is the abscissa parameter in all M dependences to be displayed.

Our PGSE experiments were usually conducted at fixed G_0 (0.01 T m^{-1}), G (1-3 T m^{-1}), and τ (5–300 ms; typically 25 or 50 ms), with δ varied to obtain reductions of echo height by a factor of at least 3, preferably 10. Figure 1 shows the echo attenuation for the largest 18-armed star at 0.5 wt %. After sample contamination and convection effects were eliminated and dispersity was accounted for, no multiple diffusion rates were ever observed. Several additional PGSE experiments checking D vs. τ in our

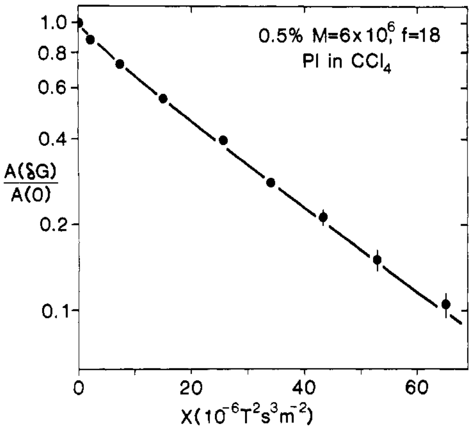

Figure 1. Spin-echo attenuation for 0.5% $f = 18$ polyisoprene star of $M = 6 \times 10^6$ (sample 18-IXAAAA) in CCl_4. Except where indicated, uncertainties are less than the size of the symbols. Line (slightly curved) is polydispersity model (ref 31) fitted to data.

largest linear and 18-armed star polymers failed to detect any time dependence of D.

III. Results and Discussion

The spin-echo attenuations for all our specimens had the general appearance of Figure 1, giving evidence of their slight polydispersity (accounted for by our data reduction model[31]). This nearly single-component, Fickian behavior persisted at all polymer concentrations examined ($c \lesssim 60$ kg m^{-3}).

Concentration dependences of D for the four largest polymers are shown in Figure 2. The diffusion of the biggest $f = 18$ star ($M = 6 \times 10^6$) is shown between 0.1 wt % and the maximum concentration ($\cong$3.6 wt %) permitting precise diffusion measurements. It should be noted that even in this specimen no asymptotic approach to a lower limit in D is observed. This fact indirectly attests to the near-monodispersity of the polymers;[17,34] it also demonstrates that segmental motions are probably not reflected in the measured D, the latter describing pure center-of-mass translation.[12,15,16,30]

Figure 3 shows the reciprocal diffusivity as a function of concentration for six of the seven 18-armed stars. D_0 and k_F were determined from such plots via eq 7 by applying standard statistical procedures (Gauss criterion[16,35]) to delimit the initial linear region and finding its slope and intercept by least-squares techniques.[16]

The scaling concept implies that a plot of D/D_0 vs. c/c^* should give a common curve for all samples of a given architecture. The overlap concentration c^* is inversely proportional to $[\eta]$, but because intrinsic viscosities in CCl_4 were not available, k_F or $M^{-1}D_0^{-3}$ had to be substituted as proportional (see eq 8); of these, the latter offers higher precision. As shown in Figure 4, scaling behavior is clearly observed, separate for $f = 2$ and $f = 18$, except for some scatter about each curve due to imprecision in the extrapolations of D_0, to which this plot is very sensitive. Examination of the slopes of Figure 4 shows that most of the measurements in the larger molecules fall well into the semidilute regime.[10,14,33] Our data are, however, not in agreement with the "naive"[33] semidilute concentration scaling model calling for a slope of −1.75 in Figures 2 and 4; a finite scaling region of constant slope is again[10,16] not observed.

The $f = 2$ and $f = 18$ data in Figure 4 may be brought into congruence by a horizontal displacement by a factor of about 2.5 (see also Figure 2). Thus, while the magnitude of the friction coefficient $F(c)$ is affected by the architecture-dependent coiled dimension of the molecules, its rate of increase with concentration, −d(log D)/d(log c), is dominated by the monomeric friction constant and the degree of polymerization[9,15,32] and is essentially independent of architecture, at least below the onset of entanglements as in the present case.

Table IV
Diffusion Results for Linear Polyisoprenes in CCl_4

sample	log (D_o, m^2 s^{-1})	log (k_F, m^3 kg^{-1})
PI-895	−9.36 ± 0.015	−2.40 ± 0.02
NH-1	−9.51 ± 0.015	−2.26 ± 0.02
NH-3	−9.65 ± 0.015	−2.25 ± 0.02
PI-3000	−9.73 ± 0.015	−2.18 ± 0.02
4A-5000	−9.78 ± 0.015	−2.02 ± 0.02
NH-2	−9.80 ± 0.015	−1.93 ± 0.03
8A-7500	−9.86 ± 0.015	−1.96 ± 0.03
6A-10000	−9.89 ± 0.015	−1.88 ± 0.03
NH-7	−9.95 ± 0.015	−1.89 ± 0.03
4A-15000	−10.1 ± 0.02	−1.77 ± 0.03
4A-30000	−10.23 ± 0.02	−1.42 ± 0.04
PI-3	−10.34 ± 0.025	−1.42 ± 0.05
PI-2	−10.40 ± 0.03	−1.20 ± 0.04
PI-1	−10.80 ± 0.03	−0.56 ± 0.05
PI-L-14	−10.82 ± 0.04	−0.67 ± 0.06

Table V
Diffusion Results for 4-Armed Star Polyisoprenes in CCl_4

sample	log (D_o, m^2 s^{-1})	log (k_F, m^3 kg^{-1})
PI-4A5	−10.04 ± 0.025	−1.60 ± 0.02
PI-SPI-4AA	−10.11 ± 0.03	−1.33 ± 0.03
PI-4A15	−10.27 ± 0.03	−1.27 ± 0.03
PI-SPI-7AA	−10.30 ± 0.03	−1.18 ± 0.03
PI-4A30	−10.40 ± 0.03	−0.92 ± 0.03

Table VI
Diffusion Results for 18-Armed Star Polyisoprenes in CCl_4

sample	log (D_o, m^2 s^{-1})	log (k_F, m^3 kg^{-1})
18-VIIA	−10.14 ± 0.03	−1.61 ± 0.03
18-VIIIAA	−10.23 ± 0.03	−1.47 ± 0.03
18-VIAA	−10.43 ± 0.03	−1.12 ± 0.03
18-IIAA	−10.53 ± 0.03	−1.28 ± 0.04
18-IAAA	−10.56 ± 0.04	−0.94 ± 0.05
18-IIIAA	−10.80 ± 0.05	−0.70 ± 0.05
18-IXAAAA	−11.32 ± 0.08	+0.17 ± 0.08

Table VII
Molecular-Weight Dependences of Dilute Diffusion of Polyisoprenes in CCl_4

architecture	D_o,[a] m^2 s^{-1}		k_F,[b] m^3 kg^{-1}	
	log A	s	log B	a
$f = 2, M <$ 5000	−7.73 ± 0.08	−0.54 ± 0.04	−4.08 ± 0.08	0.54 ± 0.03
$f = 2, M >$ 5000	−7.47 ± 0.05	−0.61 ± 0.01	−5.04 ± 0.04	0.80 ± 0.15
$f = 4$	−7.53 ± 0.15	−0.57 ± 0.03		
$f = 18$	−7.22 ± 0.12	−0.61 ± 0.03	−5.54 ± 0.06	0.82 ± 0.03

[a] $D_o = AM^s$ (eq 6). [b] $k_F = BM^a$ (eq 8).

The molecular-weight dependences of D_0 and k_F are given in Tables IV–VI. The results for D_0 are shown in Figure 5. For $f = 4$ and $f = 18$ the plots are consistent with straight lines, but for the linear isoprenes the slope changes in the vicinity of $M = 5000$. Standard least-squares methods were used to divide the $f = 2$ data into two linear segments; the optimal crossover was the fifth data point, sample 4A-5000. Table VII gives the results of the least-squares fits in terms of the parameters of eq 6.

Systematic decreases in the Mark–Houwink[22] exponents a_η are known to occur[36] in linear polymers below $M \cong 3 \times 10^4$. Because s and a_η are related, corresponding changes would be expected in s, modified by spatial crossover ef-

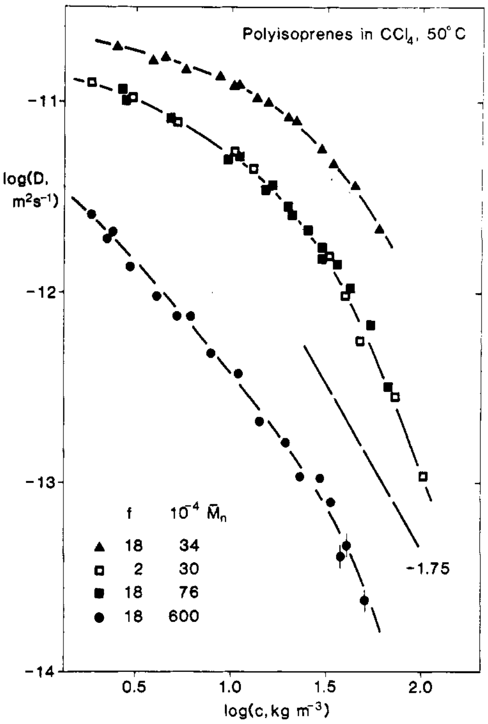

Figure 2. Concentration dependence of diffusion of the four largest polyisoprenes. Most uncertainties are somewhat smaller than the symbols. Samples are 18-IAAA, PI-L-14, 18-IIIAAA, and 18-IXAAAA. Lines are hand drawn; dashed line has slope −1.75.

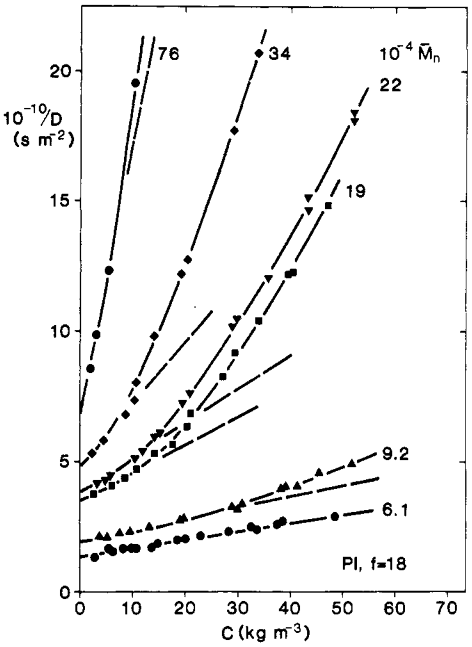

Figure 3. Concentration dependence of reciprocal diffusivity of 18-armed stars (all samples in Tables III and VI except 18-IX-AAAA). Solid lines are hand drawn; dashed straight lines are fits (see text) to the initial linear regions.

fects.[37] Also, changes in s ought to be reflected in exponent a of eq 8. Results of the least-squares fits for exponents and intercepts of the k_F data are included in Table VII and shown together with the data in Figure 6. Equation 8a postulated by the Pyun–Fixman model is, indeed, satisfied in each case within the combined experimental error; for the linear polymers it holds separately below and above $M = 5000$.

Because the high-M values for s are consistent with −0.60 (corresponding to $a = 0.80$), Flory's theory[18] suggests that

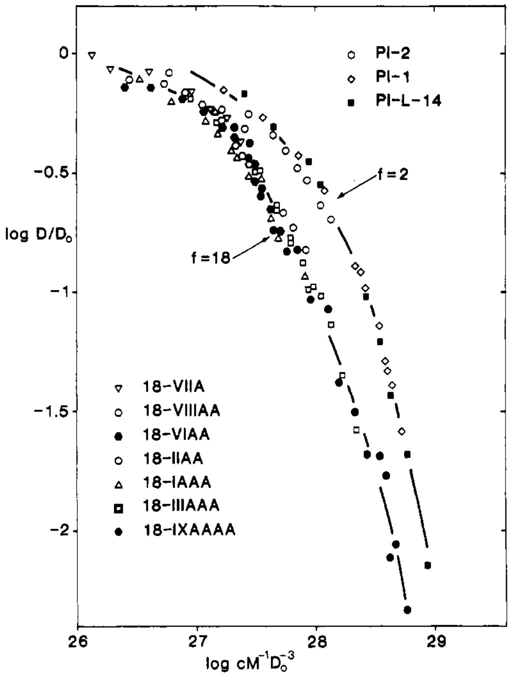

Figure 4. Scaling behavior for linear and 18-armed polyisoprenes. Data include all 18-armed stars (Tables III and VI) but, to avoid clutter, only the three largest linear specimens (Tables I and IV). Error bars are omitted. Abscissa is analogous to log c/c^*; units are kg m^{-3} for c, dalton for M, and m^2 s^{-1} for D and D_0. Using ck_F as abscissa results in a very similar plot but with more scatter.

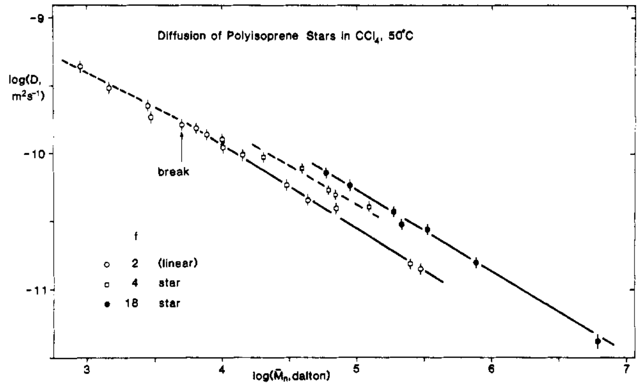

Figure 5. Molecular-weight dependence of trace diffusion. Straight lines (or segments) are fits (see text) to data, listed in Tables I–III ($\bar{M}_n$) and Tables IV–VI ($D_0(\bar{M}_n)$).

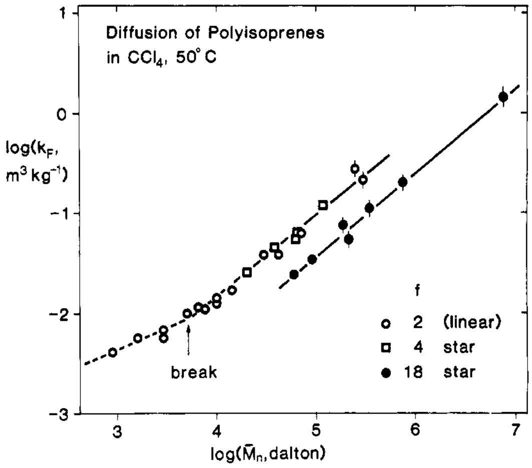

Figure 6. Molecular-weight dependence of k_F. Straight lines are fits (see text) to data for linear and 4-armed polymers combined and 18-armed polymers. Data are listed in Tables I–III ($\bar{M}_n$) and Tables IV–VI (k_F).

Table VIII
Hydrodynamic Constants of Polyisoprene Stars

f	h(exptl)[a]	h(theor)[b]	g'(exptl)	g'(theor)[g]
4	0.71 ± 0.1	0.892	0.72[c] 0.76[d]	0.754
18	0.52 ± 0.04	0.528	0.22[e] 0.31[f]	0.334

[a] Via eq 2 (good solvent), present work. [b] Equation 3 (Θ conditions). [c] Via eq 4 (good solvent), ref 25. [d] Via eq 4 (Θ conditions), ref 25. [e] Via eq 4 (good solvent, toluene), ref 38. [f] Via eq 4 (Θ conditions), ref 38. [g] Equation 5 with $m = 0.6$.

CCl_4 at 50 °C is a good solvent for polyisoprene in our range of M and f.[15] The differences in vertical intercepts of Figure 6 lead to a determination of the hydrodynamic constant h via eq 2. Their values, shown in Table VIII, are derived for $M \cong 10^5$, but no M dependence is evident since differences among s for different f are not significant. For comparison, measurements and predictions of g' are also listed.

It is seen that the values of h, especially $h(f = 18)$, are in agreement with the Stockmayer–Fixman prediction, eq 3. Thus, the effects of departures from Gaussian chain statistics due to crowding of the inner segments are not evident at our high M, or else are offset by the departure from Θ conditions.[11]

The exact value of P in eq 8 is not theoretically predicted,[20,21] but ratios between expressions for different f are quantitatively meaningful. Thus

$$\frac{k_F(f,M)}{k_F(2,M)} = \frac{P(f)}{P(2)}\left[\frac{D_0(f,M)}{D_0(2,M)}\right]^{-3} \tag{11}$$

Substituting our results (Table VII or Figures 5 and 6) near $M = 10^5$ one obtains

$$P(4)/P(2) = 2.6 \pm 0.7; \quad P(18)/P(2) = 2.6 \pm 0.5 \tag{12}$$

with no significant M dependence. The increases of $P(f)$ over $P(2)$ imply that $P(f)$, which should strongly depend on the extent of mutual interpenetrability of the coiled polymer molecules,[21] undergoes significant changes (toward the hard-sphere, i.e., impenetrability, limit) for $f > 2$. This observation is in qualitative agreement with other work.[7,11]

It should again[16] be pointed out that other models for k_F, e.g., by Yamakawa,[39] offer no clarification or improvement: if their additional terms were large enough to affect the predicted magnitudes of k_F, this would result in M dependences of k_F less steep than observed. Finally, it seems empirically significant that increasing M by a factor of 2.8 ± 0.3 changes $D_0(2)$ into $D_0(18)$ (see Figure 5) and simultaneously changes $k_F(2)$ into $k_F(18)$, over a wide concentration range (see Figure 6 and also Figure 2). This factor approximates what might be expected on the basis of Gaussian subchain statistics given the f ratio of 9, but ignoring mass differences and architecture-induced changes in polymer–solvent and polymer–polymer hydrodynamic coupling. That the adherence to this simple picture is probably fortuitous is shown by the $f = 4$ case, where no common factor connects the D_0 and the k_F.

IV. Concluding Remarks

To our knowledge, this investigation reports the first PGSE measurement of a hydrodynamic ratio h different from unity. Because of the high degree of branching, the measured D values reflect pure center-of-mass motion even at the highest molecular weights and concentrations. No multiple or non-Fickian diffusion components were observed after trace contaminants and convection problems were eliminated and the effect of the small polymer dispersity was accounted for. Flory's dilute solution theory and the Pyun–Fixman model adequately describe the dilute solution behavior of both linear and star molecules. Comparison between linear and star trace diffusion rates suggests that most of the difference is accounted for by the smaller coiled dimension of the stars at a given molecular weight. The lower limits of M in our stars appear to be too high to permit the observation of departures from Gaussian subchain statistics, although in the linear specimens deviations from high-M behavior became apparent below $M \cong 5000$. The behavior of the 4-armed stars is in several respects intermediate between that of the linear and the 18-armed polymers. While trace diffusion is significantly faster than that of linear molecules of equal M (and even marginally faster than predicted by theory), the concentration dependence of $k_F(4)$ is identical with that of $k_F(2)$. Consequently our results, interpreted in terms of the Pyun–Fixman model, suggest that a significant decrease in polymer–polymer molecular interpenetration occurs as a result of star branching, but that this change is essentially completed by $f = 4$.

The influence of polymer architecture on dilute diffusion is being explored further in a study of poly(n-alkyl methacrylates) of variable main-chain and side-chain length,[40] where the stiffening effect on the main chain due to increasing side chain length is directly observable.

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Registry No. Polyisoprene (homopolymer), 9003-31-0.

References and Notes

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Wholly Aromatic Polyamide Hydrazides. 2. Rheological Properties of Poly(4-(terephthaloylamino)benzoic acid hydrazide) in Moderately Concentrated *N*,*N*-Dimethylacetamide Solutions

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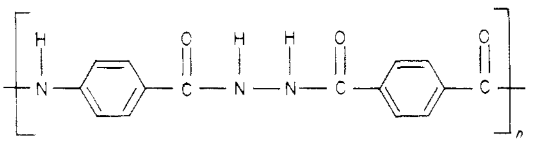
ABSTRACT: The steady state shear rheological properties of a semiflexible polyamide hydrazide, poly(4-(terephthaloylamino)benzoic acid hydrazide) (PTIPH), in moderately concentrated, 7% (w/v), *N*,*N*-dimethylacetamide (DMA) solutions were studied as a function of polymer molecular weight ($\bar{M}_w$), which ranged from 2×10^3 to 2.1×10^4, using the cone-and-plate geometry. The results obtained showed that within the investigated shear rate range, $1.8 \times 10^1 < \dot{\gamma} < 1.8 \times 10^3$ (s^{-1}), first indication of the non-Newtonian flow behavior could be observed for $\bar{M}_w \simeq 9 \times 10^3$ at $\dot{\gamma} > 1 \times 10^3$ s^{-1}. Comparison of the experimental results with the Graessley master curve (for $\bar{M}_w/\bar{M}_n = 2$) showed very good agreement with theory, but the ratio of the experimental and Rouse relaxation time (τ_0/τ_R) was found to be independent of the polymer molecular weight, probably because insufficiently high molecular weights were involved. No resemblance to the so-called "B. effect" earlier observed for the solutions of the same polymer in dimethyl sulfoxide (Me_2SO) could be observed. A plot of the zero-shear viscosity (η_0) vs. the Bueche contact parameter ($c\bar{M}_w$) revealed typical "entangled behavior", focusing further attention upon determination of the PTIPH chain length parameters critical for the onset of such behavior. To accomplish this, four different methods reported earlier in the literature were used. With the exception of the critical number of chain atoms (Z_{wc}) calculated from the critical value of the dimensionless chain length parameter χ_{wc}, proposed earlier by Fox and Allen, all of these methods led to the results which agreed within less than 10% of the average Z_{wc} value which was accepted for a critical number of chain atoms: $Z_{wc} = 253$ (corresponding to a critical entanglement molecular weight ($\bar{M}_{wc}$) of about 7000). Above these critical values, zero-shear viscosity (η_0) was found to be proportional to a polymer chain length parameter raised to the power of 4.0.

Introduction

Solution properties of wholly aromatic polyamide hydrazides, and among those in particular poly(4-(terephthaloylamino)benzoic acid hydrazide), I (PTIPH),[1] have attracted considerable research attention in recent years. The main reason for this originated from the discovery that these semiflexible polymers[2] could be successfully used for production of ultrahigh-modulus fibers when spun from organic solvents such as dimethyl sulfoxide (Me_2SO) or *N*,*N*′-dimethylacetamide (DMA),[3-5] similar to the well-known behavior of a number of rigid-rod aromatic polyamides, for example poly(*p*-benzamide) (PBA)[6-9] and poly(*p*-phenyleneterephthalamide) (PPTA).[10]



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The molecular mechanism responsible for the development of high-modulus properties in polymer fibers has generally been associated with the ability of their macromolecules to achieve unusually high degrees of chain orientation, i.e., high degrees of long-range molecular order, during the spinning process.[11] Such chain orientation is greatly facilitated by processing polymer solutions which, even in unperturbed, or quiescent, state form a nematic mesophase, or in other words, which are liquid crystalline. In such cases spinning and stretching operations induce further orientation of the liquid crystals uniaxially aligning

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