Self-Diffusion and Viscoelastic Measurements of Polystyrene Star Polymers

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ABSTRACT: A series of hydrogenous and deuterated four-arm polystyrene stars with low polydispersity have been synthesized by anionic polymerization. Self-diffusion data have been obtained using helium-3 nuclear reaction analysis, and rheology has been employed to obtain the zero shear viscosity. Both diffusion and viscosity data have been compared to results predicted by recent theories in order to test the alternative models of diffusion cases, i.e., arm retraction followed by the core hopping either a diluted or an undiluted tube diameter. The exponential dependence on molecular weight can be conveniently removed by taking the product of the self-diffusion and the viscosity, making it possible to determine which model is more appropriate. Our data show good agreement with the undiluted tube model over a range $3.5 > N/N_e < 9$. At low molecular weight the data show the model failing at $N/N_e < 3$, in agreement with theoretical predictions.

1. Introduction

The dynamics of linear polymer molecules are now well described at least qualitatively by the tube model and the concept of reptation proposed by de Gennes[1] and Doi and Edwards.[2] The polymer molecule is considered to be confined to a hypothetical tube defined by the surrounding chains and moves via curvilinear diffusion within this tube. However, to obtain good quantitative agreement between the theoretical framework and experimental data, other factors have to be introduced,[3,4] namely contour length fluctuations, where the tube surrounding the chain ends are redefined by movement due to thermal fluctuations, and constraint release, where the surrounding polymer matrix allows transverse motion of the diffusing species.

In the case of nonlinear architecture (e.g., star polymers) reptation is prevented by the branching as there is no single tube along which motion can occur. It was proposed by de Gennes[5] that translational chain motion may occur via the retraction of all but two of the arms back to the junction point. This would enable the core to hop the distance of a tube diameter, a_0, in an arbitrary direction. Klein[6] derived expressions to describe such diffusion for star-shaped polymers within a lattice of fixed obstacles. Since the retraction of an arm is entropically unfavorable, for large degrees of polymerization it is an activated process with an exponential dependence on the degree of polymerization. Consequently the longest relaxation time is determined by the arm length. It was later shown[7] that the diffusion coefficient has a much weaker dependence on the functionality, f (number of arms), than expected, suggesting that the simultaneous retraction of all but two arms is not necessary for diffusion to occur. Ball and Mcleish[8] then introduced the concept of dynamic dilution. Exponential dependence of the arm retraction time on the degree of polymerization, N, results in a large range of relaxation time scales for different segments of the arm. The arm will retract short distances on fast time scales but will only occasionally retract to a larger extent back toward the junction point. These faster moving short distance relaxations mean that the slower retracting arms effectively see a more diluted entanglement network. Consequently, the effective tube diameter increases (i.e., $>a_0$), implying that once an arm has fully retracted the core of the star may hop a distance of the order of a diluted tube diameter, a_d, rather than the original undiluted diameter, a_0.

To date, there have been a number of studies performed to determine diffusion coefficients in a number of different star polymer species (3−12-arm polystyrene,[7,9−11] 3-arm polyethylene-like,[12,13] and 3-arm polyethylene-*alt*-proplyene[14] stars). These have been over a wide range of arm molecular weights from unentangled to highly entangled. However, most of these have been for tracer diffusion where a mobile star polymer diffuses into a high molecular weight (MW) or cross-linked matrix to remove the contribution from constraint release. Only one experiment has studied self-diffusion in symmetric 3-arm butadiene stars although the data were obtained by an indirect method[15] (small-angle neutron scattering), and the system is described as being "thermorheologically complex" (i.e., time−temperature superposition is not obeyed).

Our work has been partly motivated by recent developments in the theory of star polymer diffusion.[16,17] ^{3}He nuclear reaction analysis (NRA)[18] has been used to determine the diffusion of deuterated polystyrene in a hydrogenous polystyrene matrix. Rheology has also been employed to obtain dynamic moduli and viscosities. Polystyrene is considered a thermorheologically simple molecule in both linear and star forms; therefore, time−temperature superposition can be applied. The recent theoretical development is reviewed in the next section followed by details of the synthesis and experimental techniques employed in this study.

2. Theoretical Background

The self-diffusion constant due to arm retraction is given by the mean-square distance a junction point is able to hop within an arm retraction time τ_{arm}.

$$D = \frac{(pa)^2}{6\tau_{\mathrm{arm}}} \qquad (1)$$

where a is a tube diameter. Since the mean hopping distance

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Table 1. Molecular Weight Data for Hydrogenous Polystyrene Arms and Four-Arm Stars Obtained by Triple Detection SEC

	molecular weight data of arm			molecular weight data of star			
star	M_n/g mol^{-1}	M_w/g mol^{-1}	PDI	M_n/g mol^{-1}	M_w/g mol^{-1}	PDI	functionality of star, f^c
h14K[a]	13 200	13 700	1.04	50 800	52 800	1.04	3.9
h27K[a]	26 800	27 300	1.02	95 500	102 000	1.06	3.7
h60K[a]	57 100	59 200	1.04	219 000	234 000	1.07	4.0
h110K[a]	107 000	110 000	1.03	412 000	441 000	1.07	4.0
h137K[a]	133 000	138 000	1.03	512 000	541 000	1.06	3.9
h186K[a]	181 000	186 000	1.03	761 000	781 000	1.03	4.2
h193[b]	189 000	193 000	1.02	802 000	822 000	1.03	4.2
h293K[b]	279 000	293 000	1.05	1 120 000	1 150 000	1.02	3.9

[a] Star synthesized with core 1. [b] Star synthesized with core 2. [c] $f = M_w(\text{star})/M_w(\text{arm})$.

during time τ_{arm} could be a fraction of a full tube diameter, the junction point is assumed to hop a distance pa, where p is a dimensionless constant of order unity.

Milner and Mcleish[19] developed a theory for the relaxation time which successfully integrates dynamic dilution in order to describe the rheological behavior of star polymers. Following this, Frischknecht and Milner[20] derived expressions for the self-diffusion constant (D_0) and the zero shear viscosity (η_0).

In the case of the diffusion, to calculate D_0, both the tube diameter and the arm retraction time in the diluting network need to be known. The difference between dilute and undiluted tube models is significant with a_d scaling as $a_0N^{2/7}$.

In the situation where the core hops a diluted tube diameter, a_d (magnitude $> a_0$)

$$D_0 \sim \left(\frac{N}{N_e}\right)^{-3/2} \exp\left(-\frac{27N}{56N_e}\right) \tag{2}$$

whereas for a hop distance of an undiluted tube diameter (magnitude $\sim a_0$)

$$D_0 \sim \left(\frac{N}{N_e}\right)^{-29/14} \exp\left(-\frac{27N}{56N_e}\right) \tag{3}$$

The zero shear viscosity for both dilute and undiluted hopping models is given by

$$\eta_0 \sim \left(\frac{N}{N_e}\right) \exp\left(\frac{27N}{56N_e}\right) \tag{4}$$

where N and N_e are the degree of polymerization of the arm and its entanglement value, respectively.

The exponential dependence of both the diffusion coefficient and the viscosity makes it difficult to determine the scaling of the prefactor of the diffusion coefficient with MW. Hence, diffusion experiments alone are unable to verify whether the undiluted or diluted tube hopping model is most appropriate. A further problem is the dependence of both quantities on the monomeric friction coefficient. However, by taking the product of the diffusion coefficient and the viscosity, both the exponential terms and the monomeric friction coefficients are eliminated. This simple and elegant fact is the basis for the studies reported in this paper.

3. Experimental Section

I. Materials. Benzene (HPLC grade, Aldrich), styrene (Aldrich), and perdeuterated styrene (Cambridge Isotopes) were dried and degassed over CaH_2 (Aldrich); styrene and d_8-styrene were further purified with dibutylmagnesium immediately prior to use. *sec*-Butyllithium (1.4 M solution in cyclohexane), tetravinylsilane, chlorodimethylsilane, and chloroplatinic acid, all Aldrich, were used as received. 1,6-Bis(dichloromethylsilyl)hexane (Fluorochem) was also used as received.

Synthesis of Tetrafunctional Chlorosilane. A tetrafunctional chlorosilane coupling agent was prepared by the hydrosilylation of tetravinylsilane with chlorodimethylsilane using chloroplatinic acid as a catalyst according to the procedure of Hadjichristidis et al.[21]

Synthesis of Star-Branched Polystyrene. A series of four-arm polystyrene stars have been prepared with arm molecular weights from 13 000 to 300 000 g mol^{-1}. A series of analogous four-arm perdeuterated polystyrene stars have similarly been prepared with arm molecular weights from 14 000 to 160 000 g mol^{-1}. In each case the "arm first" approach has been used, and the arms have been synthesized by living anionic polymerization using standard high-vacuum techniques. A typical reaction was as follows. Benzene (250 mL) and styrene (34 g, 0.24 mol) were distilled, under vacuum, into a 500 mL reaction flask. To the monomer solution was injected *sec*-butyllithium (1.87 mL, 2.62×10^{-3} mol of a 1.4 M solution in cyclohexane) as the initiator for a target M_n of 13 000 g mol^{-1}. Upon addition of the initiator to the monomer solution, the orange/red color of living polystyryllithium was observed. The solution was stirred for 2 h at room temperature to allow complete propagation before a small aliquot of polymer solution was removed for molecular weight analysis. To the remaining living polymer solution was added 1,6-bis(dichloromethylsilyl)hexane (0.16 g, 5.24×10^{-4} mol). The reaction mixture was stirred at room temperature for 3 days to allow complete coupling of the arms to the core. The unreacted "excess" of polystyryllithium was terminated with nitrogen-sparged methanol and the polymer recovered by precipitation into methanol and collected by filtration. The polymer was dried in vacuo. The star-branched polymer was separated from the unreacted linear polystyrene by fractionation, using toluene as the solvent and methanol as the nonsolvent. The yield of purified star was 12.0 g (35%). Molecular weight of arm: M_n 13 200 g mol^{-1}, M_w 13 700 g mol^{-1}, PDI 1.04. Molecular weight of star: M_n 50 800 g mol^{-1}, M_w 52 800 g mol^{-1}, PDI 1.04. Functionality (f) of star (average number of arms) given as $M_w(\text{star})/M_w(\text{arm})$ $f = 3.9$.

Reaction times of both polymerization and coupling reactions vary according to molecular weight and are discussed later. In certain cases, for example where the molecular weight of arm is very high, a synthesized chlorosilane core was used. The reasons for this are discussed later.

Measurements. Molecular weight analysis was carried out by size exclusion chromatography (SEC) on a Viscotek TDA 302 with refractive index, viscosity, and light scattering detectors. A value of 0.185 (obtained from Viscotek) was used for the dn/dc of polystyrene. 2 × 300 mm PLgel 5 μm mixed C columns (with a linear range of molecular weight from 200 to 2 000 000 g mol^{-1}) were employed; THF was used as the eluent with a flow rate of 1.0 mL/min at a temperature of 30 °C. The extent of the coupling reactions and fractionations were monitored by SEC using a Viscotek 200 with a refractive index detector and 3 × 300 mL PLgel 5 μm 10^4 Å high-resolution columns (with an effective molecular weight range of 10 000−600 000 g mol^{-1}); THF was used as the eluent at a flow rate of 1.0 mL/min.

Results and Discussion. Synthesis. A series of four arm polystyrene stars have been synthesized by the arm first approach. Similarly, a series of analogous perdeuterated polystyrene stars have been prepared with arms of approximately the same dimensions

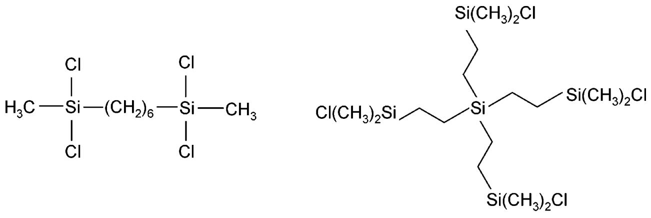
Table 2. Molecular Weight Data for Deuterated Polystyrene Arms and Four Arm Stars Obtained by Triple Detection SEC

	molecular weight data of arm			molecular weight data of star			
star	M_n/g mol^{-1}	M_w/g mol^{-1}	PDI	M_n/g mol^{-1}	M_w/g mol^{-1}	PDI	functionality of star, f^c
d14K^a	14 100	14 400	1.02	50 900	53 800	1.06	3.7
d28K^a	26 900	27 800	1.03	91 200	98 000	1.07	3.5
d71K^b	68 900	71 000	1.03	270 000	282 000	1.05	4.0
d97K^b	94 100	97 100	1.03	377 000	395 000	1.05	4.1
d160K^b	154 000	160 000	1.04	660 000	685 000	1.04	4.3

Table 3. Constituents of the Polymer Couples Used in Self-Diffusion Measurements along with the Annealing Temperature Ranges Used for Each Couple

couple code	dPS upper layer	hPS matrix	annealing temp [K]
14K	d14K	h14K	390, 400, 410, 420
27K	d28K	h27K	390, 400, 410, 420, 430
60K	d71K	h60K	420, 430, 440
110K	d97K	*h*110K	420, 430,440
140K	d160K	h140K	420, 430, 440

(see Tables 1 and 2). The “arms” have been synthesized by living anionic polymerization and as such are well-defined in terms of both molecular weight and polydispersity. The time required for the polymerization of the styrene varies with molecular weight. Arms with molecular weights up to 100 000 g mol^{-1} were polymerized for 2−3 h at room temperature, and for molecular weights greater than 100 000 g mol^{-1} the polymerizations were allowed to proceed overnight. The arms have then been coupled together to form a star using one of two tetrafunctional chlorosilane coupling agents, nominally designated core 1 and core 2 (see Figure 1 for structures).



Core 1 Core 2

Figure 1. Tetrafunctional chlorosilane coupling agents used for synthesis of polystyrene star branched polymers.

It was found that for the lowest molecular weight arms (stars h14K and h27K, Table 1) the coupling reaction was complete in 3−4 days. In these cases a modest excess of arm with respect to Si−Cl bonds (25 mol %) was sufficient to drive the coupling reaction to completion. However, as the molecular weight of the arm increases so does the time required for complete coupling. Arms with molecular weight 100 000 g mol^{-1} and larger required up to 4 weeks to reach completion, and this presented a problem. As the arm molecular weight increases, the concentration of “living” chain ends drops. This lower concentration of chain ends must be kept free from impurities for progressively longer to allow complete coupling. Eventually under the standard reaction conditions, all the living polymer was terminated before complete coupling occurred. To circumvent this problem, we increased the amount of polymer from 20 to 30 g to 70−90 g, thereby offering some “economy of scale”. The stoichiometry of the coupling reaction was also changed; increasing the molar excess of arms with respect to Si−Cl bonds from 25% to 50%. Both of these modifications extended the lifetime of the coupling reactions, and as a result the reaction to make star h186K (Table 1) still had living polymer present (as evidenced by the yellow/orange color of living polystyryllithium) after 30 days. However, the cost of deuterated styrene precluded the use of 70−90 g of monomer per reaction. To avoid the use of such large quantities of monomer, the use of a second coupling agent was investigated. The principal reason that the coupling reactions take such a long time is that as the number and MW of arms around the core increase, so does the steric hindrance. Mays et al.[22] found that during the synthesis of six-arm polystyrene stars using 1,2-bis-(trichlorosilyl)ethane the first four arms attached very rapidly, in less than an hour; however, it required 5 weeks to complete the coupling of all six arms. Furthermore, it should be noted that in their work the steric hindrance around the core is alleviated to a great extent by the capping of the living polystyrene chains with a few units of isoprene. In our work, no such capping was attempted. The structure of 1,6-bis(dichloromethylsilyl)hexane is such that two polymer chains must react with a single silicon atom, thereby creating steric hindrance; however, the structure of the second coupling agent (core 2, Figure 1) physically separates the location of each of the Si−Cl groups, thus alleviating much of the steric hindrance and allowing more rapid coupling of arms to core. Using core 2 to make star h293K, the coupling reaction was complete in less than 10 days. Therefore, core 2 was used to synthesize stars d71K, d97K, and d160K (Table 2) from deuterated polystyrene arms with molecular weights above 50 000 g mol^{-1}.

In all cases the functionality of the synthesized stars displayed a value close to four. The variation in most cases being less than 5%. The notable exception is star d28K, which has a functionality of 3.5 (Table 2), indicating the sample contains a lower MW component. Given the time the coupling reaction proceeded and the SEC results, this lower MW component is almost certainly predominantly 3-arm stars arising from incompletely coupling. However, both the diffusion and zero shear viscosity are highly dependent on arm MW and have a far smaller dependence on total star MW and functionality. In addition, rheology was only carried out on the more abundant hydrogenous stars.[7,23,24] Consequently, the 3-arm component should not have a significant effect on the data.

II. Diffusion and Viscoelastic Measurements. Sample Preparation for Ion Beam Analysis. A thick layer of the hydrogenous polystyrene stars was spin-coated from toluene solutions on to the polished surface of a silicon wafer of 3 in. diameter and (111) orientation. Layer thicknesses were determined by optical reflectometry and were varied depending on the temperature at which the samples were to be annealed. Typically thicknesses of the order of 1−2 μm were produced. After spin-coating the samples were relaxed overnight under vacuum at 413 K. A thinner (∼40−60 nm) film of the deuterated star polymer was spun on to a glass microscope slide again from toluene solution. This thin layer was floated off the microscope slide onto the surface of high-purity deionized water and carefully picked up onto the upper surface of the polystyrene layer on the silicon wafer. The polymer couples were then dried overnight under vacuum at 348 K, and each sample wafer was cut into a number of smaller pieces ready for annealing. A range of annealing temperatures were employed for different molecular weight couples (see Table 3). Samples were placed under vacuum and annealed at the required temperature for predefined times, after which one of the samples was removed and rapidly quenched to room temperature.

Sample Preparation for Rheology. A polymer disk of 25 mm diameter and 1 mm thickness was prepared. First, ∼0.55 g of hydrogenous polystyrene star was weighed and cold pressed into a compact pellet. This pellet was placed inside an aluminum foil lined, stainless steel mold and inserted into a heated press. The press and mold were heated to 445 K and maintained in a nitrogen atmosphere with high pressure applied. Pressure was maintained for 5−10 min at a time, released, and then reapplied in order to produce transparent disks free of voids and bubbles. Pressing times varied between 20 and 45 min, depending on the molecular weight of the sample. All samples were checked for possible indications of

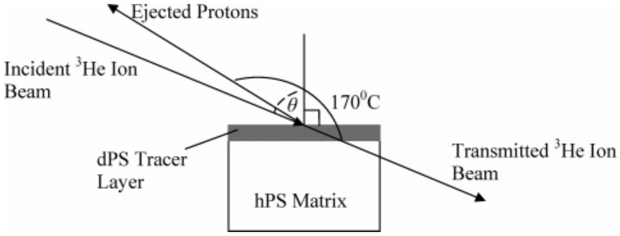


Figure 2. Detection geometry employed for NRA experiments.

polymer degradation such as discoloration. In addition, SEC analysis were ran on several of the samples to further ensure that processing had not altered the structure of the stars.

Ion Beam Analysis. Ion beam analysis was carried out using a 5SDH National Electrostatics Corp. pelletron accelerator. The annealed polymer samples from each molecular weight couple were mounted on to a movable sample stage located within the evacuated end station. A beam of $^3He^+$ ions, with typical energies and currents of 0.7−1 MeV and 10−30 nA, respectively, was directed onto the sample at an incident angle, θ, to the sample normal. These incident ions may undergo nuclear reactions with deuterium atoms within the sample, fusing to form a short-lived compound nucleus of ^{5}Li. This intermediate rapidly disintegrates to a proton and ^{4}He ion with the liberation of 18.35 MeV. Protons ejected in the backward direction are detected at 170° to the incident beam (Cornell geometry) (Figure 2).

The depth the beam penetrates into the sample and the depth resolution are determined by the beam energy and the incident angle. The closer to a grazing angle, the better the depth resolution but the smaller the beam penetration. Therefore, the incident angle employed for different samples, and annealing temperatures varied in order to allow the beam to penetrate a reasonable depth into the sample and to optimize the depth resolution. Typically, angles between 45° and 80° were employed, and the depth resolution was generally around 10% of the penetration depth.

The emitted particles were sorted according to their energies, and the data were presented as total yield as a function of channel number. The energy can then be related to the depth at which the reaction occurred, and the yield to the volume fraction of deuterated polymer at that depth using methods described in detail elsewhere.[11,18] Figure 3 shows the volume fraction distribution produced from the raw nuclear reaction analysis data using the procedure outlined above.

The profiles obtained for a series of finite annealing times, t, were interpreted with the solution to Fick's second law of diffusion:[25]

$$\phi(z) = \frac{1}{2}\left[\mathrm{erf}\left\{\frac{h-z}{w}\right\} + \mathrm{erf}\left\{\frac{h+z}{w}\right\}\right] \tag{5}$$

where h is the original thickness of the deuterated polystyrene layer and w the width of the broadened interface between the two polymers resulting from interdiffusion

$$w = (4Dt)^{1/2} \tag{6}$$

with D the diffusion coefficient. Equation 5 was convoluted with a Gaussian resolution function to account for the spatial resolution of the NRA and then fitted to the data using a nonlinear least-squares fit routine with w as an adjustable parameter.

Typical fits to the data are shown as the solid lines in Figure 3b. Values of $w^2/4$ extracted for the data for different annealing times when plotted as a function of time give linear plots (Figure 4), with the diffusion coefficient, D, given by the gradient.

Rheology. Dynamic moduli were measured using two rheometers. The initial low MW studies were performed on a Rheometric Scientific SR5; later work was carried out using an TA Instruments AR2000 with environmental test chamber (ETC). Both instruments were operated using parallel plate geometries with 25 mm diameter plates and a gap of around 1 mm. Storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli were obtained over a wide range of frequencies (typically $10^{-3} < \omega$ (s^{-1}) $< 10^2$) and over a temperature range of 403−463 K. All measurements were performed in an inert nitrogen atmosphere. Prior to experiments with a new sample, the gap was zeroed at an intermediate temperature (423 K) and corrections made for the expansion of the plates at other temperatures. Measurements at the intermediate temperature were repeated several times during the series of experiments and then finally after the highest temperature test in order to check for inconsistencies due to thermal degradation or sample loss from between the plates.

The zero shear viscosity can be extracted from the low-frequency moduli data using the relation[26]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{7}$$

4. Results and Discussion

Rheology. Example dynamic moduli for two of the hPS samples (h60K and h140K) can be seen in Figure 5a,b. As expected, the samples were all found to obey time−temperature

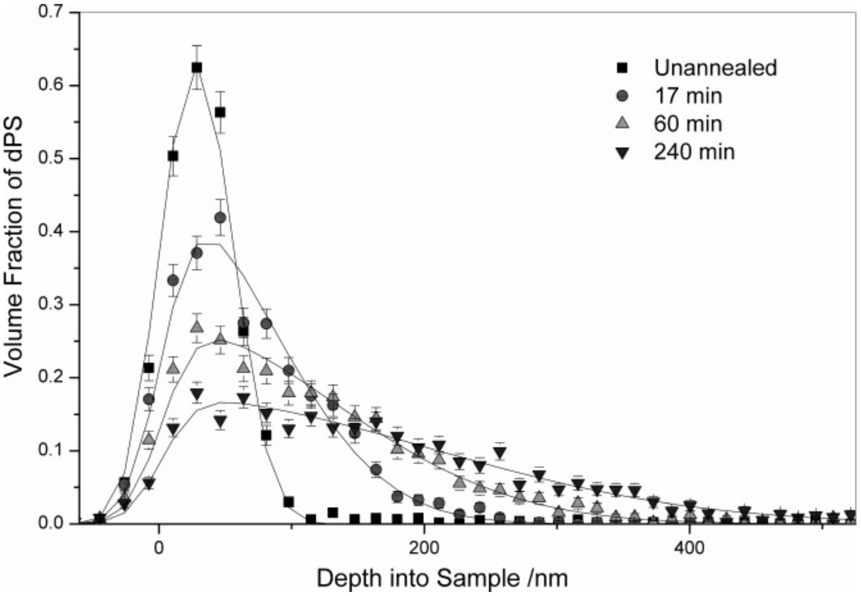


Figure 3. Typical NRA data for several annealing times. The volume fraction of dPS star as a function of depth is obtained from raw ion beam data as described in the text. The solid lines show typical fits to eq 5 convoluted with a Gaussian resolution function.

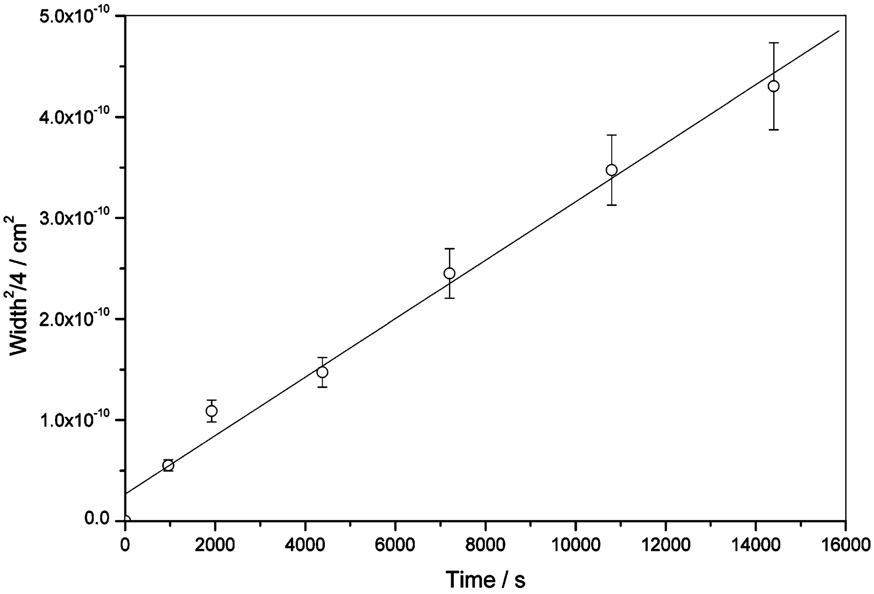


Figure 4. Typical plot of $w^2/4$ as a function of annealing time for dPS star diffusing into hPS star matrix. The diffusion coefficient is given by the slope of the line.

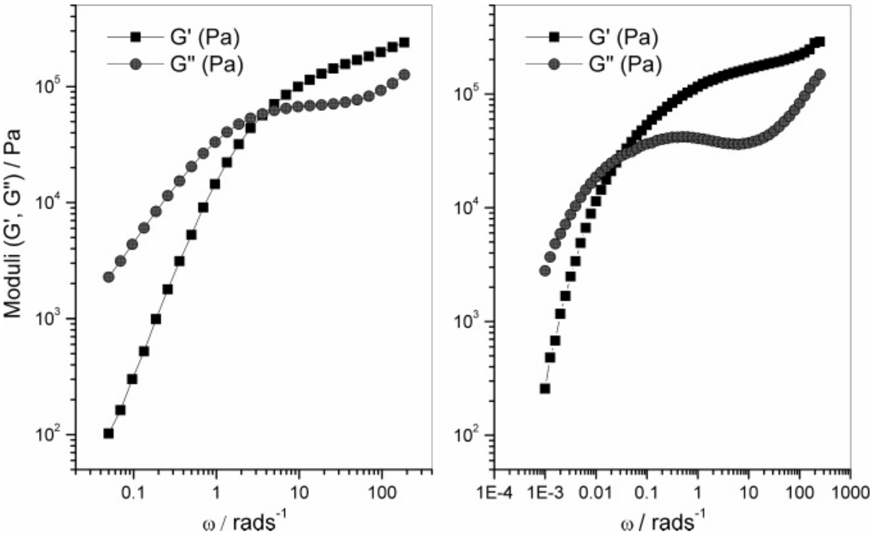


Figure 5. Example dynamic modulus curves for hPS star samples obtained at 433 K: (a) h60K sample; (b) h140K sample.

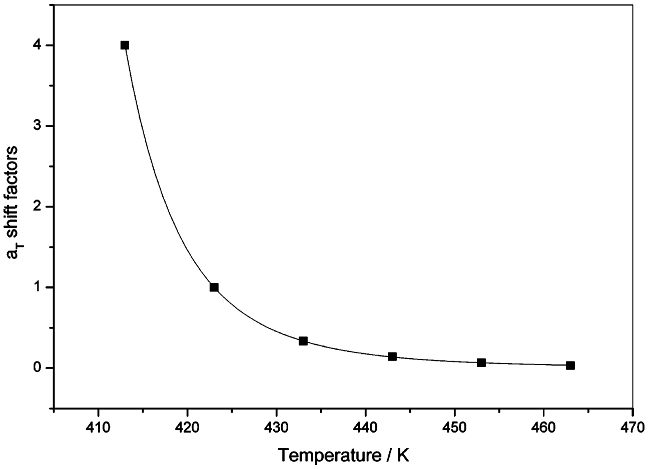


Figure 6. Shift values a_T as a function of temperature for viscosity measurements scaled using WLF to reference temperature of 423 K. The solid line shows a fit of eq 9 to the data.

superposition. Shifts in the modulus for the different temperatures were considered negligible.

Zero shear viscosities, η_0, were extracted from the low-frequency moduli obtained at different temperatures using eq 7 and plotted as a function of *N*. These plots were then scaled to a single reference temperature (423 K) using WLF form shift factors (a_T):[27]

$$\eta_0(T_{\text{ref}}) = \eta_0(T_{\text{actual}})a_T \tag{8}$$

These shift factors were plotted against temperature (Figure 6). The WLF expression

$$\log(a_T) = -C_0(T - T_{\text{ref}})/C_1 + (T - T_{\text{ref}}) \tag{9}$$

(where T and T_{Ref} are the measurement and reference temperatures) was fitted to the data, and the coefficients C_0 and C_1, determined to be 4.5 and 84.7, respectively. Figure 7 shows the averaged scaled viscosity data as a function of *N*. The plot shows reasonable agreement between data and the theory given by eq 4 (with the entanglement value $N_e \sim 150$). The notable exception is h14K, which exhibits a considerably lower viscosity than expected. However, for this sample $N/N_e < 1$, which means

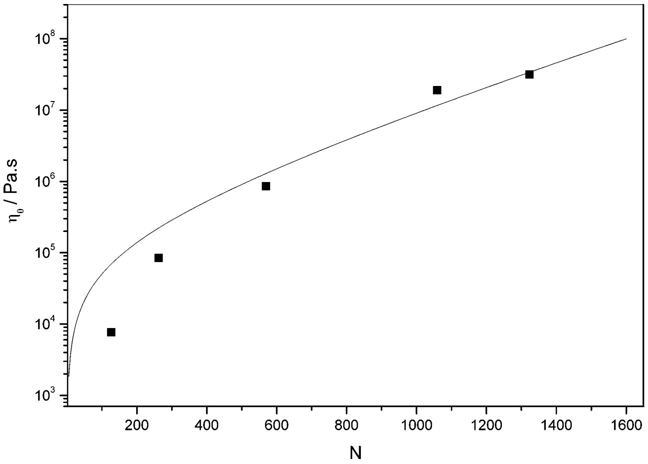


Figure 7. Zero shear viscosity (η_0) plotted as a function of degree of polymerization (N). The solid line shows the results of the Frischknecht and Milner[20] expression (eq 4).

the system will be largely unentangled, resulting in faster chain motion.

Self-Diffusion. Experimental constraints meant that only certain MW polymer couples could be studied at each annealing temperature. At the higher temperatures (433 and 443 K) the low MW couples diffused far too rapidly, and at the lower temperatures (393, 403, and 413 K) the higher MW couples moved too slowly to be to be able to accurately determine interfacial widths and diffusion rates from the data. Diffusion values for the entire range of MW couples could only be obtained at the intermediate temperature of 423 K. Consequently, 423 K was defined as our reference temperature, and all the data were scaled to this using the WLF theory with the same WLF coefficients extracted from the viscosity plots. The scaled data were averaged to produce a single plot of self-diffusion as a function of N, which is shown in Figure 8 along with the theoretical curves given by eqs 2 and 3 for the dilute and undiluted tube cases (scaled arbitrarily with identical factors). Clearly, the data show the expected exponential dependence on N. The data show excellent qualitative agreement with the undiluted tube model. Again, the most notable exception is the 14K couple, which displays a slightly greater diffusion coefficient than expected, supporting the idea that this is due to lack of entanglement in the polymeric system.

Diffusion coefficients depend on three parameters: the degree of polymerization of an entanglement length, N_e, the tube diameter, a_0, and the monomeric friction coefficient, ζ, which is embedded in the Rouse relaxation time for an entanglement segment. The viscosity depends on all the above parameters as well as the plateau modulus, G_N^0, as suggested by Milner and Frischknecht.[20] The dependence of both quantities on ζ and the dominant exponential dependence on N can be removed by taking the product of the diffusion and the viscosities, $D_0\eta_0$. Using the expressions for these quantities given by eqs 2 and 4 or eqs 3 and 4, the resulting relations are

$$\text{for dilute tubes: } D_0\eta_0 \sim (N/N_e)^{-1/2} \tag{10}$$

$$\text{for undiluted tubes: } D_0\eta_0 \sim (N/N_e)^{-15/14} \tag{11}$$

Figure 9 shows values of the product $D_0\eta_0$ as a function of N/N_e compared to values of $D_0\eta_0$ calculated using eqs 10 and 11. The magnitude of the product should be given by $a_0^2\, G_N^0$. However, using typical literature values for PS ($a_0 \sim 8$ nm, $G_N^0 \sim 0.2$ MPa), this magnitude was a factor of ~10 larger than the data. The magnitude of the theory has therefore been rescaled in Figure 9 to coincide with that of the data. The three highest MW couples (60K, 110K, 140K) clearly show good qualitative agreement with the undiluted tube case of the theory. For the 27K couple the theoretical curve is ~60% higher in value than the data and outside of the experimental errors. The most likely explanation for this that the 27K system is only partly entangled. This is possibly shown in the viscosity data for this MW, which exhibits a value that is lower than the theory by a factor of ~2.6 (40%) but not in the diffusion data. However, since in general viscosity varies more rapidly with N than diffusion, it is probable that the effects of reduced entanglement are also less obvious in the diffusion data at the MW in question. These findings are generally in agreement with the conclusions of Frischknect and Milner,[20] who compared the calculated theoretical values of $D_0\eta_0$ with data for polybutadiene from Bartels et al.[15] They also found some discrepancy between the magnitude of the theoretical curves and the data, although in their case the

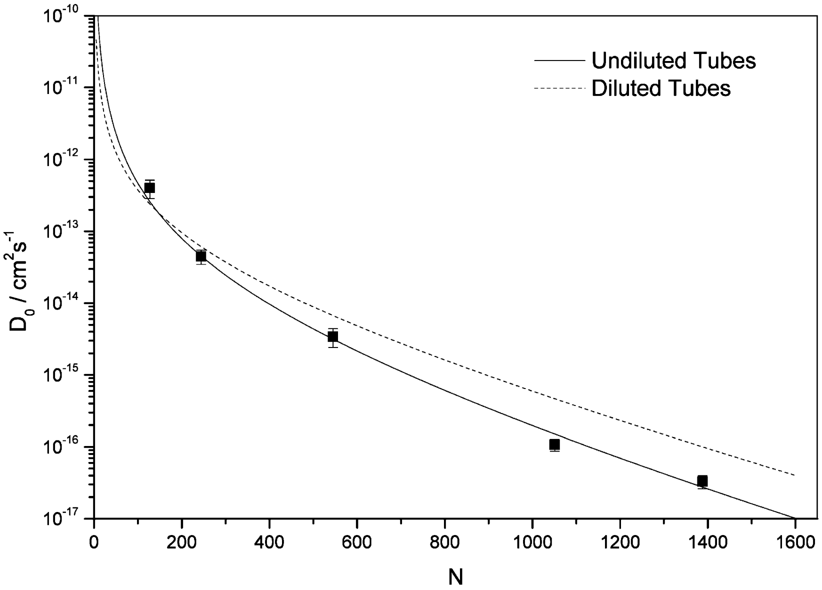


Figure 8. Self-diffusion coefficients (D_0) plotted as a function of degree of polymerization (N). The dashed and solid lines show the results of the Frischknecht and Milner[20] expressions for diluted (eq 2) and undiluted (eq 3) tubes, respectively.

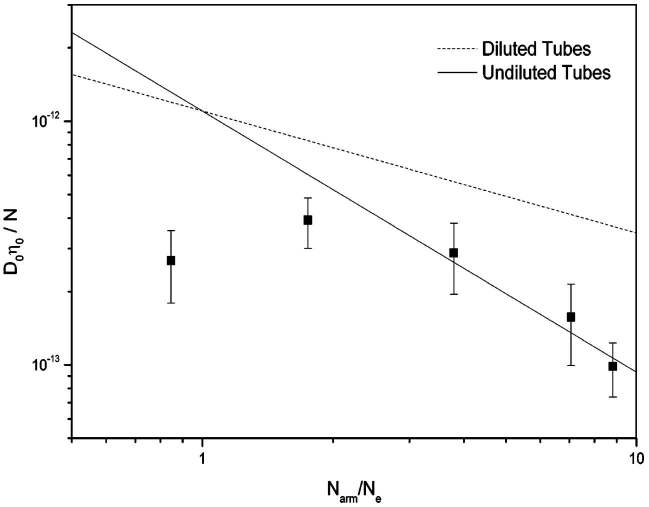


Figure 9. $D_0\eta_0$ as a function of N/N_e. The dashed and solid lines show the results of the Frischknecht and Milner[20] expressions for diluted (eq 2) and undiluted (eq 3) tubes, respectively (shifted to overlay the data).

data exceeded the theory by a factor of only ∼1.3. They attributed this to the core hopping slightly more than a undiluted tube diameter (i.e., $p \sim 1.5$; cf. eq 1). In addition, we have observed dynamic dilution effects at values of N/N_e as low as 3.8 (60K couple), whereas for $N/N_e = 1.75$ (27K couple) the data suggest that the dynamic dilution model has begun to fail. This is consistent with both the lower bound conditions used in the $D_0\eta_0$ calculations of Frischnect and Milner, the lowest data point from Bartels ($N/N_e \sim 6$), and the lower limit at which stress relaxation theory with dynamic dilution in stars has been found to work.[27]

5. Conclusion

A series of both hydrogenous and deuterated star polystyrenes have been synthesized with increasing arm molecular weight and low polydispersities. Viscoelastic measurements from rheology performed on the hydrogenous stars provided zero shear viscosity data that agrees reasonably well with expression derived by Frischknecht and Milner.[20]

The self-diffusion coefficients have also been determined for a deuterated/hydrogenous polymer couple using nuclear reaction analysis for a range of annealing temperatures. The results, when shifted to a single reference temperature and compared with the Frischknecht and Milner expressions for self-diffusion with dynamic dilution, show the data to be inconsistent with the case where the core hops a diluted tube diameter but in good quantitative agreement with the situation where it jumps an undiluted tube diameter. At the higher MWs the product $D_0\eta_0$ also appears consistent with the undiluted tube case for $N/N_e \geq 3.8$. In addition, the magnitude of the theory and data are not in perfect agreement. These findings are consistent with those of a previous study,[20] although the discrepancy between theory and experiment in the two studies are noticeably different.

It would have preferable to extend the range of MW couples to values of N/N_e greater than those used; however, this was not feasible due to the difficulties discussed in the synthesis section.

At the lower MW's the data show good evidence of the failure of dynamic dilution for values of N/N_e less than 2, i.e., when the system is no longer fully entangled, which conforms to the values expected from calculations.[27]

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References and Notes

(1) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(2) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.
(3) Watanabe, H. *Prog. Polym. Sci.* **1999**, *24*, 1253.
(4) McLeish, T. C. B. *Adv. Phys.* **2002**, *51*, 1379.
(5) de Gennes, P.-G. *J. Phys. (Paris)* **1975**, *36*, 1199.
(6) Klein, J. *Macromolecules* **1986**, *19*, 105.
(7) Shull, K. R.; Kramer, E. J.; Fetters, L. J. *Nature (London)* **1990**, *345*, 790.
(8) Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22*, 1911.
(9) Antonietti, M.; Sillescu, H. *Macromolecules* **1986**, *19*, 798.
(10) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Antonietti, M.; Sillescu, H. *Macromolecules* **1988**, *21*, 2578.
(11) Colley, F. R.; Collins, S. A.; Richards, R. W. *J. Mater. Chem.* **2003**, *13*, 2765.
(12) Fletcher, D.; Klein, J. *J. Polym. Commun.* **1985**, *26*, 2.
(13) Klein, J.; Fletcher, D.; Fetters, L. J. *Nature (London)* **1983**, *304*, 526.
(14) Gell, C. B.; Graessley, W. W.; Efstratiadis, V.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1943.
(15) Bartels, C. R.; Crist, B.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1986**, *19*, 785.
(16) Levine, A. J.; Milner, S. T. *Macromolecules* **1998**, *31*, 8623.
(17) Milner, S. T.; McLeish, T. C. B.; Young, R. N.; Hakiki, A.; Johnson, J. M. *Macromolecules* **1998**, *31*, 9345.
(18) Payne, R. S.; Clough, A. S.; Murphy, P.; Mills, P. J. *Nucl. Instrum. Methods Phys. Res. Sect. B* **1989**, *42*, 130.
(19) Milner, S. T.; McLeish, T. C. B. *Macromolecules* **1997**, *30*, 2159.
(20) Frischknecht, A. L.; Milner, S. T. *Macromolecules* **2000**, *33*, 9764.
(21) Hadjichrisitidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11*, 668.
(22) Frater, D. J.; Mays, J. W.; Jackson, C.; Sioula, S.; Efstradiadis, V.; Hadjichristidis, N. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 587.
(23) Hadjichristidis, N.; Roovers, J. *Polymer* **1985**, *26*, 1087.
(24) Fetters, L. J.; Kiss, A. D.; Pearson, D. S.; Quack, G. F.; Vitus, F. J. *Macromolecules* **1993**, *26*, 647.
(25) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: Oxford, 1975.
(26) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(27) Milner, S. T.; McLeish, T. C. B. *Macromolecules* **1998**, *31*, 7479.

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