Self-Diffusion and Spin–Spin Relaxation in Cyclic and Linear Polydimethylsiloxane Melts

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ABSTRACT: Self-diffusion and spin–spin relaxation measurements have been performed on narrow fraction linear and cyclic polydimethylsiloxane (PDMS) polymers in the melt, by pulsed nuclear magnetic resonance techniques. The effects of ring and chain molecular weight have been studied. The diffusion and relaxation data exhibit interesting molecular weight dependencies, some of which were also found in the bulk visocisty. The relaxation data show a noticeable change in molecular weight dependence at the critical molecular weight for entanglement for both the linear and cyclic polymers. The diffusion data are not, however, sensitive to this critical molecular weight effect.

Introduction

The theory of the dynamics of entangled linear polymer systems has received considerable attention in recent years.[1-4] The theories of de Gennes and Edwards have been most widely referred to and have been verified for a range of polymer systems. The scaling theory[5] proposed by de Gennes for high molecular weight linear chains, models motions by means of macroscopic deformations traveling along a curvilinear tube; this tube is formed by the constraints of the neighboring molecules. This motion is referred to as "reptation" and starts at a chain end. Cyclic polymers, on this basis, cannot reptate since they have no "free chain end" (where the perturbation would be initiated). For reptative behavior to be observed, the motion along the backbone must be highly correlated. This leads to an inverse square law dependence of the self-diffusion coefficient, D_s, on chain length, N; i.e., $D_s \sim N^{-2}$.

Studies of the dynamics of cyclic polymer systems over an extended molecular weight range, however, have received less attention.[6] To our knowledge, no explicit theoretical interpretation of the diffusion of ring polymers exists though recent computer simulation studies[7-9] have been presented. These simulations, based on the cooperative motion of loops within a condensed system with no free volume, show a dependence of the diffusion on N^{-1} for low N but on N^{-2} for higher molecular weights. No free volume effects are considered.

For $N < N_c$, the critical molecular weight for entanglement, diffusion may be represented by a much simpler treatment, the Rouse model.[10-12] In this model it is assumed that segments move isotropically; any pair of segments in a given chain move independently (cf. reptation). In this case, the diffusion coefficient scales inversely with molecular weight; i.e., $D_s \sim N^{-1}$.

Experimentally, the molecular weight exponent for D_s, for a range of polymers, varies between 1.5 and 2.4.[13-15] For polyethylene[16-18] and indeed for the lower hydrocarbons[18-21] an exponent of −2 has been found. However, as has been pointed out,[20] this does not imply that reptation occurs over the entire molecular weight range. For polystyrene melts,[22] an exponent of −2 has also been found but a free volume correction applied to the data leads to a reduced value of −1 at low molecular weight.[21] For low molecular weight poly(ethylene oxide) (PEO)[23] and poly(propylene oxide) (PPO)[24] an exponent of −1 has been reported. For PEO, above N_c, the exponent

increases to −2 though the data have been analyzed in terms of a distribution of diffusion coefficients. This is somewhat surprising as the samples are quoted to have low polydispersities. Polydispersity may also account for an exponent of −1.55 found in earlier studies of polydimethylsiloxane (PDMS) melts. For polyisoprene,[25] the evaluation of the molecular weight exponent is again dependent on a free volume correction but indicates a closer adherence to the Rouse model than to reptation.

The molecular weight behavior of the spin–spin relaxation time, T_2, in the melt is less well understood. For polyethylene, three molecular weight dependent regions may be distinguished. The critical molecular weight characterizes the transition to a stronger dependence on molecular weight associated with the onset on molecular entanglements. The molecular weight dependence then becomes less steep at a greater, undefined molecular weight. This latter behavior is still unresolved. An earlier study of polydimethylsiloxane showed a similar trend; the critical molecular weight characterized the transition to a steeper molecular weight dependence. For polystyrene, only two regions are observed, but in this instance, the transition is to a less steep dependence.

The nature of the spin–spin relaxation function has recently been studied[26-28] and found to be more sensitive to the dynamics of a polymer chain than spin–lattice (T_1) and self-diffusion measurements. A theory, enveloping a general hierarchy of polymer chain dynamics, has been proposed that reinforces the occurrence of Rouse behavior. The theory is based on the scale-invariant model of dipolar interactions[29,30] responsible for transverse relaxation. For nonentangled chains in the melt, incorporation of the Rouse model into this theory leads to exponential relaxation functions of the form

$$G(t) = \exp(-t/T_2)$$

where the relaxation rate $1/T_2 = \alpha \ln M_w + \beta$. The behavior above the critical molecular weight is more complex; nonexponential relaxation curves are proposed theoretically with much greater relaxation rates. The nonexponentiality, which increases with molecular weight, is attributed to a distribution of mobilities related to the proximity of entanglement points and the greater mobility associated with chain ends.

An ideal system for investigating the diffusional behavior of polymers is polydimethylsiloxane which can be

prepared as narrow molecular weight fractions in both linear and cyclic forms. PDMS provides an interesting class of polymers with which to study dynamics because of the high mobility of the polymer backbone. This mobility is attributable to the very flexible nature of the silicon–oxygen–silicon bond.[31] The siloxane polymeric compounds find many uses—predominantly due to their viscoelastic properties—such as lubricants, greases, and oils.

Preparation and Characterization of Polysiloxanes

Sharp fractions of cyclic PDMS were prepared by the cationic polymerization of the cyclic tetramer octamethylcyclotetrasiloxane (D_4) in a 20% w/v methylene chloride solution catalyzed by a trace amount of trifluoromethanesulfonic (triflic) acid at room temperature. The resultant linear silanol and triflate ester terminated polymers underwent equilibrium ring closure in situ as described in the mechanistic studies of Chojnowski and co-workers.[32-36] The reaction was terminated by the addition of excess sodium carbonate at approximately 45% monomer conversion. This salt was removed by filtration, and the filtrate washed repeatedly with equal volumes of deionized water to remove any trace ionic impurities which might have catalyzed reequilibration. The bulk polymer was finally isolated by evaporation of the solvent at reduced pressure. The resultant polydisperse material was then fractionated by preparative gel permeation chromatography (GPC) as previously described[37] except that the total column eluent was analyzed by the refractive index detector. This modification was expected to eliminate uncertainties found in split detection systems. The isolated fractions were analyzed by GLC and analytical GPC to determine their average molecular weights and polydispersity indices.

Sharp fractions of the analgous linear polymers were prepared by the GPC ractionation of commercial trimethylsilyl-end-capped PDMS (Dow Corning, Barry). The fractions were characterized as described above.

In both cases, GPC fractionation provided samples with a polydispersity of 1.05 or less.

NMR Experimental Studies

The measurements were performed on a JEOL FX100 high-resolution nuclear magnetic resonance spectrometer operating at 100 MHz (protons) modified to carry out self-dissusion measurements, using the pulsed field gradient technique.[38] The spectrometer has been upgraded by the addition of a Surrey Medical Imaging Systems console which replaces both the RF and computational parts. The current amplifier used to generate the field gradients was based on the design by Stilbs.[39] The unit was calibrated with a sample of known diffusivity (water), giving field gradients, G, between 1.5 and 8.0 G cm^{-1}. The data were acquired with the same diffusion time parameters; the separation of the field gradient pulses, Δ, was set at 150 ms and the width of the field gradient pulses, δ, varied between 5 and 90 ms. A glass filament containing D_2O was used as an internal lock reference for greater stability. The data in the form of partial spin echoes were transferred to a Tandy 4000 PC for computer analysis. The resultant, reconstructed (full) and integrated spin echoes both before and after Fourier transformation could be fitted to eq 1, which assumes isotropic Brownian diffusion, where γ is the magnetogyric ratio.

$$A_t = A_0 \exp[-\gamma^2 G^2 \delta^2 (\Delta - (\delta/3))D_s]$$ (1)

The samples were allowed to equilibrate, at 20 °C, and duplicate measurements were performed to check for consistency. Typical attenuation plots (A_t/A_0), are shown in Figure 1 for three different high molecular weight samples. In all cases, a good single component fit to eq 1 (solid lines) was found.

The spin–spin relaxation measurements were performed using the high-resolution CPMG sequence,[40] and the data could be fitted to a single exponential. Low-resolution CPMG traces for
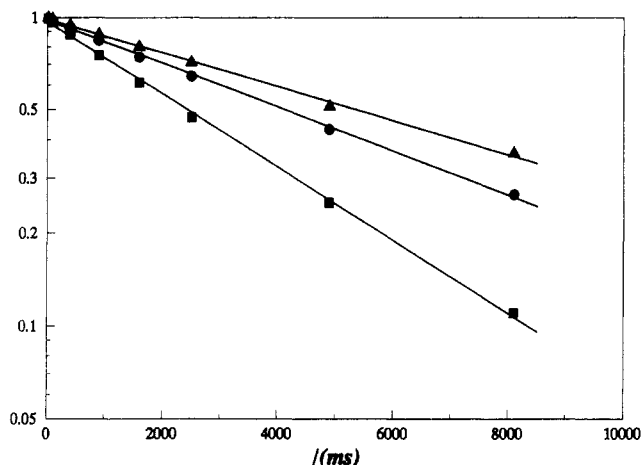

Figure 1. Typical attenuation plots, ln (A_t/A_0) vs δ^2 (ms^2) for three high molecular weight samples: L946 (squares), L1030 (circles), and L1356 (triangles).
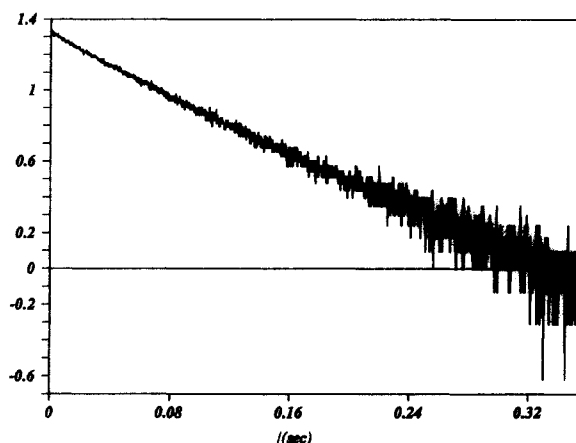

Figure 2. Typical CPMG trace for a high molecular weight sample, amplitude vs time (s).

samples above the critical molecular weight, however, could not be fitted to a single exponential. A typical trace is shown in Figure 2.

Discussion

Viscosity. The viscometric behavior of bulk polymers may be characterized by two distinct regions, above and below the critical molecular weight for entanglement. Above this molecular weight, a transient network is present and a restriction to the polymer motion arises from coupled loci, or entanglement points.[1,2,19] Viscosity, η, measurements on the present samples have been published[41] and are reproduced in Figure 3. The cyclic polymers, below N_c, exhibit a power law of the form $\eta \propto N^{0.60(\pm0.05)}$, while above N_c, $\eta \propto N^{3.46(\pm0.05)}$. The linear polymers, on the other hand, show a corresponding behavior of $\eta \propto N^{1.05(\pm0.05)}$ below N_c and $\eta \propto N^{3.21(\pm0.05)}$ above N_c. The sudden changes in the ln η vs ln N slopes are indicative of the formation of entanglement coupling, and give values of N_c, in bond numbers, of 450 (cyclic) and 440 (linear). In comparing the absolute values of η, it may be seen that the critical behavior is more pronounced in the cyclic samples. In excellent agreement with this is a similar study on linear and cyclic polystyrene in the melt,[42] where it was found that, above N_c, linears exhibit higher viscosities than the corresponding cyclics. The molecular weight dependencies in this instance, however, were $\eta_{linear} \sim N^{3.39(\pm0.02)}$ and $\eta_{cyclic} \sim N^{3.31(\pm0.03)}$.

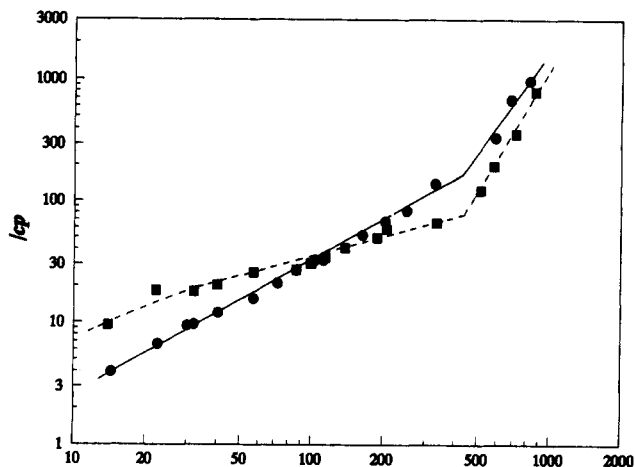**Spin–Spin Relaxation.** Spin–spin relaxation times, T_2, for the samples as a function of molecular weight are

Figure 3. Viscosity of PDMS melts, viscosity (cp) vs bond number: cyclic (squares), linear (circles).
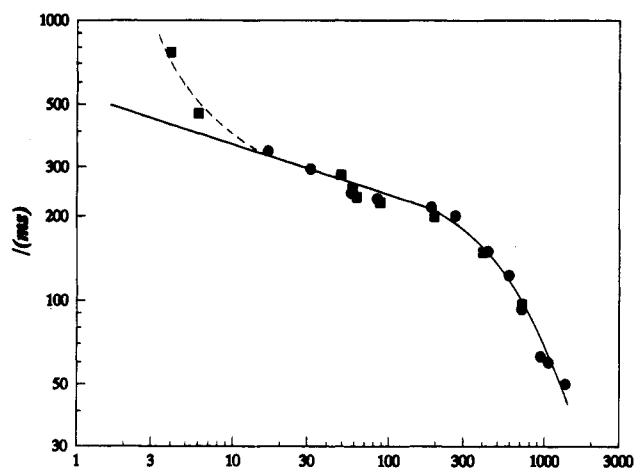

Figure 5. Brereton analysis for linear PDMS, $1/T_2$ (ms^{-1}) vs bond number.

Figure 4. Spin–spin relaxation time, T_2, in PDMS melts, T_2 (ms) vs bond number: cyclic (squares), linear (circles).

Figure 6. Self-dissusion in PDMS melts, self-diffusion coefficients vs bond number: cyclic (squares), linear (circles).

shown in Figure 4. The sharp break indicating the critical molecular weight gives a value of N_c = 400 ($\pm$20) which agrees very well with the value obtained from the viscosity data, N_c = 440 ($\pm$15) (see Figure 2). Similarly, the T_2 results presented here are in good agreement with earlier published data.[43]

Experimental results for nonentangled polyethylene melts, when discussed in terms of the Brereton model, yield the values α = 0.89 s^{-1} and β = –4.9 s^{-1}. In excellent agreement with this approach are the PDMS data presented here, which give α = 0.90 ($\pm$0.03) s^{-1} and β = –3.5 ($\pm$0.3) s^{-1} (see Figure 5). The critical molecular weight obtained from this analysis agrees very well with the value obtained previously. As predicted by the Brereton model, nonsingle exponential relaxation curves were obtained for the higher molecular weight samples used in this study and the relaxation rates were indeed much greater; α = 14.7 ($\pm$0.9) s^{-1}, and β = –149 ($\pm$10) s^{-1}.

Unlike the viscosity data, there is no obvious crossover between the linear and cyclic T_2 data, highlighting the subtle differences in the physical processes that the two measurements are sensitive to. One such process, which could affect the results in this manner, are the shear forces involved. The viscosity measurements are obtained at finite shear rates whereas the NMR relaxation measurements are a result of the thermally driven Brownian motion of the molecules. Another factor is that when $\omega_0 \tau_c \ll 1$ (where ω_0 is the resonant frequency and τ_c is a characteristic correlation time for molecular motion) T_2 also has a contribution from high frequency motion, $\sim \omega_0$, which will depend strongly on the backbone flexibility and the
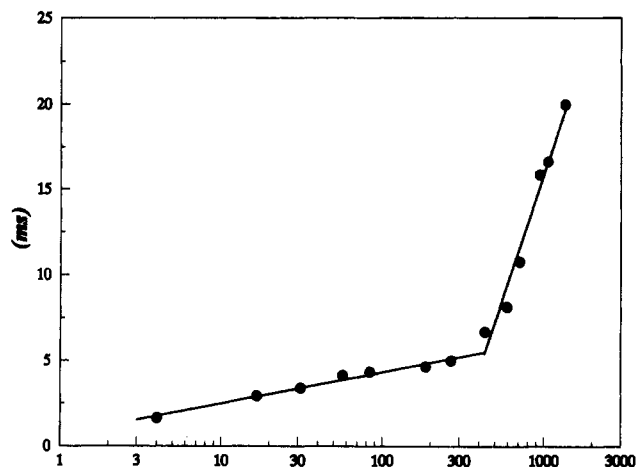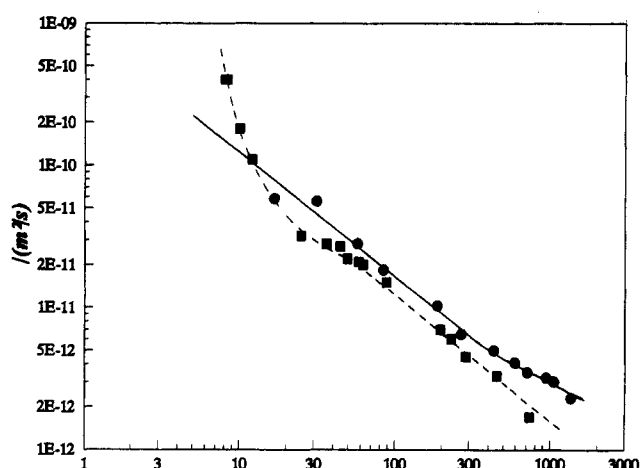
rotation of pendant groups. This rotational motion will have little effect on the bulk viscosity.

Diffusion. In Figure 6 the diffusion results for both cyclic and linear species are shown. As with the viscosity data the lower molecular weight linear species can be characterized by a scaling law of the form $D \sim N^\alpha$ where α = –1, in agreement with the Rouse model. The diffusion of the small cyclics, however, is enhanced compared to the linears due to the increased rigidity of the ring and the concomitant reduction in size. In the diffusion data for the rings there is a marked change in slope at N = 20 and a "plateau" region extending to $N \approx$ 50. The viscosity data do show this behavior but less markedly. One possible interpretation is that some cyclic molecules can "thread" through others. These associations will be rather weak and possibly disrupted somewhat in the viscosity measurements, but to a lesser extent in self-diffusion. At N = 120, the viscosity for the linear chains crosses that for the cyclic chains because of the lower dependence of η on N. No such behavior was found for the diffusion data, and for $N > 10$, D_{linear} is always greater than D_{cyclic}.

The absolute values of the molecular weight exponents for both linear and cyclic molecules for $N_c > N > 50$ are –1.0 ($\pm$0.05). This is rather different for the values found for polyethylene (PE) (–2) and polystyrene (PS) (–2)[16–18,22] and can be attributed to the larger free volume found in PDMS. Above N_c, there is no apparent change in the exponent for the cyclics but the exponent for the linears decreases ($\approx$–0.8). However, there is no indication of any higher dependence on N as seen for PS and PE. This may be rationalized by the extremely mobile nature of the

PDMS chain, enabling less anisotropic segmental motion which will preclude reptation. In comparison, the diffusion data on polyisoprene[25] are complicated as the free volume term, f, is smaller than that for PDMS. The polyisoprene experimental data show an exponent greater than -3, but after a free volume correction suggest an underlying trend of $D \sim N^{-1.0}$ for low molecular weights. This free volume correction depends on the size and mobility of the polymer end groups and molecular weight. Its physical significance is that it enhances the diffusion process.

The fractional free volume, f, at a temperature, T, takes the form[6]

$$f = f_g + \Delta\alpha(T - T_g) + \rho V_e/N \qquad (2)$$

where f_g is the free volume at the glass transition temperature, T_g. ρ is the density, V_e is the molar volume of the end group, and $\Delta\alpha$ is the free volume thermal expansivity. As molecular weight increases the value of f tends to a constant, given that T_g is largely independent of molecular weight. The free volume correction term for the diffusion coefficient has been given by Meerwall as[25]

$$D = (\varphi_0\delta^2/6N) \exp(-B_d/f) \qquad (3)$$

where φ_0 and δ are the jump frequency and jump distance, respectively, and B_d is a constant characteristic of the polymer.

For polyethylene, a relatively stiff chain, the free volume correction is negligible whereas for a much more flexible polymer, polyisoprene, the effect is significant. The absolute value of the free volume determines the ease of diffusion. However, it is the variation of the free volume with molecular weight that is important in differentiating the two types of behavior. For polyisoprene, the explicit molecular weight dependent term, $\rho V_e/N$, makes a significant contribution to the overall free volume. For cyclic PDMS, this contribution is necessarily zero since there are no end groups, $V_e = 0$, and the free volume is constant. The corresponding behavior for linear PDMS is similar due to the relative magnitudes of each contribution to the free volume; i.e., $\Delta\alpha(T - T_g)$ is much larger than $\rho V_e/N$. Consequently, the free volume term is again independent of molecular weight, except at very low molecular weights. This may be emphasized by the ratio of D_{cyclic}/D_{linear} which tends to a constant in the range $30 < N < 300$. The free volume molecular weight dependent correction is, therefore, negligible, and $D_s \sim N^{-1}$.

Conclusion

Diffusion results are presented for a series of linear and cyclic PDMS polymer melts which do not follow the reptation theory over a range of molecular weights encompassing M_c. Free volume arguments have been proposed to account for the variation in the observed molecular weight exponents for a range of polymers. It is apparent that stiff, rigid chains, with little or no free volume, exhibited an inverse square law dependence of the diffusion coefficient with molecular weight over a broad molecular weight range—above and below N_c. For less rigid chains, a transition from $D_s \sim N^{-1}$ to $D_s \sim N^{-2}$ is observed at the critical molecular weight, while for a flexible polymer, no transition to $D_s \sim N^{-2}$ is observed. In qualitative agreement with this is the comparison between the linear and cyclic PDMS forms where chain end effects are necessarily zero. In this case an identical exponent is observed. The lack of sensitivity of diffusion to the critical

molecular weight is contrasted with viscosity and spin-spin relaxation data. The spin-spin relaxation data have been sucessfully described by a recent theory based on the Rouse model.

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