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Self-diffusion and spin–spin relaxation in blends of linear and cyclic polydimethylsiloxane melts

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Self-diffusion and spin–spin relaxation measurements have been performed on a series of blends of narrow-fraction linear and cyclic polydimethylsiloxane polymers in the melt by pulsed nuclear magnetic resonance techniques. The results obtained are compared to the viscosity behaviour on the same samples and discussed in terms of the reptation and Rouse theories commonly invoked for the dynamics of single-component systems. The dynamics of the blend samples are shown to deviate from the expected behaviour above a critical ring size which can be understood through a mechanism based on ring threading. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The complex dynamics of entangled polymer systems have received considerable attention in recent years and the reptation theory[1–3] has been very informative in this context. The theory models the motion of a polymer chain as macroscopic deformations travelling along the curvilinear length of a 'tube' formed by the neighbouring polymer chains. The motion starts, and can only be perpetuated when a chain end leaves one tube and enters into another tube, so-called 'tube renewal'. This requires a high degree of motional correlation along the backbone of the polymers and, therefore, is only applicable to highly entangled systems. Consequently, the onset of reptation depends on the critical molecular weight for entanglement, M_c, of the polymer, characterized for example by the dramatic increase in the viscosity with increasing molecular weight. The mobility of the polymer chain travelling along the tube scales linearly with molecular weight, a Rouse chain, as does the curvilinear tube length. Therefore, the self-diffusion coefficient, above the critical molecular weight for entanglement, is proposed to follow an inverse square law dependence on molecular weight, $D_s \alpha M^{-2}$.

For unentangled systems, the simpler Rouse model[4] suffices, in which the polymer chain is represented as a series of beads joined by springs of an equivalent spring constant. Contrary to reptation, and central to this approach, is that the segmental motion is highly isotropic, i.e. there is no correlation along the polymer backbone over distances greater than a few Kuhn statistical segments. In this case, the self-diffusion coefficient follows an inverse dependence on molecular weight, $D_s \alpha M^{-1}$.

Experimentally, these two types of diffusion behaviour have been confirmed for a series of polymers[5–13]; entangled systems such as polyethylene (PE), polystyrene (PS) and poly(ethylene oxide) (PEO) all show the reptation exponent above M_c, whilst below M_c, PS, PE, PEO, poly(propylene oxide) PPO[14] and polydimethylsiloxane (PDMS)[15] all show the Rouse exponent.

Often, corrections must be applied to this sort of data before unequivocal observations of these exponents are seen. For example, the low molecular weight PE diffusion data show an exponent greater than −2, but when corrected to a constant monomeric friction factor, the Rouse exponent is observed[16]. Essentially, this correction normalizes all the data to a constant temperature interval above the glass transition temperature, which is molecular weight dependent. Similarly, PS and polyisoprene only show the Rouse exponent after a similar correction for the free-volume has been made. On the other hand, PEO shows the analogous transition without any such correction.

These trends are related to chain flexibility—the stiffer the chain, the greater the need for, and the greater the magnitude of, any correction[14]. With this in mind, the highly flexible polymer PDMS is of considerable interest. The first results on PDMS diffusion were obtained by McCall *et al.*[17] but their samples were rather polydisperse. Similar problems of sample polydispersity were

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encountered in later studies[18,19]. The first study of the diffusion behaviour of a wide molecular weight range of monodisperse PDMS samples was performed by Cosgrove *et al.*[15]. The effect of chain architecture could also be investigated by comparison with a parallel set of monodisperse cyclic samples. However, the reptative exponent was not observed in the diffusion data for these samples up to $5M_c$ although the spin–spin relaxation and viscosity data did show the presence of entanglements. Interestingly, the Rouse model fitted both linear and cyclic architectures; no difference in the molecular weight dependences of the self-diffusion was observed for the linear and cyclic forms except for small rings. The similarity of the diffusion data for the two forms was accounted for by the flexible nature of the backbone and, therefore, the inherently small free volume. Indeed, the spin–spin relaxation and the viscosity data (except for small rings) also showed no marked difference between the two forms, with a common value of the critical molecular weight for entanglement for the two architectures.

Stepto[20], reconsidering the Graessley–Edwards theory[21], has proposed a modification to account for the common features of the two architectures. With the exception of the small rings, the principal conclusion is that since segmental mobility is insensitive to long range chain connectivity (as shown by a rotational isomeric state (RIS) model of the two species[22]), the critical molecular weight for entanglement is more sensitive to the flexibility of the chain rather than the mobility of the whole chain: the presence of entanglements depends only on the localized segment density (which is independent of chain connectivity). This is not applicable to the case of small rings, where there is a tendency to form disc-like molecules which results in a higher diffusion coefficient and lower viscosity.

Appel and Fleischer[23], however, focusing on higher molecular weight PDMS samples, did observe the reptation exponent but only above $5M_c$, at a considerably greater molecular weight than that observed for the viscosity data. Whilst these observations initially appear to be contradictory, they can be rationalized by considering the nature of the various techniques. Viscosity measures the displacement of molecules under shear over comparatively large distances and timescales. Appel and Fleischer[23] proposed that the entanglement tubes are incompletely formed below a molecular weight equivalent to $5M_c$. The presence of these 'tubes' is, therefore, enhanced by the shear in the viscosity experiment and the effects of the entanglements become observable. Spin–spin relaxation, on the other hand, operates over a much shorter distance scale and, therefore, is sensitive to the segmental motions of the system. The presence of any tubes, whether incompletely formed or not, results in a reduction in the segmental mobility. It should be noted that spin–spin relaxation is, however, only sensitive to the dynamics of the polymer chains provided the correlation time characterizing those dynamics is comparable to the frequency of the applied field. For liquids, this requirement is easily fulfilled. Diffusion, on the other hand, as required by the reptation mechanism, only becomes anisotropic upon complete formation of the tube. Reptation as perceived by the diffusion experiment, therefore, is only observed at higher molecular weights upon complete formation of the tubes, compared to the viscosity and spin–spin relaxation.

More importantly, the reptation theory has serious limitations when considering the dynamics of cyclic molecules. Since the cyclic polymer has no 'free ends' there is no mechanism for (conventional) tube renewal. In the content of pure reptative motion, entangled cyclic polymer molecules cannot self-diffuse. Further insight into the dynamics of cyclic molecules may be obtained by studying blends of linear and cyclic polymers.

Klein[2,24] has proposed three possible molecular configurations for linear and cyclic blends: (a) the cyclic polymer is threaded by linear chains and has a rather extended conformation; (b) the cyclic polymer is unthreaded, and has large loops extending into the surrounding media; and (c) the cyclic polymer is again unthreaded but has no loops and adopts a rather compact configuration.

The dynamics of these three systems are very different. The cyclic polymer in case (a) may only rotate around the linear chains that thread it and cannot translate without their removal, whilst in cases (b) and (c) the motion is described by a 'wriggling' process between the linear chains, analogous to reptation. In particular, case (b) may be compared to the diffusion of a star polymer and case (c) contrasted with the diffusion of a much smaller linear polymer. In dilute and semidilute solutions, the diffusion of star-shaped polymers is similar to that of the linear analogue[25,26]. In the melt, however, the 'retraction' of the arm of the star seriously retards the diffusion of the polymer, effectively 'quenching' reptation. The presence of higher order motions[27], such as constraint release[1] or fluctuations in the primitive path, have been shown to account for the discrepancies between the experimental and theoretical behaviour; experimentally, a stronger molecular weight dependence is observed, $\eta \propto M^{3.4}$, with the absolute value of the viscosity slightly less than predicted. The presence of these higher order motions may hold the key to the dynamics of cyclic polymer melts—since they have no free ends, the motions must proceed through the reversible formation of loops extending through the walls of the conventional 'tube'.

It is important to understand the differences between cyclic and linear molecules and their behaviour in the melt when interpreting their dynamics. When comparing chemically identical but topologically different species (cyclics *versus* linears) of the same molar mass, differences can be observed in some bulk properties[28]. The densities of the linear fractions are always slightly less when compared to cyclic fractions of equivalent mass for the range studied up to an average number of skeletal bonds $N_{av} = 500$. For PDMS, these effects are most pronounced for oligomers (low molar mass material) and can be explained in terms of the disc-like structures that the cyclics adopt in their all-*trans* conformation, which can pack efficiently[29]. Blends containing equal portions of cyclic and linear PDMS of similar molar mass show deviations from the additive theoretical densities and viscosities[28–30]. These deviations reach a maximum at $N_{av} = 22$, suggesting that the geometry of the polymer is of importance when discussing the properties of blends and the motions in them. The cause of these deviations in blends with $N_{av} = 22$ may be due to linear chains interrupting the efficient packing of the cyclic PDMS 'discs'.

When comparing the properties of larger cyclics and linears, additional factors are introduced by threading and entanglements. It has been found that for $N_{av} > 30$ for cyclic PDMS, there is enough room for a linear PDMS chain to thread a cyclic[31]. If the linear chain is cross-linked after a cyclic has been threaded onto the linear chain, a network containing topologically trapped cyclics is formed[32,33]. It is important to note that the cyclic is not covalently bonded to the chain but is physically restrained from coming off the chain by the cross-links. Similarly, the 'entrapment' of cyclic polymers by cross-linking linear polymers is not limited to the PDMS/PDMS system. Fyvie *et al.*[34] trapped cyclic PDMS into a network formed by cross-linking poly(2,6-dimethyl-1,4-phenylene oxide), and Wood *et al.*[35] trapped some cyclic polyesters in a PDMS network.

The aim of this paper is to study systematically the dynamics of a series of linear and cyclic blends to compare the results with the single component data, and to discuss the results in terms of the Rouse or reptation models by placing special emphasis on the molecular weight dependences of the diffusion coefficient and spin–spin relaxation times.

EXPERIMENTAL

Polymer synthesis

Sharp fractions of cyclic and linear PDMS have been prepared from octamethylcyclotetrasiloxane (D_4), which was polymerized following the method proposed by Chojnowski and Wilczek[36] where a strong acid (trifluoromethanesulfonic acid) catalyses the Si–O bond cleavage and a ring–chain equilibrium is established. Full details of this reaction and the extraction and purification of cyclic PDMS are given in references 37–39.

Cyclic PDMS was fractionated using a preparative gel permeation chromatography (g.p.c.) instrument which was constructed at the University of York[40]. A series of sharp fractions with typical dispersities of $M_w/M_n < 1.2$ over a number average molar mass range $300 < M_n < 30\,000$ were obtained. Linear fractions with similar molar mass data were also prepared from commercially available linear PDMS supplied by Dow Corning Ltd.

Pulsed gradient spin-echo n.m.r. experiments

The self-diffusion coefficient measurements were performed on a SMIS-JEOL FX100 high resolution spectrometer operating at 100 MHz (protons) employing the Skejskal–Tanner sequence[41,42]. The homospoil accessory[43] was used to produce the field gradient pulses which were calibrated against known standards ($^2H_2O/H_2O$, glycerol). The experimental spin echos were Fourier transformed, integrated and the data analysed in terms of equation (1):

$$A(\delta) = A(\mathrm{o})\exp[-\gamma^2\delta^2G^2(\Delta - \delta/3)D_S] \qquad (1)$$

where γ is the magnetogyric ratio, $A(\delta)$ is the integrated peak intensity obtained by application of a pair of field gradient pulses of magnitude G, length δ, and separation Δ. $A(\mathrm{o})$ is the intensity when $G = 0$; Δ was set at 150 ms and δ varied between 5 and 90 ms.

The spin–spin relaxation times were measured on a SMIS-JEOL FX200 high resolution spectrometer operating at 200 MHz (protons). A low resolution CPMG[44] sequence was used where only the maximum of the spin echo intensity is sampled. In all cases, single exponential decays were observed.

RESULTS

In order to present a clear argument comparing and contrasting the various types of experiment and the conclusions from each, the results will be presented first and a discussion given later.

Viscosity behaviour

The average viscosity of blends of equivalent molecular weight linear and cyclic molecules have been measured[30] as a function of molecular weight. The data are reproduced in *Figure 1* and *Table 1*. Up to a ring size of 150 (±20) bonds ($M_n = 12\,300$), the experimental viscosity closely follows a simple average of the two component viscosities with one exception, that of the smallest ring. With decreasing ring size, the viscosity of the single-component system showed a slight decrease in the expected behaviour because of the increased rigidity associated with small rings. Consequently, for the smallest ring blend, the smaller than expected average viscosity is again taken to be representative of the rigidity of the small ring.

Above a ring size of 150 bonds, the viscosity of the blend follows a much steeper dependence on molecular weight with the deviation from the simple average increasing with molecular weight. Since the critical molecular weight for entanglement for PDMS is 440 bonds ($M_c = 36\,500$), this change in slope cannot be due to 'conventional' molecular entanglements. It has been proposed[31] that this effect is due to 'ring threading',

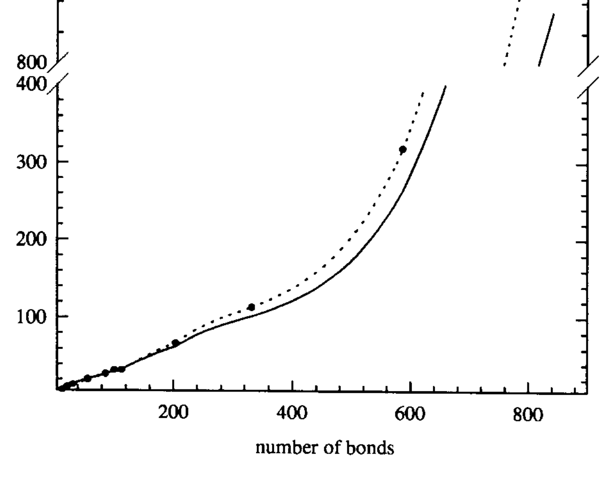

Figure 1 Viscosity of equal molar mass linear and cyclic PDMS blend samples as a function of average number of bonds: solid circles, experimental data; solid line, theoretical additive density

Table 1 Experimental and predicted values of the viscosity in PDMS melt bands

Cyclic size	Linear size	Percentage cyclic volume	η experimental	η theoretical	Percentage difference
14.0	14.5	51.24	5.47	6.83	−19.9
22.2	22.6	49.86	9.64	9.10	+5.9
32.0	32.0	50.00	12.67	13.80	−8.2
57.0	57.0	50.25	19.62	20.73	−5.4
86.0	86.0	50.49	26.82	26.89	−0.3
99.0	102.0	51.02	31.84	31.10	+2.3
114	112	49.93	32.21	33.28	−0.2
205	203	49.93	67.21	62.92	+6.8
334	330	50.37	113.35	102.00	+11.1
582	591	50.16	318.64	264.66	+19.2
866	818	50.03	1082.86	876.12	+23.6

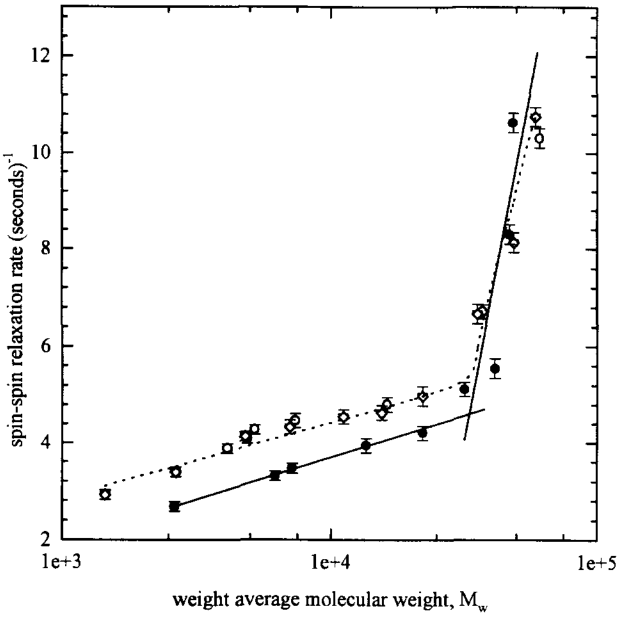

Figure 2 Spin–spin relaxation rate as a function of weight-average molecular weight for a series of PDMS samples: solid circles, blend samples; open circles, linear samples; open triangles, cyclic samples; dashed line, Brereton analysis of the single-component data; solid line, Brereton analysis of the blend data

where the ring polymer ‘lassoes’ the linear polymer. Geometric calculations suggest that a ring size of at least 30 bonds ($M_n = 2500$) is required to allow such threading mechanisms.

Spin–spin relaxation rate behaviour

The spin–spin relaxation rates, T_2^{-1}, for the pure linear and cyclic melts as a function of molecular weight are displayed in *Figure 2* according to the model of Brereton *et al.*[45,46]. In the model, the molecular configurations giving rise to the spin–spin relaxation function are based on two correlation functions characterizing the dynamics of segment and entanglement correlations which, over a suitable distance scale, describe the motion of the whole chain. Two distinct molecular weight dependences arise and the transition from one dependence to the other signifies the onset of molecular entanglements. Therefore, this gives a representation of the critical molecular weight for entanglement as perceived by the segmental dynamics. For the single-component melt PDMS data, there is excellent agreement using this approach and that obtained from the experimental viscosity data.

The spin–spin relaxation data for the melt blends are shown in *Figure 2* plotted as a function of weight-average molecular weight, M_w. There is no *a priori* reason why the relaxation data are dependent on a different molecular weight average compared to the diffusion data, although the few blend samples which consist of two very different molecular weight components show absolutely no agreement with the other similarly sized blends unless the weight-average molecular weight is used. Whilst this is not conclusive proof that this form of averaging is correct, it does lend considerable support.

The Brereton plot for the blend data shows many similarities with the pure component data. The higher molecular weight samples, above the critical molecular weight, show (a) a strong dependence of the relaxation rate on molecular weight which is equivalent not only for the linear and cyclic forms, but also for the blend data; (b) the actual values of the relaxation rates for the blend and single-component samples at an equivalent weight-average molecular weight are also comparable; and (c) the onset of this steeper dependence, characteristic of the critical molecular weight for entanglement in the pure systems, is the same for the blend and single-component data.

However, below this critical molecular weight the similarity between the blend and pure components is limited only to the molecular weight dependence—the actual relaxation rates for the blend samples are smaller than for the pure components.

Self-diffusion behaviour

Self-diffusion coefficient measurements have been performed on the same series of PDMS blends. As shown previously, the diffusion behaviour of both the linear and cyclic forms was well described by the Rouse model, $D_s \propto M^{-1}$ with no observation of the reptative exponent even up to $5M_c$. The lack of a reptative mechanism was attributed to incomplete tube formation – the motion of the chains within these tubes was not sufficiently anisotropic. For all the blends studied, no deviation from the single-component diffusion (equation

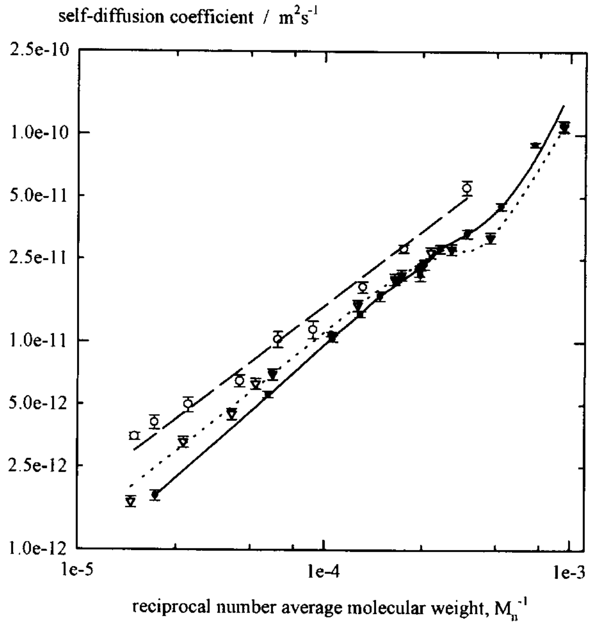

Figure 3 Self-diffusion coefficient as a function of reciprocal number-average molecular weight (Rouse behaviour) for a series of PDMS samples: solid circles, blend samples; open circles, linear samples; open triangles, cyclic samples

(1)) was observed, signifying the presence of only one diffusing species as found in other studies of this type[14,47,48]. Contrary to the relaxation rate measurements, the self-diffusion coefficient is sensitive to the number-average molecular weight in such blend samples[49,50].

The self-diffusion coefficients of the linear, cyclic and blend samples are plotted in *Figure 3* as a function of the reciprocal number-average molecular weight. At higher molecular weights, a simple power law dependence of the self-diffusion coefficient on molecular weight is observed, with a slope of −1, characteristic of Rouse motion. For the pure component data, the diffusion of the linear form is, over this molecular weight range, always greater than the cyclic equivalent. The blend data cross the cyclic data at a molecular weight of ~3000 (200 bonds) and for molecular weights below this value, the diffusion coefficient of the blend lies between the linear and cyclic forms but closer to the cyclic, the slower component. Above this molecular weight, the diffusion of the blend data is always slower than both the cyclic and linear forms.

DISCUSSION

The study of blends of polymer melts has been used to elicit information not only on the mechanism of diffusion but also on the averaging processes that occur in these blends. For example, the diffusion in blends of PPO melts[14] and the simple alkanes[48] could be superimposed on the single-component master curve after a suitable correction for the effective molecular weight. For the alkane case, the data must be further corrected to a constant monomeric friction factor.

A similar approach has been adopted in this study. However, since the blends generally consist of equivalent molecular weight components, the effective molecular weight is close to that of the two components. This facet allows the effects of the chain architectures to be extracted. (The few samples that do not comprise equivalent molecular weight components provide a useful check of the validity of the particular molecular weight averaging formalism.)

The ring-threading mechanism is proposed to occur for ring sizes greater than 30 bonds ($M_w = 2500$). This corresponds to the plateau in the self-diffusion and viscosity behaviour of the single-component cyclic form. As may be seen in *Figure 3*, this also corresponds to the (average) molecular weight where the blend diffusion becomes slower than either of the two single-component forms. No such behaviour is seen in the relaxation data, although below the critical molecular weight for entanglement, the dynamics of the blend systems are described by smaller relaxation rates and, thus, longer correlation times.

These observations lend support to the ring-threading mechanism. If we assume that a cyclic chain has been threaded by only one linear molecular, the diffusion of the linear chain can only occur if the chain end passes out through the cyclic polymer. This does not contradict the observation of Rouse motion since any of the segments can initiate this motion and can thus explore the local environment in an isotropic manner. The centre-of-mass motion will, of course, be somewhat retarded.

The Brereton model[45,46], which represents the polymer chain as a series of Rouse subunits, was invoked to discuss the relaxation of the single-component melts. The measured relaxation function is proposed to be a single exponential (below M_c) with a time constant which is dependent on molecular weight thus:

$$T_2^{-1} = \alpha \ln M_w + \beta \qquad (2)$$

The parameters α and β are related to the size of the Rouse unit such that β/α is proportional to the logarithm of the number of monomer units in a Rouse subunit. Above the critical molecular weight for entanglement, some non-exponentiality is proposed, and observed, in the relaxation function[46].

A simple inspection of the single-component and blend data below the critical molecular weight for entanglement shows that for the blend data, β must be smaller than in the single-component case. The value of α, given by the slope of the molecular weight dependence, is the same for both cases. From the ratio of the β values for the blend data, it is possible to conclude that the effective subunit size in the blend is five times larger.

The relaxation data for the blend samples strongly suggest that some form of entanglement, unrelated to conventional entanglement, is present over the entire molecular weight range studied. The smallest ring studied by relaxation was 32 bonds ($M_w = 2700$), approximately the minimum size required for ring threading. The diffusion and viscosity data also support the occurrence of an entanglement, unrelated to the conventional type, which starts at the critical ring size.

CONCLUSIONS

Viscosity, spin–spin relaxation and self-diffusion coefficient measurements have been performed on a series of blends of monodisperse linear and cyclic PDMS. Above a critical ring size, an entanglement, unrelated to the conventional type, is observed which has been attributed to the linear polymer threading the cyclic polymer.

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