Conformation of Cyclics and Linear Chain Polymers in Bulk by SANS

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Received March 4, 2004; Revised Manuscript Received July 21, 2004

ABSTRACT: Small-angle neutron scattering (SANS) has been used to investigate the conformation of linear and cyclic poly(dimethylsiloxane)s (PDMS) in chemically identical, undiluted blends. SANS measurements have been carried out on (1) linear hydrogenous (H) mixed with linear deuterated (D) PDMS and (2) cyclic H mixed with cyclic D PDMS. The conformational behavior of the cyclic and linear polymers is studied over a wide range of molar mass and composition. Isotopic blends of linear PDMS are shown to adopt conformations that agree well with theoretical predictions for Gaussian random-coil polymers and confirm previous SANS studies. As expected for chains obeying Gaussian statistics, the mean radii of gyration, R_g, scale with the weight-average molar mass as $R_g \propto M_w^{0.5}$. A detailed study of H/D cyclic PDMS mixtures is presented, and we demonstrate that, since $R_g \propto M_w^{0.4}$, highly flexible cyclic polymers in the melt adopt an even more compact conformation than that of unperturbed rings. This behavior confirms previous predictions based on computer simulations and theoretical studies. The results are in excellent agreement with computer simulations and theoretical predictions reported in the literature.

1. Introduction

The dilute solution behavior of cyclic polymers has stimulated considerable interest over many years,[1,2] with cyclic poly(dimethylsiloxane) (PDMS) being one of the most thoroughly studied systems. Extensive comparisons have been made between the properties of cyclic PDMS and those of linear chains using a wide range of experimental techniques, e.g., gel permeation chromatographic (GPC) retention volumes,[3] radii of gyration,[4] bulk viscosities,[5] and translational diffusion coefficients.[6,7] In this paper, we report on the comparison between the conformational behavior of linear and cyclic polymers in bulk, an area to date largely unexplored due to the unavailability of deuterated cyclic polymers.

This lack of suitable deuterated cyclics has limited conformational studies to investigations in dilute solutions. For example, Higgins et al.[4] carried out SANS measurements of cyclic PDMS in deuterated benzene solution. The mean-square radii of gyration of cyclic PDMS with *z*-average number of bonds between 130 and 550, $R_{g,c}^2$, were determined by SANS. In that work, Higgins et al.[4] were able to show that ring chain dimensions are considerably smaller compared to those of linear PDMS chains, i.e., $R_{g,l}^2$. The experimentally determined ratio, $R_{g,l}^2/R_{g,c}^2$, was found to be equal to 1.9 ± 0.2.[4] This result is in good agreement with theoretical predictions that $R_{g,l}^2/R_{g,c}^2 = 2^{8-10}$ for flexible polymers in the unperturbed state (at θ-point conditions). A similar value has been reported for solutions of ring and linear polystyrene.[11,12]

Experimental studies and theoretical predictions are supported by Monte Carlo calculations[13] of the mean-square radii of gyration of ring and linear molecules containing 8−100 skeletal bond atoms, unperturbed by excluded-volume effects. The ratios $R_{g,l}^2/R_{g,c}^2$ were found to be 2.0 ± 0.2 for molecules with more than 30 skeletal bonds while larger values of this ratio were obtained for rings containing fewer than 20 skeletal bonds.[13]

As pointed out by Müller, Wittmer, and Cates,[14] despite the wide range of experimental data that are available on the behavior of cyclic polymers in solution, the static and dynamic properties of ring polymers in the melt remain largely unexplored. To date, no experimental study of the radius of gyration of rings in the melt, apart from our own work, has been reported. The unavailability of deuterated cyclic polymers has been responsible for such a lack of investigations. This paper reports the first detailed comparison of the conformation and thermodynamics of cyclic and linear polymers in bulk.

[†] Tony Semlyen, who had been at the heart of a very successful long-term collaboration on understanding the behavior of the cyclic siloxanes, sadly died before the publication of this part of the work. We believe he would have been very pleased to see the fruits of his efforts, and we dedicate this paper to his memory.

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10.1021/ma049565w CCC: $27.50
Published on Web 09/16/2004

Ring polymers differ considerably from their linear counterpart as they cannot interpenetrate to the same extent. Cates and Deutsch[15] have suggested that, due to the presence of topological constraints, rings may adopt a more compact structure in the undiluted state compared to linear chains and, as a result, are partially collapsed. For cyclics, the molecular weight dependence of R_g is predicted to be less pronounced, i.e., $R_g \propto N^{2/5}$, compared to that of linear chains obeying Gaussian statistics, i.e., $R_g \propto N^{1/2}$ (N being the number of monomer units in the chain).

Recent computational studies[14,16−19] of cyclic polymers have confirmed theoretical predictions. Published work focuses on the conformational properties of rings with 16−512 monomer units and their comparison with the dimensions of linear chains. There appears to be common agreement that the conformational behavior of rings in dilute solution and in the melt differs significantly. Because of their closed structure, uncatenated, unknotted cyclic polymers cannot adopt all possible conformations such as those that lead to the formation of catenated rings or knots. For concentrated systems, these restrictions give rise to an additional topological excluded-volume interaction between neighboring chains that is only negligible for dilute solutions. The experimental results to be presented here support this view.

In this paper, we report a SANS study of mixtures of hydrogenous (H) and deuterated (D) cyclic PDMS and compare their conformational properties to those of similar mixtures of linear PDMS chains. To our knowledge, only three SANS studies of linear PDMS have been reported.[20−22] Lapp et al.[20] carried out SANS experiments on asymmetric H (M_w = 14600) and D linear PDMS (M_w = 267 000) blends at low concentration of deuterated chains (0.9 and 6%). More recently, Beaucage et al.[21] reported SANS data of symmetric 50/50 H/D PDMS blends with M_w in the range 15 000−300 000 g mol^{-1}. These measurements deal with high molecular weight PDMS samples, outside the range of molar masses for which cyclic polymers are available to us. To make direct comparison between linear and cyclic PDMS, we therefore carried out SANS measurements on low molecular weight samples, M_w < 15 000.

A study of the conformation of cyclic polymers has been presented in a separate paper.[23] In that work, through analysis of the form factors, we demonstrate that rings in the melt are partially collapsed compared to linear chains. Here we exploit this result and extend analysis of SANS data to a range of cyclic H and D PDMS blends of different molecular weights. By studying mixtures of hydrogenated and deuterated linear chains of similar M_w, we make comparisons between the mean radii of gyration of linear chains and cyclics. In a following paper we will describe the behavior of topological blends, i.e., mixtures of H and D linear chains and cyclics.[24]

2. Theory[25]

The coherent scattering from a homogeneous mixture of deuterated (D) and hydrogenous (H) polymers can be expressed by the differential scattering cross section, $d\sigma(Q)/d\Omega$. This quantity represents the number of neutrons scattered per second into a small solid angle $d\Omega$ (neutrons s^{-1}) with respect to the incident neutron flux (neutrons cm^{-2} s^{-1}) in units of cm^2. The quantity measured experimentally is the normalized differential scattering cross section per unit volume, $d\Sigma(Q)/d\Omega$, expressed in units of cm^{-1}. The differential scattering cross section $d\Sigma(Q)/d\Omega$ is a function of the scattering vector or momentum transfer Q ($= (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle and λ the neutron wavelength). It is related to the structure factor $S(Q)$ which is the Fourier transform of the density correlation function relative to the scattering units, and it is given by

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\frac{b_D}{v_D} - \frac{b_H}{v_H}\right)^2 S(Q) \quad (1)$$

The term within parentheses is the contrast, a quantity that determines the magnitude of the observed scattered intensity. As shown above, the contrast is defined from the scattering lengths of the monomer units b_D and b_H and the volumes per monomeric unit v_D and v_H of the deuterated and hydrogenated species, respectively.

In the framework of the mean-field random phase approximation (RPA) derived by de Gennes[26] and Binder,[27] the structure factor $S(Q)$ for an H/D mixture of two chemically identical polymeric species is given by

$$\frac{1}{S(Q)} = \frac{1}{\phi_D v_D N_D P_D(Q)} + \frac{1}{\phi_H v_H N_H P_H(Q)} - \frac{2\chi}{v_0} \quad (2)$$

where N_i and ϕ_i are the degree of polymerization and volume fraction of polymer i, respectively, and χ is the segment−segment interaction parameter. The reference volume v_0 is usually taken as the geometric average:

$$v_0 = \sqrt{v_H v_D} \quad (3)$$

Since the difference between the volumes of hydrogenous and deuterated species is small,[28] for a H/D blend, v_D is approximately equal to v_H. The differential scattering cross section can be obtained by combining eqs 1 and 2:

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{(1/v_0)(b_H - b_D)^2}{[\phi_D N_D P_D(Q)]^{-1} + [\phi_H N_H P_H(Q)]^{-1} - 2\chi} \quad (4)$$

For monodisperse Gaussian chains the variation of the scattered intensity with scattering vector Q represented by the form factors $P_i(Q)$ in eqs 2 and 4 is modeled by the Debye equation:[29]

$$P_i(Q) = \left(\frac{2}{Q^4 R_{g,i}{}^4}\right)[Q^2 R_{g,i}{}^2 - 1 + \exp(-Q^2 R_{g,i}{}^2)] \quad (5)$$

where $R_{g,i}$ is the radius of gyration of polymer i which is related to its degree of polymerization N_i and statistical segment length a_i:

$$R_{g,i}{}^2 = \left(\frac{N_i a_i{}^2}{6}\right) \quad (6)$$

For the flexible PDMS chains, the statistical segment length is reported to be 5.61 Å.[21]

For rings, the structure factor was calculated by Casassa,[8] and his result subsequently confirmed by several authors.[30,31] $P(Q)$ is given by

$$P(Q) = \left(\frac{2}{\sqrt{t}}\right)\exp\left(-\frac{t}{4}\right)\int_0^{t^{1/2}/2}\exp(x^2)\,dx = \left(\frac{2}{\sqrt{t}}\right)D\left(\frac{\sqrt{t}}{2}\right) \quad (7)$$

where $t = Q^2(R_{g,c})^2$ and $D(x)$ is the Dawson integral. We have already shown that the form factor $P(Q)$ given by eq 7 better describes the Q dependence of the scattered intensity than the Debye function, at least for cyclic H/D mixtures containing relatively small cyclics,[23] up to approximately 11 000 g mol^{-1}.

The radius of gyration of a cyclic molecule has been calculated by Zimm and Stockmayer[32] by neglecting excluded-volume effects. It is related to the degree of polymerization by

$$R_{g,c}^2 = \left(\frac{N_i a_i^2}{12}\right) \tag{8}$$

leading to a reduction in the average size of the polymer compared to linear chains (eq 6). A similar result had been reported by Kramers.[9] From eqs 6 and 8, the ratio $R_{g,l}^2/R_{g,c}^2$ is predicted to be 2.

The prediction that $R_{g,l}^2/R_{g,c}^2 = 2$ relies on calculations that are based on Gaussian statistics and that are assumed to be equally applicable to linear chains and rings. On the basis of Flory-like arguments, Cates and co-workers[15] first pointed out that ring polymers may adopt a more compact conformation than linear chains. For rings, the scaling exponent ν describing the molecular weight dependence of R_g was predicted to be 0.4, a result that clearly deviates from the Gaussian scaling exponent 0.5.

Various methods have been used to extract the relevant parameters from eq 4, i.e., the interaction parameter and the radii of gyration of the two components. Usually, approximate expressions are used to obtain this information from either the low-Q or the high-Q regions. As pointed out by various authors,[33,34] $P_H(Q)$ and $P_D(Q)$ in eq 4 are correlated, and therefore the two $R_{g,i}$ values cannot be determined independently. Hence, eq 6 is used considering an average statistical length which is the same for the deuterated and hydrogenous polymers. This assumption is justified for isotopic blends of the same chemical species, except when the chains become too short so that data deviate from Gaussian statistics.

In this work, to fully exploit the information available on a wide Q range, we have fitted the scattering data to the Debye equation. However, since eq 5 is strictly valid only when the hydrogenous and deuterated polymers are monodisperse, we have used a modified Debye function.[35] For a sample with a Schulz−Flory distribution of molar mass and polydispersity index u ($= M_w/M_n - 1$), the modified Debye equation is[35]

$$P_i(Q) = \frac{2}{(u+1)\gamma^2}[(1+u\gamma)^{-1/u} - 1 + \gamma] \tag{9}$$

where $\gamma = R_z^2Q^2/(1+2u)$, R_z^2 being the mean-square z-average radius of gyration of the linear chains. After substituting the appropriate expression for the form factor, eq 4 can be used to fit the experimental data using nonlinear least-squares regression analysis.

Isotopic effects have to be considered when analyzing SANS data. There exists a wealth of literature data indicating that mixtures of hydrogenous and deuterated polymers exhibit an upper critical solution temperature behavior and isotopically driven phase separation may occur on cooling. Early SANS studies on high molecular weight linear PDMS[20] indicate that the interaction parameter between hydrogenous and deuterated species is far from being negligible: $\chi = 1.7 \times 10^{-3}$; symmetric blends with $M_w > 100\,000$ should phase separate at room temperature. Recently, this expectation was confirmed by experiments[21] on high molecular weight PDMS ($M_w = 300\,000$).

Isotopic effects are negligible at low molecular weight since, at room temperature, the binary blend is far from the phase boundary. However, end group effects may alter the expected critical temperature required for phase separation, resulting in an upward shift of the phase boundary. This effect has been invoked to explain the SANS data of binary isotopic PDMS blends.[21]

By using eq 4, we have estimated the extent of the isotopic effect in H/D PDMS mixtures; comparison between the behavior of linear and cyclic isotopic blends is given in section 4.

Table 1. Molar Mass and Polydispersity of Samples Investigated by SANS[a]

hydrogenous PDMS			deuterated PDMS		
sample	M_w [g mol^{-1}]	M_w/M_n	sample	M_w [g mol^{-1}]	M_w/M_n
23HL	22900	1.04	31DL	31171	1.23
10HL	9710	1.03	12DL	11828	1.11
6HL	6280	1.15	11DL	10970	1.21
2HL	2020	1.07	6DL	6420	1.19
			2DL	1980	1.18
9HC	9000	1.05	11DC	11140	1.11
5HC	4780	1.06	9DC	8649	1.16
3HC	2750	1.03	5DC	4760	1.13
			3DC	3570	1.14

[a] Samples are coded according to their weight-average molar mass, their isotopic labeling, and finally their topology; e.g., 10HL refers to a hydrogenous linear PDMS with a weight-average molar mass of approximately 10 000 g mol^{-1}.

3. Experimental Section

3.1. Materials. The hydrogenous cyclic polymers were prepared using the ring/chain equilibration method of Brown and Sluzarczuk.[36] This produced a polydisperse sample that was solution separated and then fractionated by preparative GPC.[37,38] The hydrogenous linear polymers (which have trimethylsilyl end groups) were DC 200 series dimethylsiloxane samples supplied by Dow Corning Ltd. Linear and cyclic deuterated PDMS were synthesized using a newly developed procedure described in earlier publications.[39,40] Similarly to the hydrogenous cyclic polymers, the deuterated materials were solution separated, and after fractionation using preparative GPC, a series of well-characterized narrow fractions of deuterated linear and cyclic polymers were obtained with polydispersity in the range 1.03−1.25. Because of the synthetic procedure adopted, the linear deuterated polymers present silanol end groups.

Molar mass values for the hydrogenous linear and cyclic materials reported in Table 1 were obtained from GPC measurements after calibration with linear and cyclic PDMS narrow standards, respectively. For the deuterated polymers, the same calibration curves were used, but M_w values were corrected to account for the difference between the monomer unit masses of deuterated and hydrogenous PDMS. The error in the determination of the molar mass from the calibration curves is equal to 13% and 10% for the linear and cyclic polymers, respectively.

The H/D blends were prepared by weighing the appropriate amounts of hydrogenated and deuterated polymers into spectroscopic grade quartz cells and agitating to ensure thorough mixing. The quartz cells used had internal dimensions of 10 mm (width) × 20 mm (height) × 1 mm (path length).

For the purpose of evaluating the level of incoherent scattering in H/D PDMS mixtures, three randomly labeled H/D PDMS copolymers containing different amounts of isotopic

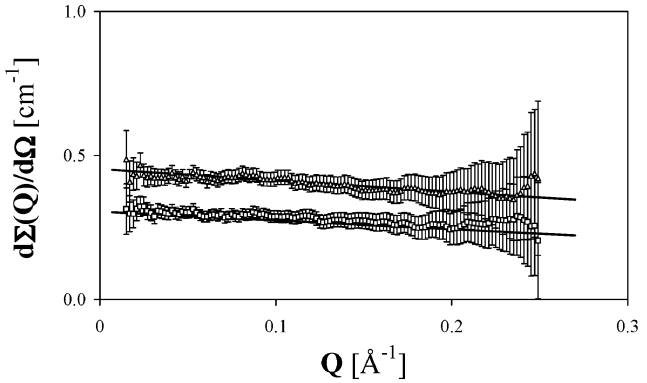

Figure 1. Scattered intensity of randomly labeled PDMS copolymers (LOQ) with volume fraction of hydrogenous monomer equal to 0.72 (△) and 0.44 (□). The continuous lines result from a linear combination of the scattering intensity from the pure hydrogenous and deuterated species, considering the volume fractions of H and D comonomers.

substitution were prepared. The amount of isotopic substitution for each of the copolymers was accurately established through NMR measurements. The volume fraction of the hydrogenous monomer in the three copolymers used here was equal to 0.44, 0.72, and 0.91.

3.2. Small-Angle Neutron Scattering. Neutron scattering measurements were carried out on the LOQ small-angle neutron scattering diffractometer at the ISIS Spallation Neutron Source (Rutherford Appleton Laboratory, UK)[42] and on the SANS instrument D22[43] (Institut Laue Langevin, France). For the measurements on LOQ, incident neutrons with wavelengths in the range $2.2 < \lambda < 10$ Å were used. SANS data were collected using both the ORDELA main detector bank and the high-angle detector bank, thus covering a Q range from 0.008 to 1.4 Å^{-1}. In this experiment we limit our discussion to data acquired on the ORDELA main area detector, i.e., covering the Q range 0.008−0.25 Å^{-1}. On D22, two different instrument configurations were used with a wavelength of 6 Å and sample−detector distances of 1.5 and 8 m to cover the Q range 0.0054−0.60 Å^{-1}.

All SANS measurements were performed at 298 K with the use of a temperature-controlled cell holder. Scattering patterns were isotropic, and therefore the raw data were radially averaged about the incident beam direction. The scattered intensities were then corrected for transmission and sample thickness, and the scattering from the empty cell was subtracted using standard RAL or ILL procedures.[44,45] The differential scattering cross section, $d\Sigma(Q)/d\Omega$ in units of cm^{-1}, was obtained after normalization with a polystyrene standard.

To subtract the incoherent background scattering, we have measured the scattered intensity of pure H and D PDMS samples. Subtraction of the incoherent scattering was performed using the appropriately volume fraction-weighted sum of the scattered intensities of the pure H and D PDMS. The validity of this method was evaluated by comparing the calculated scattering with the SANS data of the randomly labeled H/D PDMS copolymers containing different amounts of isotopic species. For these random H/D copolymers, the scattered intensities no longer contain information on the single-chain scattering, and thus SANS measurements allow us to estimate the level of the incoherent background. The scattering profiles recorded for two different copolymers are reported in Figure 1. The SANS data are compared with the scattering estimated from the appropriate volume fraction-weighted sum of the scattered intensities of the two pure H and D PDMS samples. It is evident that this method provides an accurate evaluation of the level of incoherent scattering.

4. Results

4.1. Linear Poly(dimethylsiloxane). Figure 2 shows the SANS data from LOQ of three 10HL/11DL samples with different compositions. The coherent SANS profiles

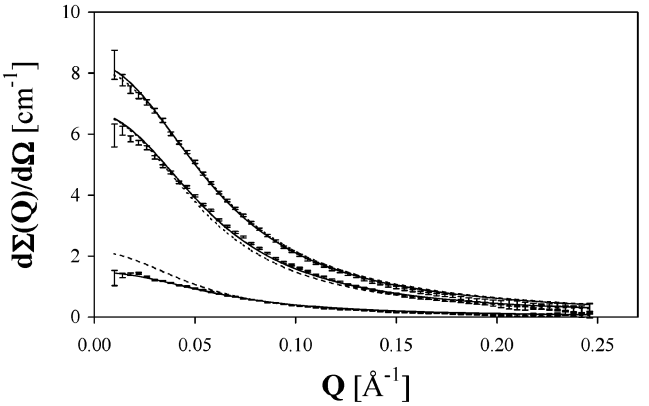

Figure 2. SANS data of 10HL/11DL after subtraction of the incoherent background (LOQ data). Error bars indicate experimental points. The three curves correspond to three different volume fractions of H PDMS: 0.06, 0.27, and 0.52 (in order of increasing scattered intensity). The continuous lines are fits to the experimental data using eqs 4 and 9 and a composition-dependent χ parameter. The dashed lines give similar fits to the data with a composition-independent χ value.

were analyzed (after subtraction of the incoherent scattering) using eq 4. For each sample, the SANS profiles relative to the three different concentrations were fitted using a simultaneous minimization procedure, with fixed M_w and M_w/M_n values determined from GPC measurements and known volume fractions. Fitting parameters were the radii of gyration and χ (the latter is computed from the extrapolated values of the scattered intensity at $Q = 0$ using M_w and the volume fractions of the H and D components).

We have adopted two fitting procedures; the corresponding results are displayed in Figure 2 as continuous and dashed lines. The latter refer to fits using composition-independent χ values while the continuous lines were generated by letting χ vary with composition. It is evident that a composition-dependent χ gives a better description of the experimental data, particularly at low concentrations.

For all linear H/D PDMS blends studied on LOQ, the modified Debye equation (eq 9) describes the Q dependence of the SANS intensity up to the highest Q values. As discussed elsewhere,[23] this observation is supported by the Q^{-2} dependence displayed at large Q values, a result that is predicted for Gaussian statistics.

The D22 SANS data for six 10HL/12DL PDMS samples are plotted in Figure 3. Contrary to the LOQ data analysis, here we plot the scattered intensity, prior to the subtraction of the incoherent scattering, and therefore an incoherent background has been added to the fits. Copolymer samples had not been available at the time of the D22 experiment. Background subtractions from the pure hydrogenous and deuterated polymers proved difficult, and the different methods that were used either under- or overestimated the level of incoherent scattering.

In agreement with the LOQ data analysis, we have used composition-dependent χ parameters to fit the D22 data. As noted for LOQ, the simultaneous fitting procedure provides excellent fits to the SANS profiles over the whole range of compositions, and the incoherent background accounts for the changes in scattered intensity which are observed in Figure 3 at high Q values.

The use of two different configurations on D22 afforded data over a wide Q range from 0.0054 to

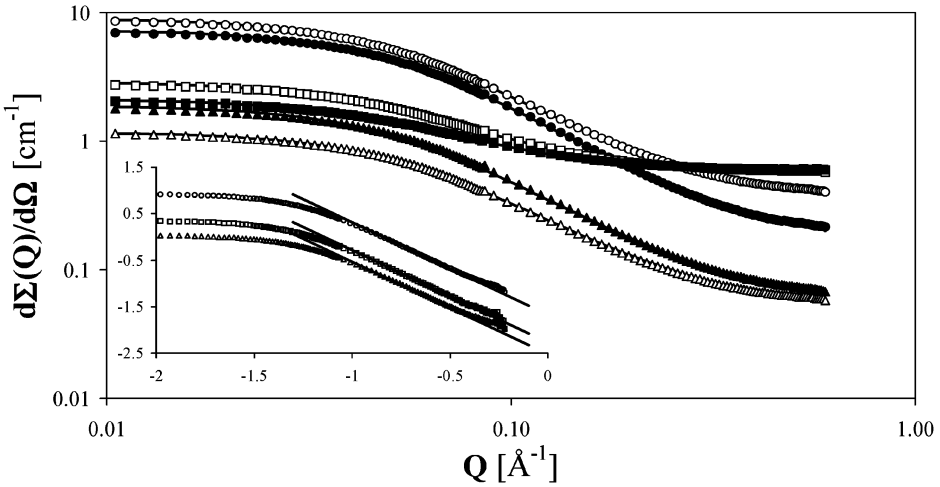

Figure 3. D22 data of 10HL/12DL prior to subtraction of the incoherent background at volume fractions of H PDMS: 0.03 (△), 0.05 (▲), 0.27 (●), 0.65 (○), 0.94 (□), and 0.96 (■). Continuous lines are fits using eqs 4 and 9, after addition of a flat incoherent background, with composition-dependent χ parameters. In the inset, selected data are plotted in a log−log scale, after subtraction of incoherent scattering, along with lines of slope −2.

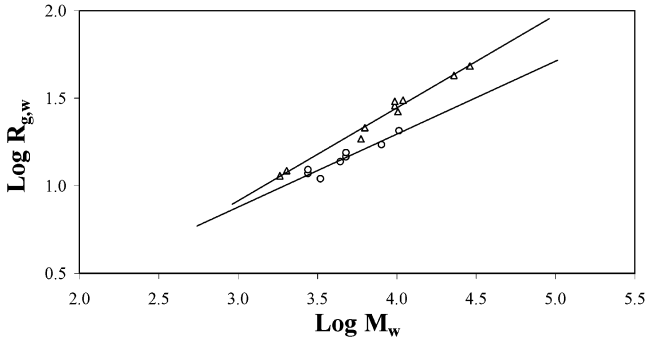

Figure 4. Weight-average radii of gyration vs M_w for the linear (△) and cyclic (○) H/D blends investigated in this work (data are displayed for both H and D components).

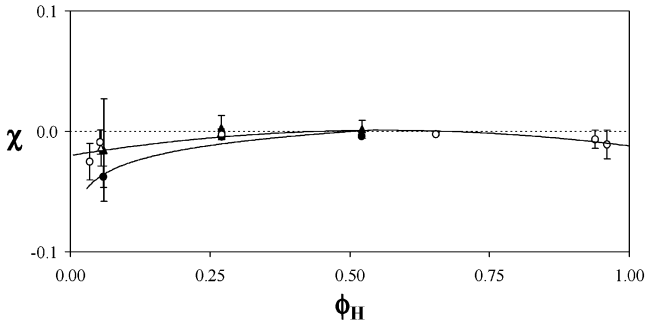

Figure 5. Interaction parameters vs blend composition as determined by SANS for mixtures of linear hydrogenated and deuterated PDMS: (▲) 2HL/2DL, (○) 10HL/12DL, (●) 10HL/11DL, (△) 6HL/6DL. The solid lines are guide to the eye and on the low ϕ_H side give an indication of the range of deviation observed.

0.60 Å^{-1}. Thanks to this feature, it is possible to verify that Gaussian scaling is retained up to high Q values. This is shown in the inset of Figure 3 where three selected curves are shown, after subtraction of the incoherent scattering, and the scattering at large Q compared to a slope of −2.

Fitting parameters extracted from the analyses of the LOQ and D22 data are combined in Figures 4 and 5. As described in section 2, SANS gives a measure of the z-average radii of gyration $R_{g,z}$, and in analogy to light scattering, weight-average values of molar mass are determined from the extrapolated intensity at $Q = 0$. To make meaningful comparison between polymer dimensions and molecular weight, the $R_{g,z}$ values need to be converted to the corresponding weight averages using the relationship

$$R_{g,w}{}^2 = \frac{u+1}{2u+1} R_{g,z}{}^2 \tag{10}$$

where u is the polydispersity index defined earlier.

$R_{g,w}$ values are plotted in Figure 4 vs M_w on a double-logarithmic plot for all blends of linear H and D PDMS investigated. The molecular weight dependence of the weight-average radii of gyration is described by

$$R_{g,w} = (0.22 \pm 0.03) M_w{}^{0.53\pm0.03} \tag{11}$$

close to the theoretical exponent of 0.50, predicted for linear chains that obey Gaussian statistics. If $R_{g,w}$ is assumed to vary as $M_w{}^{0.5}$, then the prefactor is equal to 0.28 ± 0.04, which is in good agreement with experimental values, reported to vary between 0.285[20] and 0.265.[46]

The composition dependence of the interaction parameter χ is shown in Figure 5; error bars were calculated from the error in the determination of the blend volume fractions and the error associated with the determination of the weight-average molar mass from GPC. Although the magnitude of the error in the determination of χ increases at the two extremes of the composition range, χ values seem to vary with molecular weight and blend composition. The trend is similar for both D22 and LOQ data (Figure 5). A detailed discussion of these results is presented in one of the following sections.

4.1. Cyclic Poly(dimethylsiloxane). Contrary to the linear PDMS chains, the SANS profiles of the H/D cyclic blends could not be modeled by the Debye equation. This finding has been discussed in a separate publication[23] where we show that the form factor developed by Casassa (eq 7) better describes the scattering curves over the whole experimental Q range. As shown elsewhere,[23] the discrepancy between Debye model and SANS data is large only for relatively small cyclics with M_w up to 11 000 g mol^{-1}. As the molecular weight of the cyclics increases, deviations are observed from the Casassa model, and the Debye

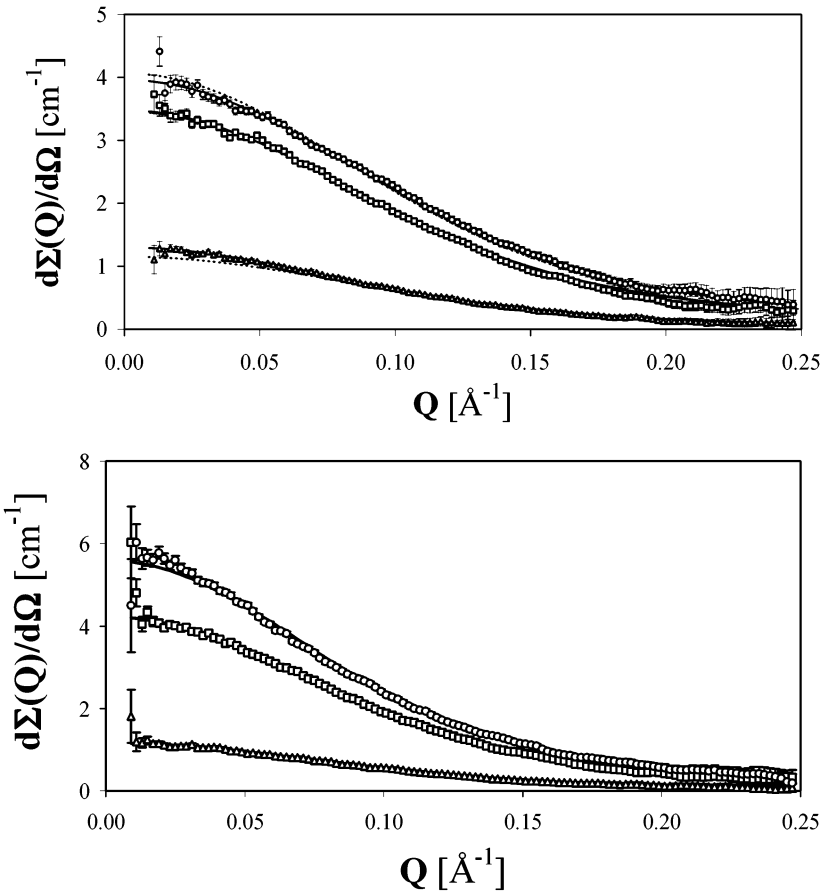

Figure 6. LOQ data of 5HC/5DC (a) and 5HC/11DC (b) after subtraction of the incoherent background at three volume fractions of H PDMS: 0.06 (△), 0.26 (□), and 0.52 (○). The continuous lines indicate fits to the experimental data using eqs 4 and 7 and a composition-dependent χ parameter. The dashed lines in (a) provide similar fits to the data with a composition-independent χ value.

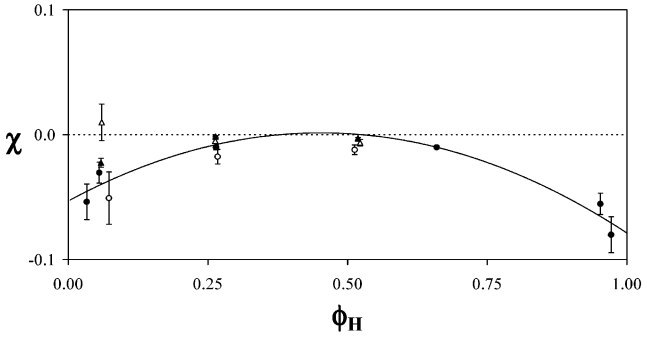

Figure 7. Interaction parameter vs blend composition as determined by SANS for mixtures of cyclic hydrogenated and deuterated PDMS: (○) 3HC/3DC, (●) 9HC/11DC, (△) 5HC/5DC. The solid line is a guide to the eye.

model better describes the SANS curves. This is largely a consequence of the inability to obtain pure high molecular weight cyclic fractions, free from linear chains.

The SANS data of the H/D cyclic blends with M_w up to 11 000 g mol^{-1} were analyzed using the Casassa form factor, following a procedure similar to that described in the previous section for the linear blends. For each blend, SANS profiles of samples with different composition were simultaneously fitted using either a constant (dashed line in Figure 6) or an adjustable χ parameter (continuous line in Figure 6). Once again, best fits are obtained when χ is allowed to vary with composition and experimental χ values are plotted in Figure 7.

Our use of eqs 7 and 9 to fit the experimental data of the cyclic and linear PDMS, respectively, may seem inconsistent. While eq 9 accounts for the polydispersity of the samples, the form factor of Casassa as expressed by eq 7 is developed for monodisperse cyclics. Here we note that, as shown elsewhere,[23] due to the narrow polydispersity of the samples used in this work, the effect on the calculated curves and therefore on the fitting parameters is negligible.

The weight-average radii of gyration of cyclics with M_w up to 11 000 g mol^{-1} are compared to those determined for blends of linear chains in Figure 4. The log−log plot gives a linear trend between $R_{g,w}$ and M_w which, for cyclics, is described by the relationship

$$R_{g,w} = (0.4 \pm 0.2)M_w^{0.42\pm0.05} \qquad (12)$$

Equation 12 indicates a less pronounced molecular weight dependence for the cyclics compared to linear chains, and it is in excellent agreement with the prediction that chain dimensions of rings in bulk should scale with their degree of polymerization as $N^{0.4}$.

5. Discussion and Conclusions

5.1. Radii of Gyration. The problem associated with ring sizes in comparison to the dimension of linear chains having the same chemical structure and degree of polymerization has stimulated theoretical and experimental work over many years. One of the first studies to be reported in the literature is the work of

Kramers,[9] who proposed that the ratio of the mean-square radii of gyration of Gaussian chains and ring polymers at theta conditions is equal to

$$\frac{R_{g,l}^2}{R_{g,c}^2} = 2 \tag{13}$$

In the same work, Kramers discussed with the expansion of rings and chains in a thermodynamically good solvent. For expanded coils, a decrease in the ratio $R_{g,l}^2/R_{g,c}^2$ to 1.9 is predicted. This result is in good agreement with data reported by Higgins et al.[4] for cyclic and linear PDMS in d_6-benzene, which is a good solvent for this polymer.

It is of interest to compare values of the radii of gyration of cyclic and linear PDMS with literature data. Scaling exponents calculated by us from the SANS data of cyclic and linear PDMS in d_6-benzene solutions at 292 K reported by Higgins et al.[4] are $\nu = 0.64 \pm 0.02$ and 0.68 ± 0.04, respectively. The similarity among ν values leads to the conclusion that cyclics and linear chains follow the same scaling law in dilute solution. This finding is in agreement with expectations based on the computer simulations of Muller et al.[14] and Monte Carlo studies of Frisch et al.[49] For isolated rings, the simulations predict ring sizes to scale as $R_g \propto N^\nu$ with $\nu = 0.595$, close to the excluded-volume exponent of 0.588 expected for linear athermal chains. Thus, results on cyclic and linear polymers in solution indicate that the static properties of the rings are not altered by the presence of topological constraints, and one expects similar swelling exponents ν for the two polymers.

Interesting conclusions can be drawn by comparing weight-average radii of gyration for rings and linear chains in the melt. Values plotted in Figure 4 indicate that both rings and linear chains follow a power law of type $R_{g,w} \propto M^\nu$. There is clear indication that the cyclic molecules in the undiluted state have smaller dimension than predicted from Gaussian statistics. While for the linear chains $R_{g,w} \propto M^{0.53\pm0.03}$, close to the result predicted from Gaussian statistics, ring dimensions (for samples with $M_w < 11\,000$ g mol^{-1}) scale as $R_{g,w} \propto M^{0.42\pm0.05}$ (Figure 4). This is an important result, in good agreement with computer simulations and theoretical predictions that chain dimension of cyclics in bulk should scale with their degree of polymerization as $N^{2/5}$.

As pointed out by Pakula et al.,[16] the ratio $R_{g,l}^2/R_{g,c}^2$ increases with increasing chain length, thus deviating from the result based on Gaussian statistics that $R_{g,l}^2/R_{g,c}^2 = 2$. Such a relationship is strictly valid only in dilute solution where topological interactions are absent.

It has been shown that, for any given number of segments N, rings in the melt are smaller and more compact than linear chains. The scaling exponent reported by Muller et al.[14] is 0.39 ± 0.03, in the limit of infinite molar masses. Similarly, using a Flory-like argument based on the free energy of a ring, Cates and Deutsch[15] predicted a scaling law $R_g \propto N^\nu$ with $\nu = 2/(d+2)$, where d is the dimensionality, and therefore for $d = 3$ we expect $\nu = {}^2/_5$.

Our results for cyclic PDMS are in very good agreement with the predicted literature values. We have shown elsewhere[23] that, due to the synthetic procedure that has been adopted for the preparation of the cyclic molecules, cyclic samples are free of contamination from linear chains up to ca. 11 000 g mol^{-1}. Therefore, we are unable to verify whether agreement between theory and experiments extends to molar masses above 11 000 g mol^{-1}.

Table 2. Comparison between χ Values Evaluated from Data Reported by Beaucage et al. for Equimolar Blends and Those Extracted in This Work (from the RPA Approach Using a Composition-Dependent χ Parameter), for Selected H/D PDMS Blends

sample	M_w^{av}	ϕ_H	$\chi_{Beaucage}$	χ_{RPA}
2HL−2DL	2000	0.52	-0.03 ± 0.01	0.002 ± 0.01
10HL−11DL	10340	0.50	-0.005 ± 0.003	-0.004 ± 0.001
10HL−12DL	10769	0.65	-0.005 ± 0.003	-0.002 ± 0.002

5.2. Interaction Parameters. The second parameter evaluated from the SANS data is the interaction parameter χ. The existence of a small positive interaction parameter between H/D mixtures of the same chemical species is well documented in the literature. Early SANS studies[20] on linear PDMS reported a χ value of 1.7×10^{-3} for high molecular weight samples, at room temperature, a result that should lead to phase separation for symmetric blends with $M_w > 100\,000$ g mol^{-1}.

For the low molecular weight linear PDMS samples investigated here, we have reported composition-dependent χ values, which are small but negative at room temperature and vary with molar mass (Figure 5). There appears to be a common trend in the composition dependence of χ; data shown in Figure 5 display a downturn curvature which for 10HL/12DL extends throughout the composition range. Similar downturn composition dependencies of the interaction parameter have been observed for other isotopic mixtures.[47−49]

The results reported here are in good agreement with χ values from Beaucage et al. for isotopic symmetric equimolar mixtures of linear H/D PDMS. In that work, interaction parameters were evaluated from the SANS profiles as a function of molecular weight and temperature, and this made it possible to establish a general relationship between χ, M_w, and T:

$$\chi(T) = A + \frac{B}{T} \tag{14}$$

$$A(n) = \frac{-2.6 \pm 0.6}{n} \tag{15}$$

$$B(n) = (0.15 \pm 0.1) + \frac{530 \pm 100}{n} \tag{16}$$

where n is the average degree of polymerization. From these relationships it is possible to evaluate the interaction parameter for the H/D blends of similar molecular weight investigated here at 298 K and at $\phi_H \approx 0.5$. Calculated values are reported in Table 2. As shown in Table 2, there is good agreement between interaction parameters, except for the lowest M_w sample investigated here. The latter result may be affected by end group effects which are negligible for the other blends. Our samples differ from those of Beaucage et al. which contain trimethylsilane end groups. While our H PDMS samples have the same functionality, the D PDMS polymers have silanol end groups. This difference may be responsible for the discrepancy between calculated and experimental χ values for the 2HL/2DL blend.

Figure 7 shows the interaction parameters determined from the RPA analysis of the H/D cyclic PDMS samples. For these blends, the downward curvature is similar to that observed previously for the linear PDMS

mixtures. Comparison between χ values leads to the conclusion that, for any given molecular weight and composition, interaction parameters are more negative for the cyclics than for the linear chains. The main difference is observed when blends of low molecular weight linear chains are compared to those of cyclic polymers with similar M_w since in the former end group effects play an important role.

5.3. Expansion Factors. Because of the small negative χ values, the polymer chains find themselves in a situation that is similar to good solvent conditions; swelling of the chain is expected compared to the unperturbed dimensions. This expectation was confirmed by calculating an effective expansion factor, α, which is defined as the ratio between the measured characteristic ratio, $C_{measured}$, to its unperturbed value (C_∞):

$$\alpha^2 = \frac{C_{measured}}{C_\infty} \tag{17}$$

$$C_{measured} = \frac{a^2}{2l^2} \tag{18}$$

where l is the Si−O bond length (1.64 Å) and a is the statistical length. For PDMS linear chains, C_∞ has been reported to be equal to 5.85.[21]

$C_{measured}$ can be readily evaluated from the experimental statistical length determined from eq 6. In practice, an average statistical length can be obtained by fitting the data to eqs 4−6 and using a single a value, which represents an average between the statistical lengths of the two components in the isotopic mixture. This analysis was carried out for two selected blends 10HL/11DL and 23HL/31DL, giving a values equal to 6.39 and 6.21 Å, respectively. From these, the effective expansion factor α is found to be 1.14 and 1.11, indicating coil expansion. Because of the narrow molecular weight range investigated here, this expansion factor appears to be almost independent of molecular weight.

In principle, a similar procedure could be used to calculate the parameter α for the cyclic blends. However, the conformation of cyclic chains is dependent upon the molecular weight and so is the expansion factor, as indicated by the relationship between R_g and M:

$$R_g \propto M^\nu = M^{0.5}\alpha^3 \tag{19}$$

Since $\nu = 0.42$ for cyclic PDMS, it follows that the expansion factor should vary as $M^{-0.08}$, thus displaying a small but nonnegligible molecular weight dependence.

6. Conclusions

We have presented an investigation of the conformational behavior of linear and cyclic PDMS in bulk, using small-angle neutron scattering. Contrary to results reported for dilute solutions of linear and cyclic chains, due to topological effects, $R_{g,l}^2/R_{g,c}^2$ is not simply equal to 2.

While isotopic blends of linear PDMS adopt conformations which obey Gaussian statistics, for H/D cyclic PDMS mixtures $R_g \propto M_w^{0.40}$, indicating that the highly flexible cyclic polymers in the melt adopt an even more compact conformation than that of unperturbed rings (already more compact than the corresponding linear chains). This behavior supports predictions from computer simulations and theoretical studies.

Acknowledgment. The authors acknowledge support by the Engineering and Physical Research Council (GR/M00596 and GR/M00725). We thank the instrument LOQ and D22 scientists, Drs. Steve King, Richard Heenan, and Isobelle Grillo for their assistance with the neutron scattering measurements, and ISIS and ILL for granting us the required beam time to carry out the experiments.

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MA049565W