Studies of cyclic and linear poly(dimethylsiloxanes): 28. Viscosities and densities of ring and chain poly(dimethylsiloxane) blends

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Two physical properties, density and low-shear viscosity, were studied in order to investigate the effects of blending chemically identical but topologically different poly(dimethylsiloxane) (PDMS) fractions (i.e. rings and chains). Deviations from a purely additive model were obtained for 50:50 (by volume) blends of cyclic and linear PDMS samples. Such investigations may be able to probe packing capabilities, the amount of free volume in a fraction and the extent and effects of chain threading.

(Keywords: density; viscosity; PDMS; blends)

INTRODUCTION

The preparation and physical investigation of sharp (narrow distribution) fractions of cyclic poly (dimethylsiloxane) (PDMS) have been reported in detail in previous papers in this series[1]. Cyclic macromolecules have been prepared with number-average degrees of polymerization up to 500, and these have been characterized by gel permeation chromatography and gas–liquid chromatography (for the low-molar-mass samples). The cyclic nature of these molecules has been verified by a range of physical studies including intrinsic viscosity, bulk viscosity, low-angle neutron scattering, quasielastic light scattering, network trapping and diffusion investigations.

Initial investigations comparing the bulk physical properties of sharp fractions of cyclic and linear PDMS have revealed differences due to the topological change from linear to cyclic molecules. Some of the effects of blending corresponding cyclic and linear PDMS samples are reported here. Such investigations should be able to probe packing capabilities, free volume in the samples and also chain threading effects. Differences between cyclic and linear systems should be revealed as a difference from the mean of the two individual values (either in their volume or weight fractions).

Since the blended fractions under investigation here involve PDMS linear chain segments interacting with similar cyclic PDMS segments, any problems associated with microphase separation are minimized, particularly since the majority of the samples are of relatively low molar mass. Single-phase blends are therefore attainable where properties are stable and reproducible.

Two physical properties, density and zero-shear-rate melt viscosity, were chosen to investigate the effects of blending chemically identical but topologically different PDMS fractions. Density values indicate the efficiency of molecular packing in a sample. Experimental data had already been obtained[2,3] for density and refractive index values, and it appeared that, in the region of less than ~40 skeletal bonds, the values obtained most likely reflected changes in configuration restrictions and molecular shapes. Since the densities of PDMS rings and chains of relatively high molar mass were known to be similar, the study of blending effects was restricted to the low-molar-mass region.

Viscosity is a measure of the frictional resistance to flow and its value is affected by molecular frictional forces, chain entanglement and free volume. Since the frictional force is, trivially, due to the sliding motion of other similar polymer segments, it is strongly dependent on the free volume available and/or steric hindrances to rotation or intermolecular forces. Zero-shear viscosity also varies as a function of molar mass. The linear monomeric friction coefficient varies at low molar mass owing to chain-end effects, and hence this results in a variation in the viscosity with molar mass. Further, for ring fractions in the low-molar-mass region there may be configurational restrictions that reduce flow and therefore increase viscosity relative to the corresponding linear molecules.

DENSITIES OF BLENDS

Experimental

Cyclic and linear PDMS fractions were prepared and accurately characterized by methods described previously[4,5] (see *Table 1*). Density measurements were determined with the use of a Digital Precision Density

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Table 1 Sample characterization and densities

n_n[a]	M_w/M_n[b]	Density (g cm^{-3})
Rings $[(CH_3)_2SiO]_x$		
12.1	1.02	0.96342
14.0	1.02	0.96800
16.0	1.02	0.97138
18.3	1.09	0.97206
22.2	1.07	0.97346
23.6	1.01	0.97254
32.0	1.06	0.97230
40.1	1.01	0.97220
Chains $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$		
12.2	1.03	0.90995
14.5	1.03	0.91512
15.3	1.02	0.91826
18.5	1.02	0.92564
22.6	1.01	0.93269
23.7	1.02	0.93443
32.0	1.04	0.94330
40.3	1.02	0.94617

[a] Number-average number of skeletal bonds

[b] The ratio of the mass-average molar mass M_w to the number-average molar mass M_n

Meter device DMAO2C (Anton Paar, Graz, Austria), which reduces the determination of the densities of liquids and gases to an electronic measurement of the frequency response period (T) for oscillation of the fluid in a small U-tube. Approximately 0.7 cm^3 of each liquid sample was used and the oscillating system was thermostatted at 298 ± 0.1 K. Each sample was thermally equilibrated for at least 30 min before density measurements were made. Density values were determined by taking the average values of at least six frequency measurements for each sample. The instrument manufacturer's error estimate during density determination is $\pm 3.5 \times 10^{-6}$ g cm^{-3}.

Blended samples were obtained by mixing ring and chain fractions of as near equivalent number of skeletal bonds as samples allowed, in a ~50:50 ratio by volume. This ratio was determined by accurately weighing the samples. The linear sample was pipetted into the cyclic fraction and the liquids were thoroughly mixed and agitated. Mixed samples were left at least 48 h before any measurements were obtained.

Results and discussion

Values for the density measurements of individual ring and chain fractions are depicted in *Figure 1*. They compare reasonably well with previously published values[2,3,6,7]. The densities of the linear fractions at 298 K increase steadily with molar mass. The densities of the cyclic fractions at 298 K increase with ring size to a maximum value of 0.97346 g cm^{-3} at $n_n \simeq 22$ and decrease slightly to a value of 0.97220 g cm^{-3} at $n_n = 40$. The density values of linear fractions were always found to be less than those of corresponding cyclic fractions.

The density values of the ~50:50 ratio (by volume) blended (cyclic and linear) PDMS fractions are given in *Table 2* and in *Figure 2*, where they appear as a function of the average number of skeletal bonds. Also shown are the positions on the plot that the blended systems would have occupied if the densities of the ring and chain portions had been purely additive, i.e. that is assuming that the rings and chains would occupy the same volume in a mixed sample as they would in their individual fractions. Blended samples with $n_{av} = 12$ and 40 have density values that correspond very closely to the calculated additive values. Moving progressively nearer to the 22-bond sample, the deviation from an additive system becomes pronounced. The maximum deviation occurs at $n_{av} \simeq 22$ and there is now a definite difference in the third decimal place, which is much greater than the error estimation.

This deviation from a purely additive system is thought to be related to the occurrence of a maximum at

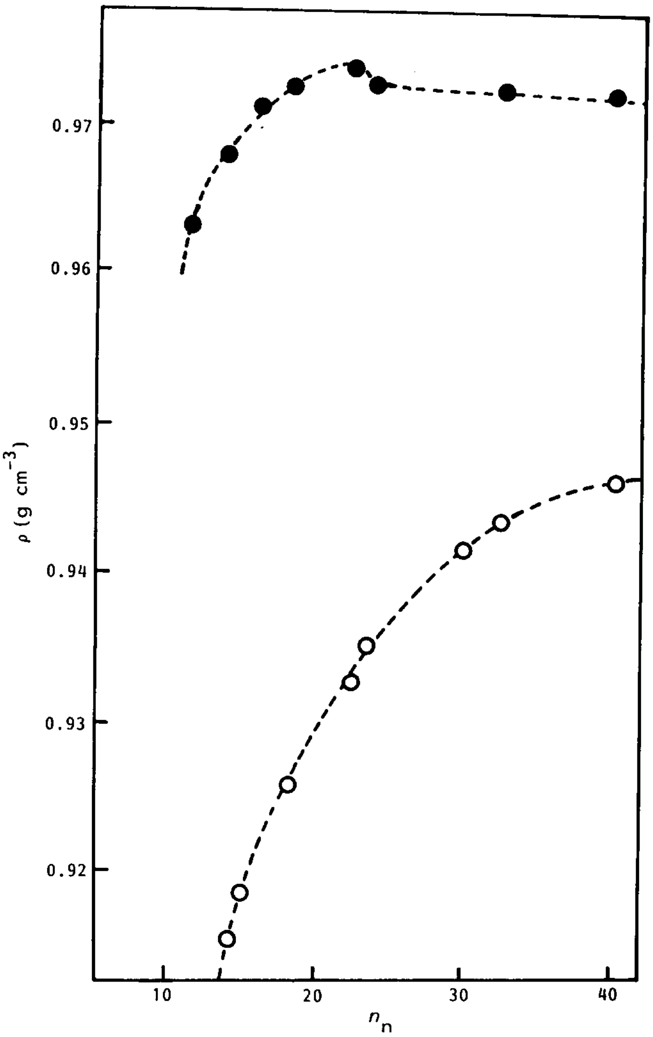

Figure 1 Densities of ring (●) and chain (○) PDMS fractions at 298 K

Table 2 Mixtures of ring and chain samples

Ring n_n	Chain n_n	Volume ratio, ring:chain	Additive density (g cm^{-3})	Experimental density (g cm^{-3})
12.1	12.2	50.01:49.99	0.93669	0.93650
14.0	14.5	51.24:49.76	0.94169	0.94170
16.0	15.3	50.10:49.90	0.94488	0.94419
18.3	18.5	49.93:50.07	0.94882	0.94830
22.2	22.6	49.86:50.14	0.95301	0.95101
23.6	23.7	49.84:50.16	0.95342	0.95200
32.0	32.0	50.03:49.97	0.95781	0.95725
40.1	40.3	50.06:49.94	0.95920	0.95890

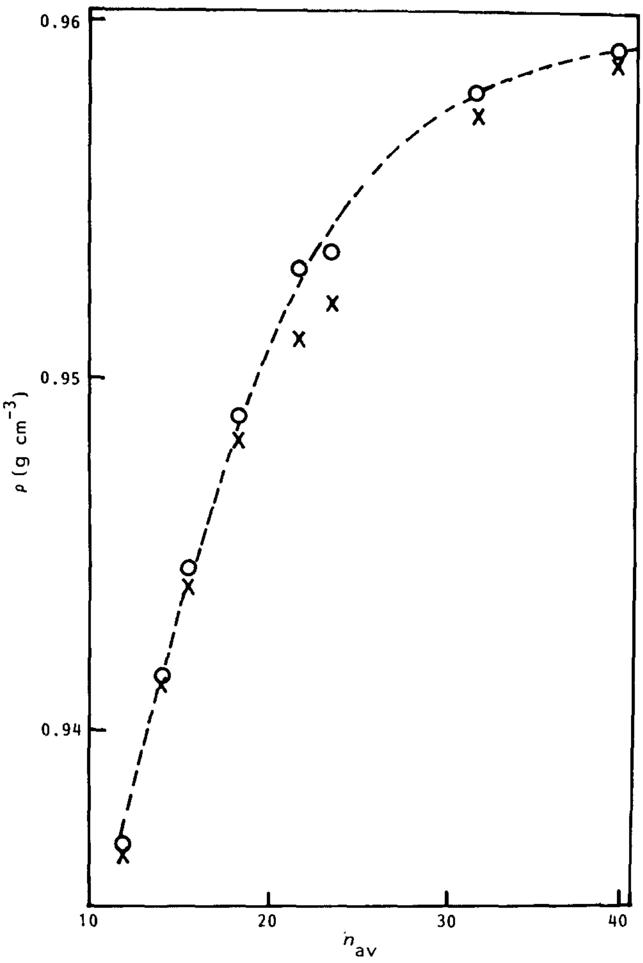

Figure 2 Experimental density values of the 50:50 v/v cyclic and linear PDMS fractions as a function of the number-average number of skeletal bonds n_{av}. The theoretical additive values (○) are compared with the experimental density values (×)

approximately 22 skeletal bonds in the ring density plot. It is believed that this behaviour is due to the potential for very favourable packing caused by the three-dimensional profile of a 22-bond siloxane ring. Calculations[8] on the shapes of cyclic and linear PDMS molecules have suggested that rings in the 20-bond region can take up near-planar configurations. These calculations involved the determination of the principal axes of an equivalent ellipsoid that represents the average shape of the molecule in question. The computations revealed that the major change on ring formation was a reduction in the longest axis of the ellipsoid, and that in the low-molar-mass region cyclic molecules are more symmetric than the corresponding linear molecules.

The shape of the all-*trans* conformation of a 22-bond ring is like a flat disc, as shown in *Figure 3*. The origin of this, and probably the reason for the near-planar molecular shapes in this ring size region, stem from the unequal skeletal silicon and oxygen bond angles for the PDMS molecule. This geometric reality is therefore a contributory factor to the appearance of the density plot. The density values reflect the changes in molecular packing that would be expected to occur given the special disc-like shape of the rings in the 22-bond region, since flat discs would be expected to pack much more efficiently in comparison to the theoretically predicted ellipsoidal-like structures of larger rings and chains. The densities of the blended fractions add further substantiation to this explanation since addition of linear molecules to a ring fraction perturbs the efficient packing.

BULK VISCOSITIES OF BLENDS

Experimental

Bulk viscosity measurements were determined by using a Contraves Low Shear 30 Rotational Rheometer. This is a highly sensitive torque-measuring device that can generate 30 fixed shear rates in a geometric progression through the range 10^2 to $10^{-2}\,s^{-1}$ for the Couette geometry employed.

Since the viscosity is heavily dependent on the friction coefficient, and the friction factor is controlled by local features such as free volume, samples of as near equivalent bond number as possible were mixed in a 50:50 ratio by volume. Characterization details of the samples are given in *Table 3*. All the siloxane samples studied here behaved as Newtonian fluids since they showed shear-rate-independent viscosities.

The volume fractions were accurately determined by precisely weighing the samples (± 0.00005 g) and applying known density values (± 0.000005 g cm^{-3}). The blends were thoroughly mixed and agitated and left for at least 48 h before any measurements were obtained.

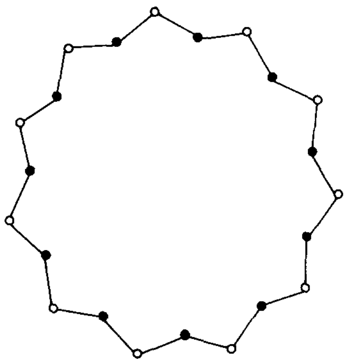

Figure 3 Skeletal structure of an all-*trans* 22-bond siloxane ring. ●, Oxygen; ○, silicon

Table 3 Sample characterization and viscosities (shear rate = 8.11 s^{-1})

Rings			Chains		
n_n	M_w/M_n	η at 298 K (cP)[a]	n_n	M_w/M_n	η at 298 K (cP)
14.0	1.02	9.51	14.5	1.03	3.94
22.2	1.02	18.25	22.6	1.01	6.64
32.0	1.06	17.92	32.0	1.04	9.67
57.0	1.03	25.72	57	1.04	15.68
			72	1.06	21.07
86	1.02	27.02	86	1.08	26.77
99	1.05	30.47			
114	1.01	34.09	112	1.06	32.48
206	1.04	58.53	203	1.05	67.30
334	1.01	65.85	330	1.05	138.69
582	1.08	194.97	591	1.04	335.30
866	1.08	783.76	818	1.12	968.59

[a] 1 cP = 10^{-3} kg m^{-1} s^{-1}

Table 4 Summary of mixed ring and chain viscosity (results at 298 K)

Ring n_n	Chain n_n	Volume ratio, ring:chain	Experimental η (cP)	Calculated η (cP)	Difference (%)
14.0	14.5	51.24:49.76	5.47	6.83	−19.9%
32.0	32.0	50.00:50.00	12.67	13.80	−8.2%
57	57	50.25:49.75	19.62	20.73	−5.4%
86	86	50.49:49.51	26.82	26.89	−0.3%
99	102	51.02:48.98	31.84	31.10	+2.3%
114	112	49.93:50.07	33.21	33.28	−0.2%
206	203	49.93:50.07	67.21	62.92	+6.8%
334	330	50.37:49.63	113.36	102.00	+11.1%
582	591	50.16:49.84	318.54	264.66	+19.2%
866	818	50.03:49.97	1082.86	876.12	+23.6%

Results and discussion

The bulk viscosity results obtained are shown along with calculated values for a purely additive system in *Table 4*. The blends generally show a lower viscosity than the calculated values below approximately 100 bonds. However, as the size of the macromolecules in the blends increases, the percentage difference from the calculated figure was found to increase steadily from a point where the experimental viscosities are below that for a purely additive situation, to a position where the bulk viscosity is much higher than that calculated additively. The results are shown graphically in *Figure 4*. The viscosity values for the cyclic and linear PDMS blended samples indicate a definite deviation from a purely additive system. This is in agreement with the data presented by McKenna and Plazek[9] for ring and chain polystyrene blends, where they also found a far from additive situation.

With reference to the density measurements, there might be some connection between the packing capabilities of small rings and chains with the negative deviation from additivity of the viscosities. However, thermodynamics of mixing as well as free volume of the systems may have an influence on the viscosity of the blend, and the results here cannot really give an indication as to the level of their importance.

One possible explanation for the viscometric behaviour observed is that the chain molecules thread themselves through the ring molecules in such a way as to change the molecular motion in the system. It is already known from network entrapment experiments[10–12] that chains can thread through rings providing the 'effective hole size' of the ring is large enough. The work of Clarson *et al.*[10,11] has shown that a dimethylsiloxane ring must have at least 38 bonds to allow threading by a hydroxyl-terminated PDMS chain. Furthermore, as the ring size increases, a higher percentage of cyclic PDMS can be topologically trapped in the network, i.e. become threaded. Mark and DeBolt[13] have carried out theoretical modelling calculations for the trapping process. They have successfully reproduced the experimental data over a large percentage of the molar mass scale for PDMS rings. The increase in threading capability with increase in ring size is believed to be reflected in the viscometric results for the blends, which show a marked rise in the viscosity of the blended fractions as the ring sizes become larger.

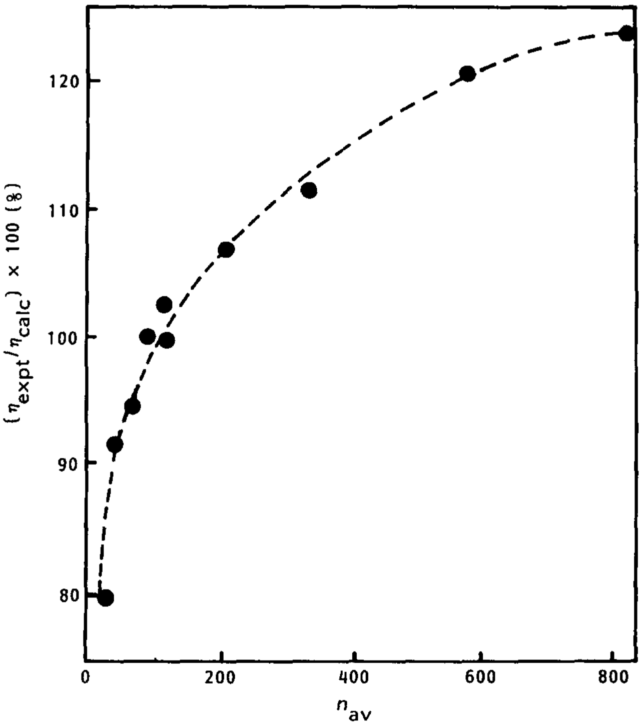

Figure 4 Ratios (%) of the experimental viscosity values to the calculated viscosity values for blended fractions of cyclic and linear PDMS shown as a function of the average number of skeletal bonds n_{av}

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