Studies of cyclic and linear poly(dimethyl siloxanes): 8. Light scattering measurements in good and poor solvents

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Weight average molar masses (M_w) and second virial coefficients (A_2) have been measured for linear and cyclic poly(dimethyl siloxane) (PDMS) fractions in toluene at 298K and for linear PDMS in bromocyclohexane at 301 K. The values of M_w are compared with those deduced previously using gel permeation chromatography, broadly confirming the values already assigned to the fractions. The values of A_2 for linear PDMS in toluene are shown to be consistent with previously published values for oligomeric linear PDMS. The values of A_2 for cyclic PDMS approach those of linear PDMS for $M_w < \sim 1000$ g mol^{-1} and decrease more rapidly as M_w increases in approximate agreement with theoretical predictions. In addition, the conventional relations between A_2 and the expansion factor α_s are shown to be inapplicable at low molar mass.

Keywords Cyclic poly(dimethyl siloxane); linear poly(dimethyl siloxane); light scattering; second virial coefficients

INTRODUCTION

This paper presents the results of a study of well-characterized cyclic and linear poly(dimethyl siloxanes) (PDMS) fractions[1-6] using classical Rayleigh light-scattering. Weight-average molar masses (M_w) and second virial coefficients (A_2) have been measured in toluene at 298 K (a 'good' solvent[5]) and bromocyclohexane at 301 K. The latter has previously been reported to be a θ-solvent for high molar mass linear PDMS[7,8].

The values of M_w of the cyclic and linear polymers are compared with those obtained from previously-calibrated gel permeation chromatographic (g.p.c.) instruments. In addition, the values of A_2 for cyclic poly(dimethyl siloxanes) are compared with those determined for the corresponding linear polymers, as well as with theoretical predictions.

EXPERIMENTAL

Preparation of samples

The preparation of the polymer samples and the purification of bromocyclohexane were as described in the previous paper[6]. The toluene was freshly distilled before use. Solutions for light scattering were clarified by filtration (Millipore, average pore size 0.22 μm).

Light scattering measurements

These were carried out using a Sofica photometer (model 42000) and unpolarized incident light ($\lambda_0 = 435.8$ nm). The temperature was controlled to ± 0.1 K using an external water bath and circulating pump. Refractive index increments (dn/dc) were measured at the same wavelength using a PCL differential refractometer. For reference purposes the values of dn/dc are given in *Tables 1* and *2*.

Since the maximum molar mass reported in this study is $\sim 30\,000$ g mol^{-1}, the angular dissymmetry of the scattered light was neglected[9] and scattered intensities were measured at 90°, with results analysed according to the standard equation:

$$Kc/R_{90} = \frac{1}{M_w} + 2A_2c, \qquad (1)$$

c is the concentration, and

$$K(=2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2 \lambda_0^{-4} N_A^{-1})$$

is the optical constant for the scattering system. Here n_0 is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_0 is the wavelength of light *in vacuo* and N_A is the Avogadro constant. For calibration purposes the Rayleigh ratio R of benzene was calculated

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Table 1 Number-average numbers of skeletal bonds (n_n), weight-average molar masses (M_w) from g.p.c. and light scattering, second virial coefficients (A_2) and refractive index increments (dn/dc) for linear and cyclic PDMS in toluene at 298 K

n_n	g.p.c. M_w (g mol^{-1})	Light-scattering M_w (g mol^{-1})	A_2 (10^{-4} cm^3 g^{-2})	mol (dn/dc) (cm^3 g^{-1})
Linear PDMS				
41	1890	1890	13.6	−0.0876
127	6000	5750	11.6	−0.0874
196	9240	9470	10.6	−0.0855
262	12200	11700	9.57	−0.0844
345	15100	15300	9.94	−0.0849
508	20900	21800	8.95	−0.0841
631	25500	27000	8.32	−0.0847
697	28100	30100	8.04	−0.0845
Cyclic PDMS				
51	2010	1980	13.0	−0.0870
66	2630	2540	11.5	−0.0868
88	3500	3320	10.5	−0.0862
115	4530	4430	10.7	−0.0863
186	7250	6920	9.23	−0.0851
251	9570	9670	8.22	−0.0850
301	11900	12300	7.55	−0.0841
389	14900	15300	7.18	−0.0837
482	18800	21800	6.76	−0.0842

Table 2 Number-average numbers of skeletal bonds (n_n), weight-average molar masses (M_w) from g.p.c. and light-scattering and second virial coefficients (A_2) and refractive index increments (dn/dc) for linear PDMS in bromocyclohexane at 301 K

Fraction n_n	g.p.c. M_w (g mol^{-1})	Light-scattering M_w (g mol^{-1})	A_2 (10^{-4} cm^3 g^{-2})	mol (dn/dc) (cm^3 g^{-1})
23	1020	930	8.42	−0.1050
69	3170	3030	2.62	−0.0932
127	6010	5710	0.00	−0.0860
267	11600	10600	0.00	−0.0832
488	19900	18800	0.00	−0.0815
818	31400	32600	0.00	−0.0817

using the relation[9] $R/\mathrm{cm}^{-1} = 10^{-6}[45.4 + 0.109(T - 273)]$ and a glass block was used as a secondary standard.

Equation 1 applies to optically isotropic particles. For anisotropic particles the Cabannes correction has to be applied to account for the elliptical polarization of the scattered light[9]. The correction increases the excess Rayleigh ratio by a factor f_c and it has previously been shown to be particularly important for solutions of low molar mass PDMS in toluene[10].

RESULTS

Molar masses of cyclic and linear PDMS

The values of the weight-average molar masses (M_w) of cyclic and linear fractions measured by light scattering in toluene at 298 K (for linear and cyclic PDMS) and in bromocyclohexane (for linear PDMS) are listed in *Tables 1* and *2* respectively. The values of M_w assigned to each fraction using previously-calibrated analytical g.p.c. instruments are also listed. These calibrations were based on information obtained using gas–liquid chromatography (for cyclic and linear fractions with n_n <100), molar cyclization equilibrium constants and vapour pressure osmometry (for cyclic fractions) and light scattering (for higher molar mass linear fractions).

In *Figure 1* the molar masses deduced by g.p.c. are plotted against the corresponding values measured by light scattering. The unbroken line in *Figure 1* has a slope of unity. There is excellent agreement between molar masses found by the two methods up to molar masses of about 20000 (corresponding to n_n values of about 500 skeletal bonds). However, discrepancies are found at higher molar masses and differences of ~10% are observed at molar masses of about 30000.

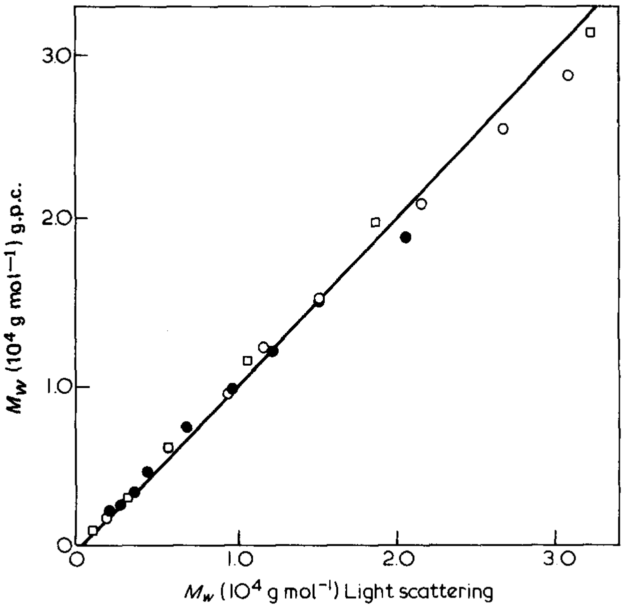

Figure 1 M_w obtained using g.p.c. plotted against values found here by light scattering for (○) linear and (●) cyclic PDMS in toluene at 298K and for (□) linear PDMS in bromocyclohexane at 301 K

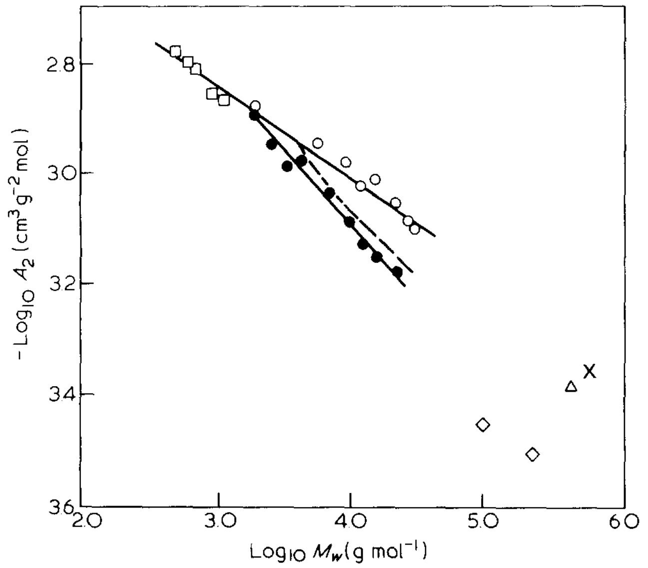

Figure 2 $\mathrm{Log}_{10}A_2$ plotted against $\log_{10} M_W$ (light-scattering) for (○) linear and (●) cyclic PDMS in toluene solution at 298 K. (□) Data of Huglin and Sokro for oligomeric linear PDMS. Data of (◇) Ref. 14, (△) Ref. 13 and (X) Ref. 15. Least-squares lines, through data (———). Calculated values of A_{2r} using Equation 6 (— — —)

Second virial coefficients in a 'good' solvent

Values of A_2 for solutions of cyclic and linear PDMS in toluene at 298 K are listed in *Table 1*. The maximum concentrations used vary from ~3% (w/w) for the highest molar mass sample to ~10% (w/w) for the samples of low molar mass. In all cases linear plots of Kc/R_{90} *versus* c were obtained, which at small values of M_w were similar to those reported by Huglin and Sokro[10].

The data in *Table 1* are plotted in *Figure 2* as $\log_{10}A_2$ *versus* $\log_{10} M_w$, where M_w is the value obtained by light scattering. The data for linear PDMS are in good agreement with data previously obtained by Huglin and Sokro for low molar mass, linear PDMS[12]. Both sets of data can be represented by an equation of the form

$$A_2 \propto M_w^{\gamma} \tag{2}$$

where $\gamma = -0.163$. The cyclic samples give values of A_2 which fall on a line of different slope with $\gamma = -0.253$. Also shown in *Figure 2* are four data points obtained by other authors[11-13] for linear PDMS of high molar mass. The points do not show any regular dependence on M_w, but it appears that our data would extrapolate to give approximate agreement with those of Price and Bianchi[11] and Kubuta, Kubo and Ogino[13].

The ratio of virial coefficients A_{2r}/A_{2l}

An expression for the ratio A_{2r}/A_{2l}, where the subscripts r and l denote ring and linear molecules respectively, has been derived by Yamakawa[14a] in terms of the modified Flory, Krigbaum, Orofino theory (F.K.O.m).

The second virial coefficient can be written as:

$$A_2 = N_A(n^2/2M^2)\beta\, h_0(\bar{z}) \tag{3}$$

where n is the number of segments in a chain of molar mass M, and β is the cluster integral representing the mutually excluded volume of a pair of segments. In the absence of values of β for cyclic molecules, it is assumed that β is unaffected by ring formation to define the ratio:

$$A_{2r}/A_{2l} = [h_0(\bar{z}_r)]_r/[h_0(\bar{z}_l)]_l. \tag{4}$$

The function $h_0(\bar{z})$ where $\bar{z} = z/\alpha_s^3$ has been calculated here using the F.K.O.m. equation[14b]:

$$h_0(\bar{z}) = \frac{1}{2C\bar{z}}\ln(1+2C\bar{z}), \tag{5}$$

with $C = 2.865$ for linear molecules.

Casassa[15] has evaluated the first-order coefficient, C in Equation 5 for a cyclic molecule and obtained the value 4.457. Thus combining Equations 4 and 5, and using the appropriate values of C one obtains:

$$A_{2r}/A_{2l} = \frac{5.73\ \bar{z}_l \ln(1+8.914\,\bar{z}_r)}{8.914\,\bar{z}_r\ \ln(1+5.73\,\bar{z}_l)} \tag{6}$$

The modified Flory equation:

$$\alpha_s^5 - \alpha_s^3 = \kappa z \tag{7}$$

forms a 'self-consistent' pair of equations[14c] with Equation 5 and allows the ratio A_{2r}/A_{2l} to be calculated from experimental values[3,5] of α_s. For a linear molecule $\kappa = 1.276$[14d] and Casassa[15] has calculated $\kappa = \pi/2$ for a cyclic molecule.

The dashed curve in *Figure 2* shows the calculated values of A_{2r}, relative to the least-squares line through the linear data. The agreement with experiment is good considering the assumption of constant β and the approximate nature of Equation 6. The ratio A_{2r}/A_{2l}, as defined in Equation 6, is predicted to become equal to unity as $\alpha_s \rightarrow 1$, that is $A_{2r}/A_{2l} \simeq 1$ for $M_w < 4000$ g mol^{-1}.

Approximate correlations of A_2 *and* α_s *for cyclic and linear PDMS*

Zimm, Stockmayer and Fixman[16] obtained a relation between $A_2M^{\frac{1}{2}}$ and (α_s^2-1) by eliminating z between series expansions for these functions and by assuming that for small z, $h_0(z)=1$, namely[17]: $A_2M^{\frac{1}{2}} = \{4\pi^{3/2}N_A(\langle s_0^2\rangle/M)^{3/2}/\kappa\}(\alpha_s^2-1)$. (8)

κ is the constant which appears in the modified Flory equation relating z and α_s (equation (7)). *Figure* 3 shows a plot of $A_2M^{\frac{1}{2}}$ *versus* (α_s^2-1) for cyclic and linear PDMS, using the experimental values of A_2 listed in *Table 1* and the values of α_s derived from neutron scattering[3] and diffusion measurements[5]. The two straight lines in *Figure 3* would be expected to pass through the origin on the basis of conventional theories of polymer solutions[17], with $\alpha_s \rightarrow 1$ as A_2 or $M_w \rightarrow 0$. However, as we have seen before, α_s becomes equal to unity for molar masses below ~4000 g mol^{-1} and so the data in *Figure 3* intersect the $A_2M_w^{\frac{1}{2}}$ axis at 0.0671 cm^3 g$^{-\frac{3}{2}}$ mol$^{\frac{1}{2}}$ and 0.0833 cm^3 g$^{-\frac{3}{2}}$ mol$^{\frac{1}{2}}$ respectively, for cyclic and linear molecules. This illustrates the transition from 'polymer-like' behaviour at high molar mass ($M_w > 4000$ g mol^{-1} for the present systems) to 'small molecule' behaviour at low molar mass, where the conventional theories of A_2 and α_s no longer apply.

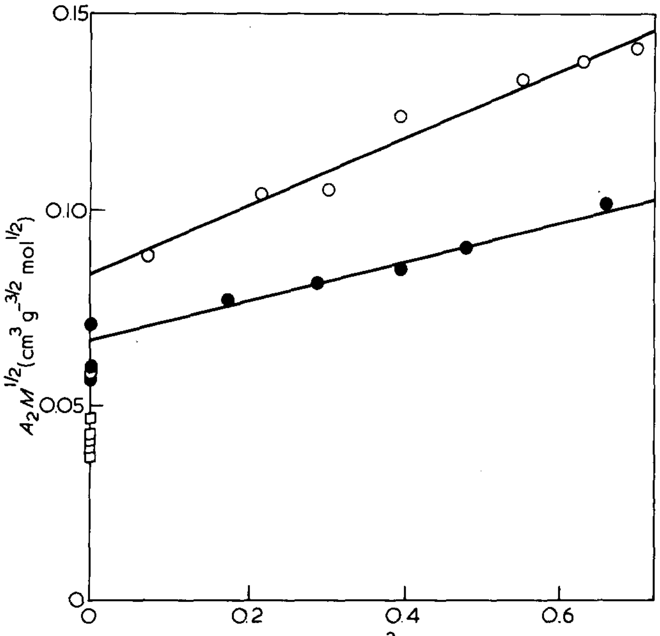

Figure 3 $A_2M^{1/2}$ plotted against (α_s^2-1) for (○) linear and (●) cyclic PDMS in toluene at 298 K. (□) Data of Huglin and Sokro for oligomeric linear PDMS[10]. Least-squares lines through data for which $\alpha_s > 1$, (——)

A further example of the departure from 'polymer-like' behaviour at low molar mass is provided by measurements of A_2 for linear PDMS in bromocyclohexane at 301 K. This solvent has previously been shown to be a θ-solvent[18] for high molar mass linear PDMS at 301 K. The data in *Table 2* confirm this observation with zero second virial coefficients for $M_w > 3000$ g mol^{-1}. However at lower molar mass, large positive second virial coefficients are measured, which increase with decreasing molar mass. This is in qualitative agreement with previous measurements by Adank and Elias[19] who also found significant second virial coefficients for low molar mass linear PDMS under these solvent conditions.

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