Studies of cyclic and linear poly(dimethyl siloxanes): 13. Static dielectric measurements and dipole moments

M. S. Beevers and S. J. Mumby
Department of Chemistry, The University of Aston in Birmingham, Birmingham, B4 7ET

and S. J. Clarson and J. A. Semlyen
Department of Chemistry, University of York, York, YO1 5DD
(Received 30 March 1983; revised 24 May 1983)

The static dielectric permittivities, refractive indices and densities of undiluted oligomeric cyclic and linear dimethyl siloxanes and narrow fractions of cyclic and linear poly(dimethyl siloxanes) have been measured for number-average molar masses $\bar{M}_n$ in the range $160 < \bar{M}_n < 7700$ at temperatures from 298 to 313 K. Measured total dielectric polarizations have been resolved into their electronic, atomic and orientation components and dipole moments have been derived. The dipole moments of cyclic oligomers $((CH_3)_2SiO)_x$ (for example, with $x=4, 5$) are markedly lower than the dipole moments of the corresponding linear oligomers containing the same number of siloxane bonds. However, for $x \geqslant 10$, the dipole moments of cyclic dimethyl siloxanes are identical, within experimental error, to those of the corresponding linear dimethyl siloxanes. Measured static dielectric permittivities of the dimethyl siloxanes and poly(dimethyl siloxanes) in solution in cyclohexane are markedly different from the corresponding values for the undiluted siloxanes. These differences are interpreted as resulting from the specific solvent effects.

Keywords Cyclic poly(dimethyl siloxane); linear poly(dimethyl siloxane); dielectric cell; static dielectric permittivity; dipole moment; specific solvent effect

INTRODUCTION

Previous papers in this series have been concerned with the preparation and characterization of the first cyclic polymers containing hundreds of skeletal bonds as well as with studies of their properties and theoretical investigations[1-12,13]. These polymers are poly(dimethyl siloxanes) and they consist of mixtures of large ring molecules $[(CH_3)_2SiO]_x$[1]. Sharp fractions of such mixtures containing (on average) up to 700 skeletal bonds have been obtained, each on a scale of several grammes, by preparative gel permeation chromatography[2]. They have been characterized and investigated by a range of experimental methods including dilute solution viscometry[1], light scattering[8], low-angle neutron scattering[3], photon correlation spectroscopy[9] and classical diffusion measurements[5,7]. The viscometric[4] and thermal properties[6] of the liquid cyclic polymers have also been studied.

In this paper, the static dielectric properties of a series of sharp fractions of cyclic and linear poly(dimethyl siloxanes) are reported. Some earlier studies[14-19], concerned mainly with linear dimethylsiloxanes, have demonstrated the important contribution of atomic polarization to the total dielectric polarization and for this reason the total distortion polarizations have been measured for both cyclic and linear siloxanes. The majority of previous studies concerned with the comparison of the dielectric properties of cyclic and linear dimethylsiloxanes have been restricted to low molecular weight samples containing less than 16 siloxane bonds[15,16,20]. The fractions of cyclic and linear dimethyl siloxanes taken for the present comparative study are in the number-average molar mass range $160 < \bar{M}_n < 7700$ and have heterogeneity indices $\bar{M}_w/\bar{M}_n$ in the range 1.0–1.2. Static dielectric permittivities, refractive indices and densities were measured for undiluted cyclic and linear dimethyl siloxanes and poly(dimethyl siloxanes) at 298 K and 313 K. The dielectric behaviour of some cyclic and linear dimethylsiloxanes and poly(dimethyl siloxanes) in solution in cyclohexane was also investigated. For all the siloxanes considered, the total dielectric polarizations were resolved into their electronic, atomic and orientation components and their dipole moments were then derived. The dipole moments of the linear oligomers and the polymers are compared with some values for cyclic and linear oligomers quoted in the literature. To allow dielectric measurements to be carried out on small quantities of siloxanes a novel dielectric cell was designed and constructed for this investigation and it is described in detail in the text. One of the main purposes of this investigation was to discover whether there is any difference between the dipole moment of a polar cyclic polymer and the dipole moment of the corresponding linear polymer. Cyclic and linear poly(dimethyl siloxanes) containing up to 200 skeletal bonds were used for this purpose.

EXPERIMENTAL

Materials

Most of the cyclic and linear dimethylsiloxanes and poly(dimethyl siloxanes) used in the present study were

0032–3861/83/121565–06$03.00

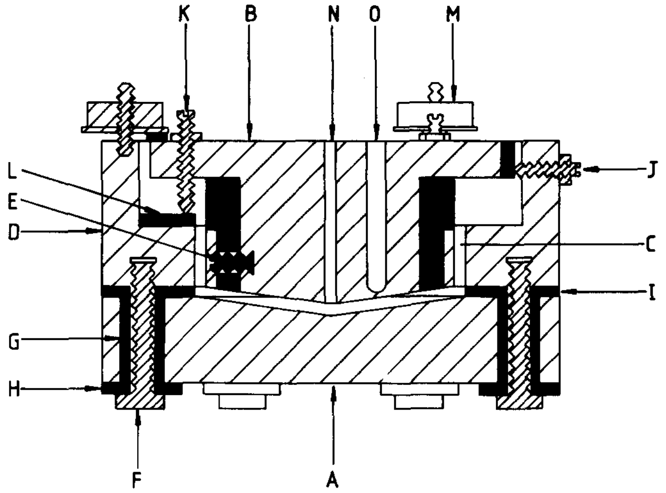

Figure 1 Cross-sectional diagram of the dielectric cell (see text)

prepared by methods described previously[1,2]. These include cyclic siloxane fractions R4-R12 and linear siloxane fractions L7-L13. Cyclic siloxane fractions R1-R3 were prepared by the fractional distillation of the products resulting from the aqueous hydrolysis of dichlorodimethylsilane[21]. Linear siloxane fractions L1-L6 were prepared by fractional distillation of the products resulting from the acid-catalysed equilibration reaction between octamethylcyclotetrasiloxane and hexamethyldisiloxane[21]. As before[1-12], the number of skeletal bonds, n, for the cyclic molecules $[(CH_3)_2SiO]_x$ is taken to be $2x$. For the linear dimethylsiloxane molecules $(CH_3)_3Si[OSi(CH_3)_2]_yOSi(CH_3)_3$ the number of skeletal bonds, n, is taken to be $2y+2$ which represents a departure from previous studies[1-4] but allows a comparison to be made between the dielectric behaviour of cyclic and linear siloxanes with the same number of skeletal bond dipole moments.

Densities

The density of each sample was measured at several different temperatures using an Anton Paar D.M.610 densitimeter in conjunction with a D.M.601 measuring cell. The temperature of the cell was maintained to within ±0.01 K of the set temperature and the densities are quoted to five significant figures.

Refractive indices

The refractive indices of the samples were measured at wavelengths of 632.8 nm (He/Ne laser) and 435.96 nm (Hg discharge lamp) using a Zeiss Abbe refractometer (Model A. Series 7). The temperature of the sample was 298±0.01 K. The refractive indices are quoted to five significant figures and were corrected for the dispersion characteristics of the refractometer.

Static dielectric permittivities

Dielectric cell. A three-terminal dielectric cell was constructed for this study. It had a sample volume of ≈ 1 cm^3 and this could be adjusted over the range 0.5–1.5 cm^3. A cross-sectional diagram of the cell is shown in *Figure 1*. The high-voltage electrode (A), low-voltage electrode (B), inner guard ring (C) and the outer guard ring (D) were turned from solid cylinders of stainless steel. The high-voltage electrode forms the base of the cell and the outer guard ring constitutes the wall of the cell. The inner guard ring was fixed by three nylon screws (E) to the low-voltage electrode and secured in position by filling the small intervening gap with an epoxy-based resin. The inner and outer guard rings were connected electrically by a short length of PTFE-coated wire. The outer guard was securely fixed to the high-voltage electrode by six 6 mm diameter Allen bolts (F). Each bolt was fitted with a sleeve of PTFE (G) and a disc of Tufnol (H) to ensure electrical isolation between the bolts and the high-voltage electrode. The outer guard and the high-voltage electrode were electrically insulated from each other by a thin sheet of epoxy-impregnated paper (I) which was cured *in situ* at 353 K for 24 h. The paper was dried for several hours at 393 K prior to immediate use. The horizontal position of the low-voltage electrode/inner guard ring assembly, relative to the outer guard ring, could be adjusted by three screws (J) set in the wall of the cell. The size of the gap between the high-voltage electrode and the low-voltage electrode was set by three screws (K) located in the rim of the low-voltage electrode. To maintain electrical isolation between the electrodes each adjustment screw impinged on a glass insulator (L). All the adjustment screws were fitted with lock-nuts. The low-voltage electrode/inner-guard ring assembly could be locked in position by three knurled discs of brass (M), mounted on threaded studs set in the outer guard ring, which engaged with the upper surface of the low-voltage electrode via glass insulators. The facing surfaces of the low-voltage and high-voltage electrodes were conical in profile to facilitate filling and emptying the cell. A hyperdermic syringe was used to fill and empty the cell via a small hole (N) located at the centre of the low-voltage electrode. A larger hole (O) in the low-voltage electrode accommodated either a thermometer or a thermocouple junction. The electrical capacitance of the empty cell, when adjusted for a sample volume of ≈ 1 cm^3, was approximately 70 pF. The temperature of the cell was controlled to within ±0.1 K over the range 283–333 K by a purpose-built oven.

Measurement of static dielectric permittivities. The electrical capacitance of the dielectric cell was measured when empty and when filled with freshly distilled samples of cyclohexane, toluene, octamethylcyclotetrasiloxane and hexamethyldisiloxane using a Marconi Universal Bridge (Type T1313A) at a frequency of 10 kHz. A substitution method described in ref. 22 was used to calculate the static dielectric permittivities of the liquids listed, assuming a value of 2.0199 for the static dielectric permittivity of cyclohexane[22] at 298 K. This value, in conjunction with the value of -1.60×10^{-3} K^{-1} for the temperature coefficient ($d\varepsilon/dT$) of cyclohexane[23], was also used to calculate the static permittivities of the liquids at 313 K. The static dielectric permittivities of the fractions of cyclic and linear dimethylsiloxanes at 298 K and 313 K were also obtained using this procedure. The dielectric permittivities of the cyclic and chain fractions were estimated to have experimental errors of 0.05% and 0.1%, respectively.

RESULTS AND DISCUSSION

The measured static dielectric permittivities of toluene (2.273), octamethylcyclotetrasiloxane (2.383) and hexamethyldisiloxane (2.170) at 298 K were found to be close to

Table 1 Number-average number of repeat units $\bar{x}_n$, heterogeneity indices $\bar{M}_w/\bar{M}_n$, static permittivities ε_0, densities ρ, temperature coefficients of volume expansion β and refractive indices n_λ for undiluted cyclic dimethylsiloxanes $[(CH_3)_2SiO]_x$ at 298 K

Fraction	$\bar{x}_n$	$\bar{M}_w/\bar{M}_n$	ε_0 298 K	ε_0 313 K	ρ (Kg m^{-3})	$10^3\beta$ (K^{-1})	n_1 632.8 nm	n_2 436.0 nm
R1[a]	4.0	1.00	2.383	2.343	950.56	1.2023	1.3927	1.4040
R2[a]	5.0	1.00	2.491	2.457	953.47	1.1790[b]	1.3947	1.4064
R3[a]	6.0	1.00	2.606	2.557	962.87	1.0344	1.3995	1.4120
R4	7.35	1.05	2.683	2.626	967.76	0.9867	1.4020	1.4138
R5	9.85	1.07	2.745	2.689	972.98	0.9382	1.4039	1.4155
R6	11.9	1.05	2.754	2.698	974.19	0.9274	1.4041	1.4157
R7	15.6	1.03	2.755	2.699	973.57	0.9156	1.4034	1.4153
R8	17.5	1.02	2.757	2.703	973.06	0.9181	1.4031	1.4150
R9	19.1	1.02	2.765	2.709	972.96	0.9197	1.4029	1.4147
R10	22.0	1.02	2.770	2.714	973.02	0.9224	1.4027	1.4143
R11	54.5	1.03	2.763	2.706	971.46	0.9183	1.4026	1.4139
R12	95.0	1.04	2.757	2.701	971.67	0.9222	1.4025	1.4140

[a] Single component
[b] Ref. 24

Table 2 Number-average number of repeat units $\bar{y}_n$, heterogeneity indices $\bar{M}_w/\bar{M}_n$, static dielectric permittivities ε_0, densities ρ, temperature coefficients of volume expansion β and refractive indices n_λ for undiluted linear dimethylsiloxanes $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ at 298 K

Fraction	$\bar{y}_n$	$\bar{M}_w/\bar{M}_n$	ε_0 298 K	ε_0 313 K	ρ (Kg m^{-3})	$10^3\beta$ (K^{-1})	n_1 632.8 nm	n_2 436.0 nm
L1[a]	0	1.00	2.170	2.145	758.45[b]	1.3212[b]	1.3734	1.3856
L2[a]	1	1.00	2.297	2.255	815.36	1.2415	1.3809	1.3928
L3[a]	2	1.00	2.390	2.344	850.63	1.1659	1.3864	1.3978
L4[a]	3	1.00	2.456	2.407	872.08	1.1116	1.3897	1.4010
L5[a]	4	1.00	2.499	2.450	885.70	1.0807	1.3919	1.4032
L6[a]	5	1.00	2.550	2.490	899.40	1.0392	1.3931	1.4045
L7	7.27	1.02	2.583	2.543	915.29	1.0446	1.3954	1.4072
L8	9.86	1.01	2.628	2.579	928.31	1.0176	1.3970	1.4094
L9	11.2	1.01	2.650	2.610	933.77	1.0030	1.3980	1.4107
L10	15.2	1.01	2.673	2.621	941.96	0.9755	1.3985	1.4111
L11	19.8	1.01	2.698	–	949.44	0.9699	1.3997	1.4121
L12	51.5	1.20	–	–	958.99	0.9538	1.4011	1.4131
L13	102	1.17	2.752	–	966.08	0.9276	1.4015	1.4136

[a] Single component
[b] Ref. 24

Table 3 Solute dielectric polarizations P_T of cyclic and linear dimethylsiloxanes in solution in cyclohexane and in the undiluted state at 298 K

Fraction	$10^6 P_T$ (m^3 mol^{-1}) Undiluted	Solution
L1[a]	60.07	59.67
L10	546.5	638.4
L13	2944	3569
R1[a]	98.41	108.0
R10	622.7	750.3
R11	1534	1863
R12	2673	3274

[a] Single component (see *Tables 1* and *2*)

the values quoted in the literature: toluene (2.2725)[22], octamethylcyclotetrasiloxane (2.382 and 2.385)[16,20] and hexamethyldisiloxane (2.166 and 2.167)[16,20].

The number-average number of repeat units ($\bar{x}$ and $\bar{y}$), heterogeneity indices ($\bar{M}_w/\bar{M}_n$), static dielectric permittivities (ε_0), refractive indices (n_λ) and densities (ρ) measured for fractions of cyclic and linear dimethylsiloxanes are listed in *Table 1* and *Table 2*, respectively. The static dielectric permittivities of the linear dimethylsiloxanes in the range $y = 1$–5 are generally in very good agreement with values measured by other workers[16–20,25]. However, the permittivities obtained by Sutton and Mark[19] for linear dimethylsiloxanes with $y = 5$, 7 and 9 are significantly larger than the corresponding values found in the present study. The static permittivities of several cyclic dimethylsiloxanes ($x = 4$–8) measured by Sauer and Mead[20] concurred with the values measured in the present study.

The dielectric behaviour of several fractions of cyclic and linear dimethylsiloxanes was also examined in solution in cyclohexane at 298 K. Cyclohexane has been shown previously to be a 'good' solvent for poly(dimethyl siloxanes)[1]. The total solute dielectric polarizations P_T for the siloxanes in this solvent are shown in *Table 3*, together with the corresponding total polarizations found for the undiluted samples. The values of P_T found for the solutions were found to be independent of the concentration of solute over the concentration range 10–50% wt/vol. Similar differences between values of P_T for undiluted and diluted samples were found for the cyclic and linear siloxanes. This behaviour has been observed previously for linear dimethylsiloxanes[26] and has been attributed to specific solvent effects[27].

Figure 2 shows the static dielectric permittivities at 298 K plotted against the average number of skeletal

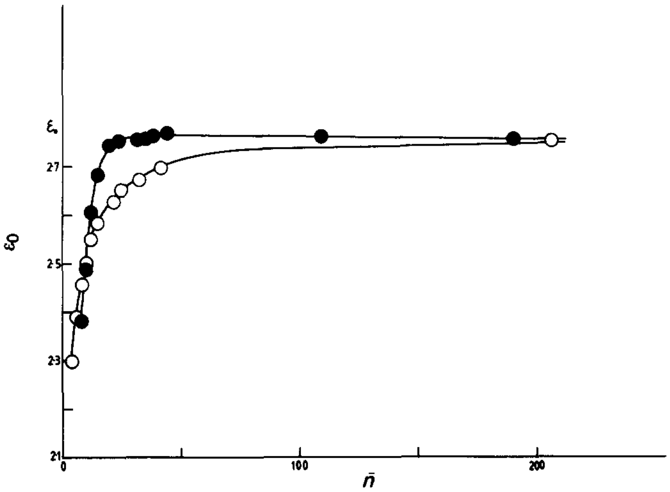

Figure 2 Static dielectric permittivities (ε_0) of cyclic dimethylsiloxanes (●) and linear siloxanes (○) in the undiluted state at 298 K

bonds for undiluted cyclic and linear dimethylsiloxanes. For oligomers with less than ≈ 50 skeletal bonds the permittivities of the cyclic siloxanes and the nearest equivalent (equal number of skeletal bonds) linear siloxanes differ markedly. These differences are a result of variations in the densities of the samples of the cyclic and linear siloxanes together with differences in their respective molecular dipole moments. For the cyclic dimethyl siloxanes the permittivity attains a maximum value of 2.77 in the region of 50 skeletal bonds and this is very close to the value of 2.76 obtained for a fraction of cyclic molecules with $\bar{n}=190$ (see *Figure 2*). This behaviour contrasts with that exhibited by the linear dimethylsiloxanes and poly(dimethyl siloxanes). The dielectric permittivities of the low molecular weight linear oligomers ($\bar{n}\leqslant 50$) are significantly smaller than the nearest equivalent cyclic oligomers and they increase smoothly to the value of 2.75 obtained for a fraction of chains with $\bar{n}=204$.

The total dielectric polarization P_T of each sample was calculated from the corresponding static dielectric permittivity using the familiar relation[28]:

$$P_T=\frac{(\varepsilon_0-1)}{(\varepsilon_0+2)}\frac{M}{\rho} \tag{1}$$

where M is the mean molar mass and ρ is the density. Number-average mean molar masses were measured by gas–liquid chromatography and/or gel permeation chromatography and the densities were measured as described previously. The electronic polarizations P_E were obtained using the Lorenz–Lorentz relation[28]:

$$P_E=\frac{(n_\infty^2-1)}{(n_\infty^2+2)}\frac{M}{\rho} \tag{2}$$

The infinite-wavelength refractive indices n_∞ required for the calculation of P_E using equation (2) were obtained from the two-term Cauchy expression[28]:

$$n_\infty=\frac{(\lambda_1^2 n_1-\lambda_2^2 n_2)}{(\lambda_1^2-\lambda_2^2)} \tag{3}$$

using the refractive indices n_1 and n_2 measured at visible wavelengths λ_1 and λ_2, respectively (see previously). The total distortion polarizations P_D were derived from measurements of P_T carried out at 298 K and 313 K using the method of Debye[28] and the atomic polarizations calculated assuming $P_A=P_D-P_E$.

In *Figure 3* the experimental atomic polarizations of cyclic and linear dimethylsiloxanes are plotted against the average number of skeletal bonds. The atomic polarizations of the cyclic siloxanes were well described by a single line of regression (see *Table 4*). The atomic polarizations of the linear siloxanes are slightly larger than the nearest equivalent cyclic siloxanes and were also reasonably well described by a single line of regression, assuming the same gradient as that found for the cyclic data. The two lines of regression were used to obtain atomic polarizations that were either not available or where it was evident that the experimental value of P_A was associated with an atypically large error. The fractions of linear siloxanes L8, L11 and L13 and the fractions of cyclic siloxanes R4 and R8 were the only samples affected by this procedure in subsequent calculations of the root-mean-square dipole moments. The atomic polarizations of the linear siloxanes were also calculated using the relation $10^6P_A=7.80+5.65y$ derived by Sutton and Mark[19] for the P_A values obtained by Dasgupta and Smyth[17] for linear dimethylsiloxanes with numbers of skeletal bonds in the range $2\leqslant n\leqslant 16$. Also, it seems reasonable to assume that for sufficiently large cyclic dimethylsiloxanes their atomic polarizations may be estimated using the similar relation $10^6P_A=5.65\bar{x}$. The various polarization components obtained using the methods described are listed in *Table 4* and in *Table 5* for the cyclic and linear siloxanes, respectively. The contributions of the orientation polarizations P_O to the total polarizations were obtained assuming $P_O=P_T-P_D$ and the root-mean-square dipole moments calculated using the relation $\langle\mu^2\rangle=9P_0kT\varepsilon/N$ ($\varepsilon=8.854\times10^{-12}$ Fm^{-1}). As P_O is readily calculated from the tabulated values of P_T, P_E and P_A the different values of P_O corresponding to the different values of P_A are not listed.

In *Figure 4* the experimental mean-square dipole moments are shown plotted against the mean number of skeletal bonds $\bar{n}$ for cyclic and linear dimethylsiloxanes at 298 K. For cyclic and linear siloxanes with a mean number of skeletal bonds not exceeding ≈ 15 there are significant differences between their dipole moments, with the chains possessing the higher values. As the number of skeletal bonds increases the mean-square dipole moments of cyclic and linear siloxanes converge and become identical within experimental error for $\bar{n}\geqslant 20$.

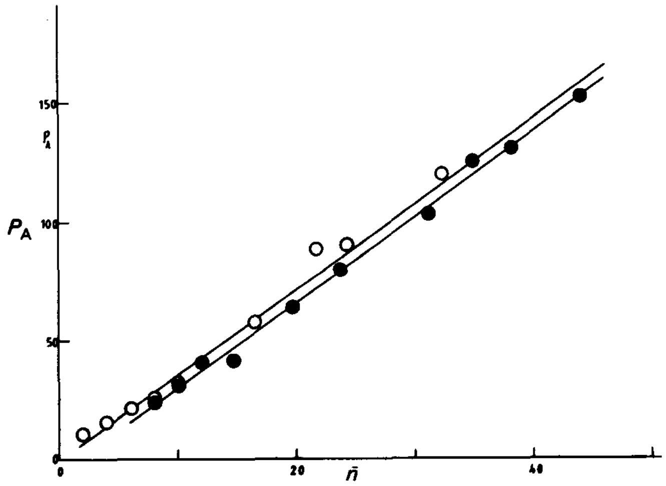

Figure 3 Experimental atomic polarizations P_A ($\times 10^6$ m^3 mol^{-1}) of cyclic dimethylsiloxanes (●) and linear dimethylsiloxanes (○)

Table 4 Polarizations P_T, P_E, P_A (I, this study; II, Dasgupta and Smyth[17] (see text)), infinite-wavelength refractive indices n_∞ and root-mean-square dipole moments $\langle\mu^2\rangle^{1/2}$ for cyclic dimethylsiloxanes at 298 K

	$10^6 P_T$ (m³ mol⁻¹)				$10^6 P_A$ (m³ mol⁻¹)		
$\bar{x}$	298 K	313 K	n_∞	$10^6 P_E$ (m³ mol⁻¹)	I	II	$10^{30}\langle\mu^2\rangle^{1/2}$ (C m)
4[a]	98.5	98.2	1.3825	72.7	21.6[b]	22.6	1.50
5[a]	129.0	128.5	1.3841	90.9	27.8	28.3	2.37
6[a]	164.5	163.7	1.3882	111.4	36.6	33.9	3.00
7.35	203.0	201.5	1.3913	134.3	37.3[c]	41.5	3.80
9.85	276.6	274.7	1.3934	179.6	57.4	55.7	4.64
11.9	334.4	332.2	1.3936	216.6	71.8	67.2	5.00
15.6	439.1	436.1	1.3926	283.7	92.8	88.2	5.84
17.5	491.7	488.7	1.3923	317.2	107.8[c]	98.7	6.03
19.1	538.8	535.2	1.3922	346.5	117.7	107.9	6.37
22.0	622.7	618.6	1.3922	399.8	137.0	124.4	6.84
54.5	1534	1524	1.3924	987.9	324.8	308.1	11.0
95.0	2673	2655	1.3921	1724	574.7	537.1	14.3

[a] Single component
[b] From 5 point plot of P_T *versus* $1/T$
[c] Calculated using $10^6 P_A = 3.24\,\bar{n} - 5.46$ (see *Figure 3*)

Table 5 Polarizations P_T, P_E, P_A (I, this study; II, Dasgupta and Smyth[17] (see text)), infinite-wavelength refractive indices n_∞ and root-mean-square dipole moments $\langle\mu^2\rangle^{1/2}$ for linear dimethylsiloxanes at 298 K

	$10^6 P_T$ (m³ mol⁻¹)				$10^6 P_A$ (m³ mol⁻¹)		
$\bar{y}$	298 K	313 K	n_∞	$10^6 P_E$ (m³ mol⁻¹)	I	II	$10^{30}\langle\mu^2\rangle^{1/2}$ (C m)
0[a]	60.07	59.91	1.3624	47.53	9.44	7.80	1.30
1[a]	87.6	87.18	1.3701	65.7	14.0	13.5	2.07
2[a]	115.6	115.0	1.3761	84.0	19.2[b]	19.1	2.60
3[a]	144.2	143.3	1.3795	102.3	23.1	24.8	3.21
4[a]	172.7	171.6	1.3817	120.5	29.2	30.4	3.54
5[a]	201.9	200.6	1.3828	138.2	36.8	36.0	3.83
7.27	321.6	263.1	1.3847	218.1	52.2	48.9	4.24
9.86	395.3	335.8	1.3858	263.9	69.4[c]	63.5	4.83
11.2	432.7	373.9	1.3865	286.8	81.3	71.1	4.98
15.2	546.5	488.4	1.3871	359.4	107.9	93.7	5.73
19.8	677.1	–	1.3885	442.6	134.0[c]	119.7	6.66
51.5	–	–	1.3903	980.9	338.8[c]	298.9	–
102	2944	–	1.3906	1896	667.3[c]	584.5	14.4

[a] Single component
[b] From 5 point plot of P_T *versus* $1/T$
[c] Calculated using $10^6 P_A = 3.24\,\bar{n} - 0.962$ (see *Figure 3*)

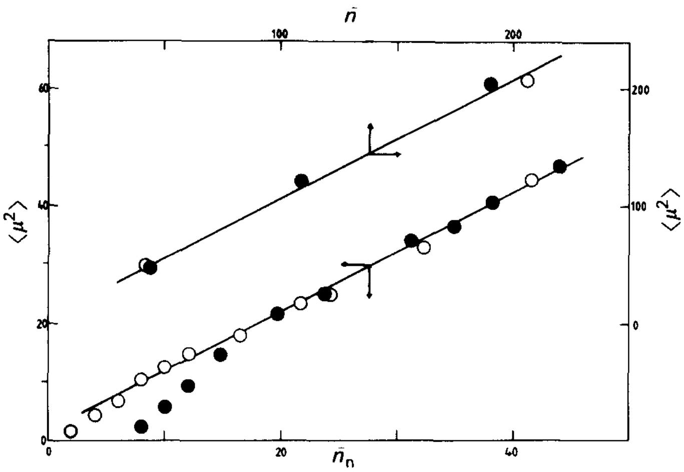

Figure 4 Mean-square dipole moments $\langle\mu^2\rangle$ ($\times 10^{30}$/Cm) for cyclic dimethylsiloxanes (●) and linear dimethylsiloxanes (○). The points are plotted along the axes shown

A quantity which is very sensitive to the conformational properties of flexible polymer molecules is the dipole moment ratio[29] $\langle\mu^2\rangle/nm^2$ where m is the link dipole moment. Experimental values of this ratio for cyclic and linear dimethylsiloxanes and poly(dimethyl siloxanes) calculated using $m = 2.0 \times 10^{-30}$ Cm (ref. 30) are plotted in *Figure 5* and are compared with values found by Dasgupta, Garg and Smyth[16], Dasgupta and Smyth[17] and Sutton and Mark[19]. Included in this comparison are theoretical values of $\langle\mu^2\rangle/nm^2$ calculated for chains of poly(dimethyl siloxane) at 298 K using the rotational isomeric state model of Flory, Crescenzi and Mark[26]. For the small cyclic molecules ($\bar{n} < 20$) the dependence of the dipole moment ratio on the number of skeletal bonds is different to that observed for the corresponding linear molecules. The dipole moment ratio has a maximum value at $\bar{n} = 8$ for linear siloxanes whereas for the cyclic siloxanes the ratio simply increases steadily with increasing ring size and approaches the value (≈ 0.26) found for the long chain molecules of dimethylsiloxane. There is a very good agreement between the experimental and theoretical values of $\langle\mu^2\rangle/nm^2$ for the linear dimethylsiloxanes over the entire range of $\bar{n}$ considered in the present study.

The small differences between the dipole moment ratios obtained for the linear siloxanes in the present study (see *Figure 5*) and those found in earlier studies are mainly due to the various methods used to estimate or measure the

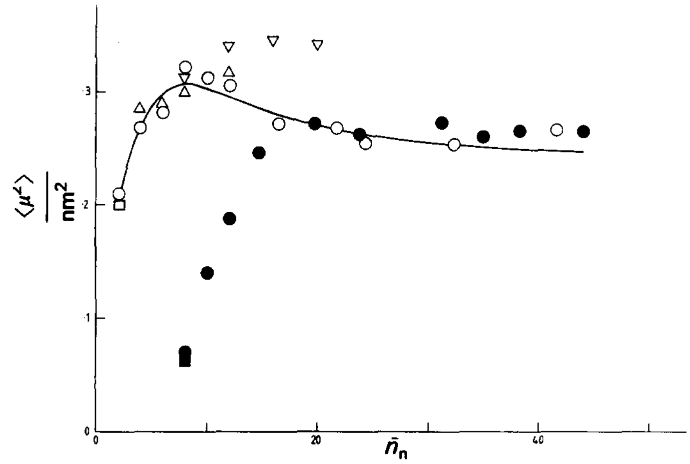

Figure 5 Dipole moment ratio $\langle\mu^2\rangle/nm^2$ for cyclic dimethylsiloxanes (●, present study; ■, Dasgupta, Garg and Smyth[16]) and for linear dimethylsiloxanes (○, present study; □, Dasgupta, Garg and Smyth[16], △, Dasgupta and Smyth[17]; and ▽, Sutton and Mark[19]) in the undiluted state. The unbroken line was calculated for poly(dimethyl siloxanes) using the theory of Flory, Crescenzi and Mark[26] at 298 K

atomic polarization P_A. Thus, the values of P_A quoted by Sutton and Mark[19] for the linear dimethylsiloxanes in the undiluted state were obtained from a linear extrapolation of a relation derived by these authors based on values of P_A measured for low molecular weight linear dimethylsiloxanes with $\bar{n} \leqslant 14$ (see previously). The validity of this extrapolation over an extended range of molecular weight for which n considerably exceeds 14 requires further examination.

It is important to appreciate the limitations of the Debye method when it is used to measure the atomic and orientation polarizations of flexible, polar molecules. The validity of this approach rests upon two main assumptions. The first assumption concerns the constancy of the mean-square dipole moment $\langle\mu^2\rangle$ of the materials over the range of temperature in which P_T is measured. For the poly(dimethyl siloxanes) in the undiluted state the temperature coefficient $d \ln \langle\mu^2\rangle/dT$ has been shown to be quite small[17,30] although it is predicted to vary with chain length[30]. The second assumption relates to the neglect of internal reaction fields in the dielectric theory and to the neglect of directional correlation between the dipole moment vectors in addition to the directional correlations imposed by the molecular structure. Dipole moments, corrected for the effects of reaction fields, may be obtained using the relation $\langle\mu^2\rangle_{\text{corr}}/\langle\mu^2\rangle = (2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_0 + 2)/3\varepsilon_0(\varepsilon_\infty + 2)$ based on the theory of Onsager[31]. The calculated ratios $\langle\mu^2\rangle_{\text{corr}}/\langle\mu^2\rangle$ were less than 1.04 for all of the samples of cyclic and linear siloxanes considered in the present study and reflects the small dipole moment of the Si–O bond (2.0×10^{-30} Cm)[16,30]. It is noted that the Debye method will not be applicable for the determination of P_A and P_O for 'flexible' polar molecules possessing large link dipole moments, as well as large temperature coefficients $d \ln \langle\mu^2\rangle/dt$ over the temperature range used to measure P_T.

The main conclusion of the present investigation is that in this first comparison of the dipole moments of a synthetic polar cyclic and linear polymer, the dipole moments increase with the number of skeletal bonds but cyclic and linear polymers containing the same number of skeletal bonds have identical dipole moments within experimental error. Further measurements of the static dielectric permittivities of other cyclic and linear siloxanes are planned.

ACKNOWLEDGEMENTS

The authors would like to thank the Science and Engineering Research Council for research grants (to S.J.M. and S.J.C.), Mr P. McGuire for the construction of a dielectric cell, the University of Aston in Birmingham for the provision of computing facilities, Ms C. Cade for the preparation of figures and Mr T. M. Elsworth (University of York) for assistance in the preparation of cyclic and linear polymers. The authors are grateful to Dr R. A. Pethrick (University of Strathclyde) for making facilities available for the measurement of densities.

REFERENCES

1 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
2 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
3 Higgins, J. S., Dodgson, K. and Semlyen, J. A. *Polymer* 1979, **20**, 553
4 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **21**, 663
5 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1980, **21**, 781
6 Bannister, D. J. and Semlyen, J. A. *Polymer* 1981, **22**, 377
7 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 865
8 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 869
9 Edwards, C. J. C., Bantle, S., Burchard, W., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 873
10 Edwards, C. J. C., Rigby, D., Stepto, R. F. T., Dodgson, K. and Semlyen, J. A. *Polymer* in press
11 Edwards, C. J. C., Rigby, D., Stepto, R. F. T. and Semlyen, J. A. *Polymer* in press
12 Higgins, J. S., Ma, K., Nicholson, L. K., Hayter, J. B., Dodgson, K. and Semlyen, J. A. *Polymer* in press
13 Semlyen, J. A. *Pure Appl. Chem.* 1981, **53(9)**, 1797
14 Holland, R. S. and Smyth, C. P. *J. Am. Chem. Soc.* 1955, **77**, 268
15 Kurita, Y. and Kondo, M. *Bull. Chem. Soc. Japan* 1954, **27**, 160
16 Dasgupta, S., Garg, S. K. and Smyth, C. P. *J. Am. Chem. Soc.* 1967, **89**, 2243
17 Dasgupta, S. and Smyth, C. P. *J. Chem. Soc.* 1967, **47**, 2911
18 Dasgupta, S. and Smyth, C. P. *J. Chem. Phys.* 1971, **54**, 4648
19 Sutton, C. and Mark, J. E. *J. Chem. Phys.* 1971, **54**, 5011
20 Sauer, R. and Mead, D. J. *J. Am. Chem. Soc.* 1946, **68**, 1794
21 Patnode, W. and Wilcock, D. F. *J. Am. Chem. Soc.* 1946, **68**, 358
22 Le Fèvre, C. G. and Le Fèvre, R. J. W. in 'Physical Methods of Chemistry', vol 1 (IIIc), (Eds. A. Weissberger and B. W. Rossiter) John Wiley, New York, 1972
23 Weast, R. C. (Ed.) 'Handbook of Chemistry and Physics' C.R.C. Press Inc., 1974
24 Hurd, C. B. *J. Am. Chem. Soc.* 1946, **68**, 364
25 Baker, E. B., Barry, A. J. and Hunter, M. J. *Ind. Eng. Chem.* 1946, **38**, 1117
26 Flory, P. J., Crescenzi, V. and Mark, J. E. *J. Am. Chem. Soc.* 1964, **86**, 146
27 Liao, S. C. and Mark, J. E. *J. Chem. Phys.* 1973, **59**, 3825
28 Smyth, C. P. 'Dielectric Behaviour and Structure', McGraw Hill, New York, 1955
29 Mark, J. E. *Acc. Chem. Research* 1974, **7**, 218
30 Mark, J. E. *J. Chem. Phys.* 1968, **49**, 1398
31 Onsager, L. *J. Am. Chem. Soc.* 1936, **58**, 1486