Polymer Vol. 37 No. 13, pp. 2597–2602, 1996

0032-3861/96/$15.00 + 0.00

Cyclic polysiloxanes: 6. Dielectric relaxation of polymethylphenylsiloxanes

Andy A. Goodwin* and Martin S. Beevers†
Department of Chemistry, Aston University, Birmingham B4 7ET, UK

and Stephen J. Clarson
Department of Materials Science and Engineering and Polymer Research Center, University of Cincinnati, OH 45221-0012, USA

and J. Anthony Semlyen
Department of Chemistry, University of York, York YO1 5DD, UK
(Received 12 April 1995)

The dielectric α-relaxation of a series of linear polymethylphenylsiloxanes (PMPSs) has been investigated as a function of frequency in the temperature range 155.5–262 K. The breadth of the relaxation process, according to the empirical Kohlrausch–Williams–Watts and Havriliak-Negami functions, increases as the molecular weight increases. The apparent activation energy passes through a maximum at $n_n = 10$ which reflects the contribution of the whole molecule rotation to dipolar relaxation. A maximum in the dipole moment ratio occurs at $n_n \sim 50$ due to dipole reinforcement. A similar investigation of a cyclic PMPS with $n_n = 10$ indicates the effectiveness of dipolar cancellation in small siloxane rings. Copyright © 1996 Elsevier Science Ltd.

(Keywords: dielectric relaxation; polymethylphenylsiloxane; dipole moment)

INTRODUCTION

Polymers containing organosiloxane backbones are an important class of inorganic polymers which have been widely studied for many years and have resulted in the development of a variety of interesting commercial products based on low-viscosity fluids, elastomers and crosslinked resins[1]. A useful property of these materials is that they show better thermal stabilities when compared with the corresponding organic polymers. Prominent among the polysiloxanes is polymethylphenylsiloxane (PMPS) which has the general repeat unit –(RR'SiO)–, where R = CH_3 and R' = C_6H_5.

A number of studies of the molecular dynamics of this polymer, in the undiluted state, have been carried out by using techniques such as ultrasonic relaxation and depolarized light scattering, which probe localized rotational dynamics at high frequencies and temperatures above the glass transition temperature (as measured by differential scanning calorimetry (d.s.c.)). At very short times, rapid localized motions of the phenyl ring can be observed[2].

On the low-frequency side of the spectrum, dielectric relaxation spectroscopy (d.r.s.) and photocorrelation spectroscopy (p.c.s.) have been used by Boese *et al.*[3] to study the α-relaxation in PMPS which results from large-scale Brownian motions of the polymer chains and is related to the glass transition of the material. At a given temperature two well-separated peaks are observed in a combined plot of correlation function against relaxation time; the 'slow' (low-frequency) component is detected by p.c.s. and the 'fast' (high-frequency) component by d.r.s. The low-frequency component is assigned to normal mode motions, with these motions not being dielectrically active in PMPS since the dipole moment components parallel to the chain axis cancel to zero. However, the dipolar components perpendicular to the chain axis are additive, which therefore makes segmental rotations dielectrically active, and they are accordingly assigned to the high-frequency component. It was found that the mean relaxation times for the two components, as well as having identical shape parameters that defined the relaxation time distributions, also exhibited the same time–temperature dependence. This prompted the conclusion that p.c.s. and d.r.s. were probing one and the same relaxation process, but on different time scales.

Baird and Sengupta[4] have studied the α-relaxation process in an amorphous PMPS with a number-average molecular weight (M_n) of 1060 and a d.s.c. glass transition temperature of −37°C. This polymer showed an asymmetric loss peak with a high-frequency skew. The maximum value of the dielectric loss was in the range 0.04–0.10, and the activation energy for the relaxation process was 320 kJ mol^{-1}. The width of the loss peak, at half-height, was equivalent to a β-value in the Kohlrausch–Williams–Watts (KWW)

---

* Present address: Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia

† To whom correspondence should be addressed. Present address: Department of Chemical Engineering and Applied Chemistry, Aston University, Birmingham B4 7ET, UK

function of 0.62, indicating the cooperativity of the relaxation process.

The effects of fourteen different diluents on the α-relaxation of this polymer has also been examined by Baird and Sengupta[5]. The diluents consisted of non-polar and polar materials and were found to have a plasticizing effect on the polymer as they shifted the dielectric loss peak to higher frequencies (or the equivalent, i.e. lower temperatures). The loss plots were also observed to broaden as the concentration of diluent increased, although they still exhibited a high-frequency skew and gave satisfactory fits to the KWW function. The dielectric loss, frequency of maximum loss, and β-values were affected most by the straight-chain diluents, but none of these diluents had very much effect on the magnitude of the dielectric relaxation. The polar diluents gave the broadest loss curves (e.g. 0.33 for benzyl alcohol) and the largest activation energies (e.g. 244 kJ mol^{-1} for phenol). The broadening of the loss curves for the polymer/diluent mixtures, compared with the undiluted homopolymer, was attributed to time-dependent fluctuations in the concentrations of diluent interacting with the polymer chain segments.

All of the above studies have been confined to individual samples of a particular molecular weight or a few oligomeric species. In this present paper we investigate the effects of a systematic variation in molecular weight on the dielectric properties of sharp fractions of linear oligomers and polymers of methylphenylsiloxane. The dielectric properties of a cyclic MPS oligomer have also been studied.

EXPERIMENTAL

Materials

The cyclic PMPS, $[(CH_3)(C_6H_5)SiO]_5$, was isolated from a ring–chain equilibrium reaction in toluene at 110°C, as described previously[6]. The trimethylsilyl-terminated linear PMPS, $(CH_3)_3SiO[(CH_3)(C_6H_5)SiO]_y$-$Si(CH_3)_3$, was prepared by a ring-opening polymerization of a mixture of cyclic oligomers ($x = 3, 4, 5$), with the polymerization being terminated and the polymer end-blocked by using hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$. The linear PMPS was then fractionated by preparative gel permeation chromatography, as described in detail previously[6]. Values for the molar masses of the siloxanes and the polydispersity (M_w/M_n) were determined by using a gel permeation chromatograph which had been calibrated using standard siloxane samples, and the chromatograms that were obtained were corrected for axial broadening effects. The characterization data for the cyclic PMPS and linear PMPS fractions are summarized in *Table 1*. It should be noted that for the linear PMPS samples the number-average number of skeletal bonds n_n is defined for this study differently to that used in our previous convention for the series, in that here $n_n = y + 2$ where y represents $(CH_3)_3SiO[(CH_3)(C_6H_5)SiO]_ySi(CH_3)_3$. The materials were all clear viscous liquids at room temperature. The samples have also been characterized by a variety of chromatographic techniques, low-angle laser light scattering, mass spectrometry and small-angle neutron scattering[7]. High-resolution nuclear magnetic resonance (n.m.r.) studies have shown that these materials are stereochemically atactic[7]. The linear samples had spectroscopic number-average number of skeletal bonds (n_n) in the range from 4 to 1370 and for the heterogeneity index value for the (M_w/M_n) in the range from 1.00 to 1.16, with just one sample having a broader distribution (2.00).

Table 1 Mean-square dipole moment (μ^2) per repeat unit for linear and cyclic PMPS

	n_n	M_w/M_n	μ^2 (10^{-31} cm)
Linear			
	4	1.00	5.01
	6	1.00	7.34
	8	1.00	6.67
	10	1.00	8.01
	31	1.08	7.00
	50.5	1.04	7.00
	82	1.14	6.34
	153	1.16	6.34
	284	1.12	6.34
	1370	2.00	6.34
Cyclic			
	10	1.00	5.01

Dielectric measurements

Electrical capacitance (C) and dissipation factor ($\tan\delta$) values were measured by using a GenRad 1689 Precision RLC Digibridge over the frequency range 12–10^5 Hz and the temperature range 155.5–262.0 K, using an average value from ten consecutive measurements. The dielectric cell was constructed from brass plates measuring 4 cm by 1 cm with PTFE spacers being used to maintain a gap of 0.25 mm. The cell was enclosed in a glass tube and had a volume of ~0.1 cm^3. The electrical capacitance of the empty cell was 25 pF. This value was used in the calculation of the dielectric loss. Electrical connections between the cell and the Digibridge were made by a two-terminal, guarded GenRad 1657-9600 extender cable. Prior to a connection being made between the Digibridge and the cell a zeroing procedure was carried out on the bridge and extender cable to compensate for stray capacitances. Temperature control in the range 203–298 K was achieved by using a 'Minus Seventy' Thermostat Bath, Bridge Control Model (Townson and Mercer Ltd, UK) with acetone and solid CO_2 used as the coolant. For measurements below 203 K a specially constructed double-Dewar system was used with liquefied N_2 as the coolant. Heating was provided by a series of resistors connected to a stabilized voltage supply. An iron-constantan thermocouple was attached to the back of one electrode and the thermocouple e.m.f. was measured by a Keithley 616 Digital Electrometer. All measurements were carried out in an isothermal mode, and empty cell stray capacitances were calculated by using toluene as a standard dielectric ($\epsilon_s = 2.379$ at 298 K).

RESULTS AND DISCUSSION

Dielectric loss and α-relaxation

Isothermal plots of normalized dielectric loss *versus* log frequency in the glass–rubber (α) relaxation region for two linear fractions of PMPS are shown in *Figures 1* and *2*. These plots are representative of the samples examined in this study and exhibit high frequency

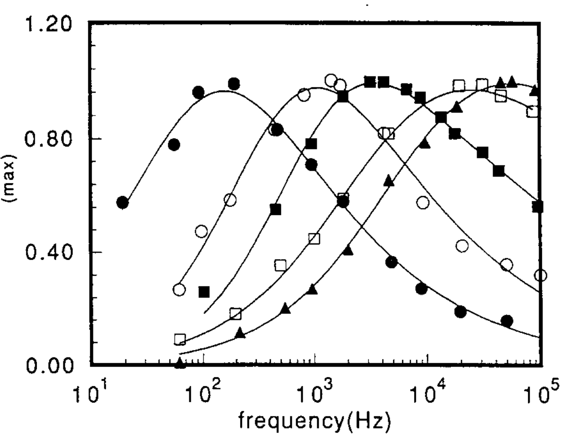

Figure 1 Frequency dependence of $\epsilon''/\epsilon''_{max}$ for a linear PMPS fraction with $n_n = 4$: (●) 155.5; (○) 158.0; (■) 159.5; (□) 161.5; (▲) 162.5 K (solid lines are HN fits)

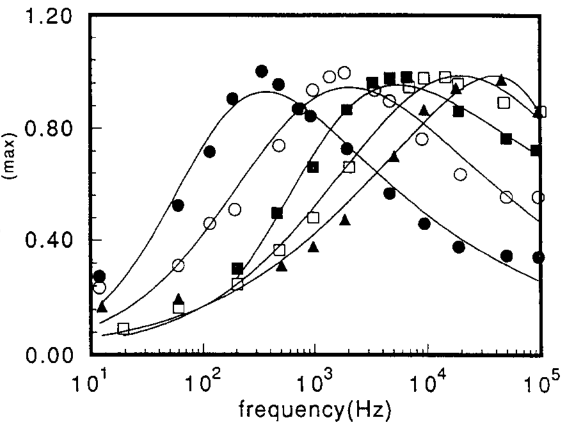

Figure 2 Frequency dependence of $\epsilon''/\epsilon''_{max}$ for a linear PMPS fraction with $n_n = 1370$: (●) 251.0; (○) 255.0; (■) 258.0; (□) 260.0; (▲) 262.0 K (solid lines are HN fits)

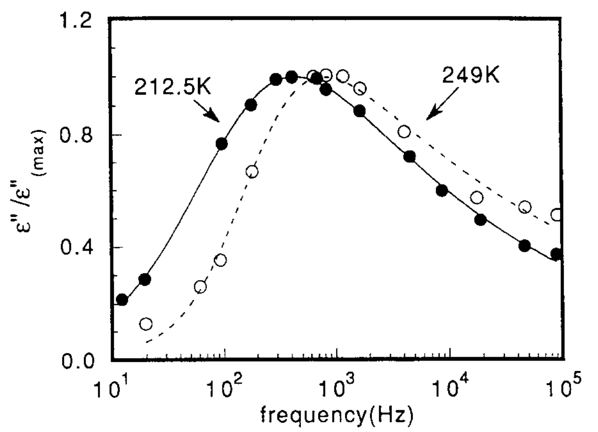

Figure 3 Frequency dependence of $\epsilon''/\epsilon''_{max}$ for cyclic (●) and linear (○) PMPS fractions (solid lines are HN fits)

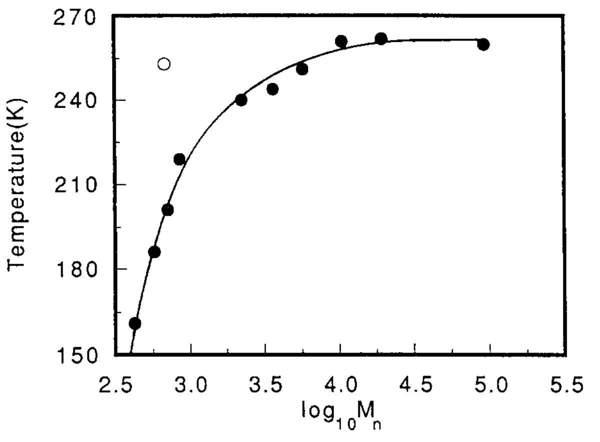

Figure 4 Molecular-weight dependence of the temperature corresponding to ϵ''_{max} at 1 kHz for linear (●) and cyclic (○) PMPS fractions (solid line is given as a guide to the eye)

skewing which is characteristic of the dielectric response of amorphous polymers. The greater dipolar mobility of the linear oligomeric chains is apparent from a comparison of the relaxation plots shown in *Figure 3*. These materials possess an equal number of skeletal bonds ($n = 10$) but the cyclic sample requires temperatures approximately 35 K higher for the α-process to appear within the experimental frequency window. For the linear samples there is a steady shift towards higher temperatures, with increasing molecular weight, of the temperature corresponding to a maximum dielectric loss at 1 kHz, as shown in *Figure 4*. This parameter shows an initial steep increase at low values of the molecular weight, followed by a levelling off towards asymptotic values as the number-average molecular weight increases beyond 10 000. This trend is in good agreement with the molecular-weight dependence of the d.s.c. glass transition[7].

The dielectric loss curves for all samples were analysed by using the empirical Havriliak–Negami (HN) function[8], as follows:

$$\frac{(\epsilon^*(\omega) - \epsilon_\infty)}{(\epsilon_0 - \epsilon_\infty)} = \frac{1}{[1 + (i\omega\tau)^\beta]^\alpha} \qquad (1)$$

where ϵ^* is the complex dielectric constant $i = \sqrt{-1}$, ϵ_0 and ϵ_∞ are the relaxed and unrelaxed values of the dielectric constant, respectively, ω is the angular frequency, τ is the central relaxation time, and β and α characterize the broadening and skewing, respectively, with $0 < \beta \leqslant 1$ and $0 < \alpha \leqslant 1$. When $\beta = 1$ the HN function reduces to the unsymmetrical Davidson–Cole function[9], while for $\alpha = 1$ a symmetrical Cole–Cole[10] dispersion is obtained. If $\alpha = \beta = 1$, this corresponds to a single-relaxation-time Debye process. The parameters relevant to the HN function were determined by a non-linear, least-squares fitting procedure and the best-fit curves which resulted are shown as solid lines in *Figures 1* and *2*.

Relaxation strength and maximum dielectric loss

For each sample, the relaxation strength ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$), which is proportional to the effective dipole moment of the sample at a particular temperature and pressure, exhibits the expected inverse dependence on temperature, while the values of the maximum dielectric loss ϵ''_{max}, measured at the loss peak (corresponding to each isothermal temperature), remain invariant with temperature. Both parameters show a strong dependence on molecular weight, as can be seen in *Figure 5*. The $\Delta\epsilon$ values used in this figure correspond to the maximum value for each sample and were recorded at the lowest measurement temperature for each of these.

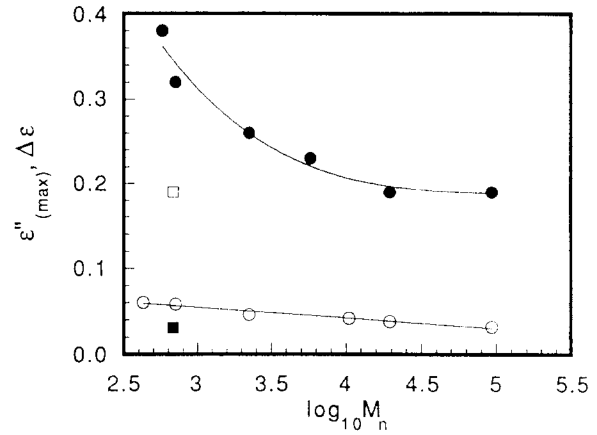

Figure 5 Molecular-weight dependence of ϵ'' for linear (●) and cyclic (■) PMPS fractions (solid line is the linear fit), and of $\Delta\epsilon$ for linear (○) and cyclic (□) PMPS fractions (solid line is the second-order polynomial fit)

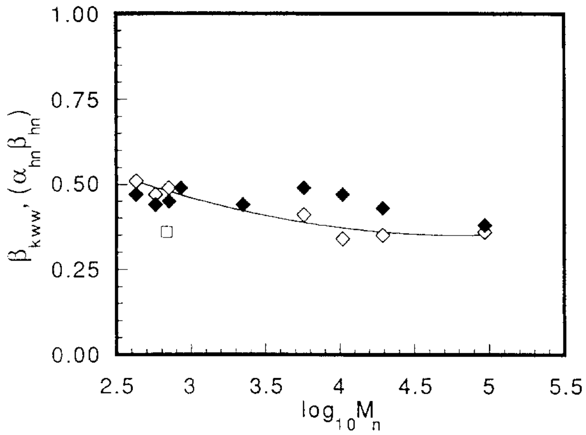

Figure 6 Molecular-weight dependence of β_{kww} for linear (◇) (solid line is given as a guide to the eye) and cyclic (□) PMPS fractions and of $\alpha_{\mathrm{hn}}\beta_{\mathrm{hn}}$ for linear (◆) PMP fractions (error in values is ± 0.02)

$\epsilon''_{\max}$ shows a linear dependence on $\log M_n$, with a slope equal to -0.012, an $\epsilon''_{\max}$ value of 0.091 corresponding to $M_n = 0$, and a $\log M_n$ value of 7.6 corresponding to zero dielectric loss. As the latter condition is unlikely to be observed experimentally it is reasonable to assume that the dielectric loss would tend towards a low asymptotic value at molecular weights beyond those examined here. The relaxation strength, $\Delta\epsilon$, shows a non-linear dependence on $\log M_n$ and can be satisfactorily fitted by a second-order polynomial which asymptotes to a $\Delta\epsilon$ value of 0.19. The low-molecular-weight limit for $\Delta\epsilon$ is predicted to be 1.26. The cyclic oligomer of MPS has a $\epsilon''_{\max}$ of 0.031 and a $\Delta\epsilon$ of 0.19. These values are approximately half of those measured for the linear MPS with an equivalent number of skeletal bonds. The PMPS studied by Boese *et al.*[3] ($M_n = 27\,300$) exhibited $\Delta\epsilon$ values between 0.42 (at −25.1°C) and 0.25 (at 28.7°C), and ϵ'' values of 0.11 (at −25.1°C) and 0.05 (at 28.7°C). Similarly, the relaxation strength for the PMPS studied by Baird and Sengupta[4] ($M_n = 1060$) reached a maximum of 0.4 at −33°C, while the loss maxima, in the temperature range from −41 to −10.5°C, varied between 0.04 and 0.10.

Distribution of relaxation times

Dielectric data in the frequency domain can also be satisfactorily represented by the 'stretched exponential' Kohlrausch–Williams–Watts (KWW) function[11] as follows:

$$\phi(t) = \exp[-(t/\tau)]^{\beta} \tag{2}$$

where $\phi(t)$ is a relaxation function, τ is a characteristic relaxation time and β is a broadening and skewing parameter, where $0 < \beta \leqslant 1$. The values of β in this present study were determined by using the method of Moynihan for evaluating the Fourier transform[12], which requires measurement of the width of the loss peak at $\epsilon''_{\max}/2$. *Figure 6* is a plot of the variation with log molecular weight of the product $(\alpha_{\mathrm{hn}}\beta_{\mathrm{hn}})$ and the β-parameter from the KWW function (β_{kww}). The parameter β_{hn} shows an erratic dependence on the molecular weight, varying between 0.96 and 0.62, and is not plotted here. The plotted values are averages taken over the experimental temperature range for each sample. The parameter β_{kww} shows a steady decrease over a narrow range from 0.51 at the lowest molecular-weight level, to 0.36 at the highest molecular-weight value. This trend gives very satisfactory agreement with $\alpha_{\mathrm{hn}}\beta_{\mathrm{hn}}$, which varies between 0.49 and 0.35. These values, along with those of β_{hn}, are in excellent agreement with the findings of Boese *et al.*[3], who reported that β_{hn} varied between 0.76 at −22.8°C and 0.99 at 28.7°C, $\alpha_{\mathrm{hn}}\beta_{\mathrm{hn}}$ varied between 0.29 and 0.43 over the temperature range of study and β_{kww} was invariant with temperature, with an average value of 0.45. Baird and Sengupta[4] reported $\beta = 0.62$ for the PMPS sample referred to above. The parameter β_{kww} for the cyclic MPS oligomer is significantly lower than that found for the corresponding linear MPS. This reflects the greater degree of cooperativity required for dipolar rotation in a small-ring molecule in which the dipoles are brought into close proximity by virtue of the chain ends being 'tied' together. The relationship between the HN and KWW parameters has previously been considered by Alvarez *et al.*[13]. Since both parameters are known to yield accurate descriptions of the experimental data they carried out dielectric studies in the time and frequency domains for a poly(hydroxy ether of bisphenol A) in the region of the glass transition. From an analysis of the data they derived a relationship between the two parameters, such that $(\alpha_{\mathrm{hn}}\beta_{\mathrm{hn}})^{x} = \beta_{\mathrm{kww}}$ where $x \sim 1$. No such correlation between the HN and KWW parameters was found in this present study, although $(\alpha_{\mathrm{hn}}\beta_{\mathrm{hn}})$ and β_{kww} exhibit a similar dependence on the molecular weight.

Dielectric relaxation activation energy

Values for the apparent activation energy $(\Delta E_{\mathrm{act}})$ for the α-relaxation process were calculated from the slopes of linear Arrhenius plots of $\log f_{\max}$ against $1/T$, where $f_{\max}$ is the frequency corresponding to maximum dielectric loss at temperature T. Activation energies are plotted in *Figure 7*, along with the error associated with each value. The values lie in the approximate range 170–240 kJ mol^{-1} and are significantly lower than the value of 320 kJ mol^{-1} reported for the PMPS investigated by Baird and Sengupta[4]. Their sample, however, contained phenyl end-groups which would be expected to exert a

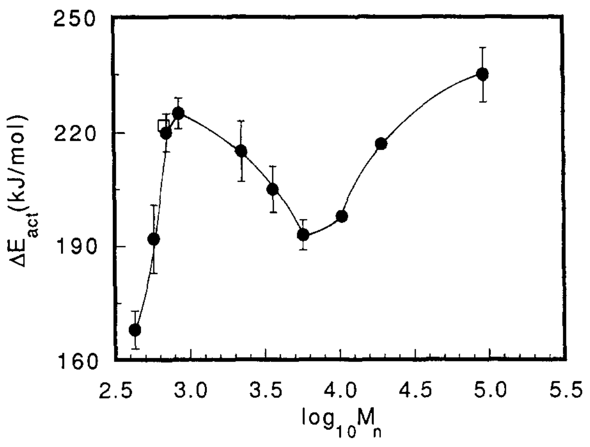

Figure 7 Molecular-weight dependence of activation energy for linear (●) and cyclic (□) PMPS fractions (solid line is given as a guide to the eye)

relatively strong influence on the relaxation behaviour of a small molecule, whereas the samples studied here were terminated by smaller and more mobile methyl groups. The limited effect that the trimethyl end-groups have on the dielectric relaxation of these materials is demonstrated by the fact that the apparent activation energies for the linear and cyclic oligomers with an equal number of skeletal bonds are identical (within experimental error).

Figure 7 can be divided into three distinct regions: (i) an increase in ΔE_{act} as M_n increases from 430 to 850, (ii) a decrease in ΔE_{act} as M_n reaches 5730, and (iii) an increase in ΔE_{act} as M_n reaches the upper limit of 93 000. Taking into account the short chain lengths of the oligomers contained within (i) ($n_n = 4$–10), and the presence of rigid phenyl groups attached to the siloxane backbone, the increase in ΔE_{act} in this region is consistent with the notion that the dominant part of the dielectric relaxation process is a rotation of the whole molecule. Previous dielectric studies[14] on dimethylsiloxane oligomers reported that the experimental data was satisfactorily represented by the superposition of two relaxation processes; the longer-relaxation-time process was attributed to a whole molecule rotation while the more rapid process was believed to be due to segmental relaxation. The activation energy for the longer-relaxation-time process was found to increase with increasing chain length, as observed in this present study. Within (ii) ($n_n = 31$–82) there is likely to be a tendency for the apparent activation energy to decrease as the whole molecule rotation becomes increasingly difficult for the longer siloxane chain and dipolar relaxation then occurs as a consequence of the more rapid segmental motions. This is in line with the dimethylsiloxane study referred to above, which reported a decrease in ΔE_{act} with increasing chain length for the fast (segmental) relaxation process. Finally, within (iii), at higher molecular weights ($n_n > 82$), chain entanglements would be expected to influence and restrict the segmental contribution to the dielectric relaxation and thus result in the observed increase in apparent activation energy.

Dipole moment and dipole moment ratio

The dielectric relaxation strength, $\Delta\epsilon$, can be used to calculate a mean-square molecular dipole moment, μ^2, by incorporation into the Onsager equation[15], as follows:

$$\Delta\epsilon = \frac{12\pi N_v\epsilon_0}{3kT(2\epsilon_0+\epsilon_\infty)}\left(\frac{\epsilon_\infty+2}{3}\right)^2\mu^2 \qquad (3)$$

where N_v is the number of dipolar molecules per unit volume and k is the Boltzmann constant. From a knowledge of N_v, calculated from density values[16] and molecular weight, as well as $\Delta\epsilon$, the molecular dipole moments were calculated for each sample. For comparative purposes these were then converted into the mean-square dipole moments per repeat unit shown in *Table 1*. The maximum value of μ^2 occurs when $n_n = 10$. At longer chain lengths, μ^2 declines to a constant value of 6.34×10^{-31} cm. The minimum values of μ^2 are found for the linear MPS oligomer with $n_n = 4$ and the cyclic MPS where $n_n = 10$. A quantity which is very sensitive to the conformational properties of flexible polymers is the dipole moment ratio, $\langle\mu^2\rangle/nm^2$, where n is the number of skeletal bonds and m is the link dipole moment. The product nm^2 represents an idealized view of a polymer chain in which the dipoles are freely jointed and can rotate independently of each other. The dipole moment ratio, therefore, represents the extent to which the experimental mean-square dipole moment of the actual chain departs from the idealized view. Using the values of μ^2 listed in *Table 1* and a value for m of 0.6, the dipole moment ratios were calculated, and the variation with the number of skeletal bonds is shown in *Figure 8*. This value of m has previously been used in similar calculations for polysiloxanes with different substituents[17]. The dipole moment ratio shows an initial increase with chain length, reaches a maximum of 0.28 at $n_n = 51$ and then decreases to an asymptotic value of 0.26 at the highest molecular-weight value. This is in good agreement with earlier studies which utilized a rotational isomeric state model and reported a theoretical long-chain limit of the dipole moment ratio of 0.27, compared with an experimental value of 0.31[18]. The relatively small values of the dipole moment ratio reflect the effective cancellation of dipole vectors which are normal to the chain backbone, as is the case with PMPS. Theoretical calculations[19] have shown that *trans*-conformational sequences are energetically preferred in dimethylsiloxane chains, and that such sequences will result in a maximum value of the

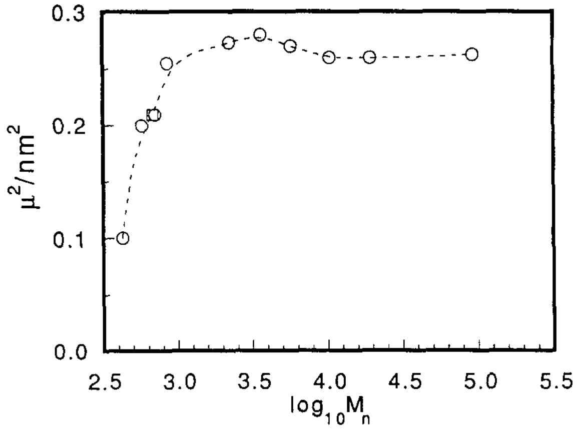

Figure 8 Molecular-weight dependence of dipole moment ratio for linear (O) and cyclic (□) PMPS fractions (dashed line is given as a guide to the eye); error in values is ±0.05

dipole moment ratio at a particular chain length at which mutual cancellation of dipole vectors is least effective. At longer chain lengths the alternate values of 110 and 143° for the skeletal bond angles in these molecules results in the all-*trans*-conformation forming a closed structure with a smaller dipole moment. The effectiveness of dipolar cancellation in closed structures is apparent from a comparison of the dipole moment ratio of the linear and cyclic MPS oligomers with an equal number (i.e. 10) of skeletal bonds. There is a significant difference in the values for these two molecules, with the linear oligomer having a dipole moment ratio of 0.26, compared with 0.21 for the cyclic oligomer, which suggests more effective dipolar cancellation in the cyclic oligomer. This result can be explained by the nature of the chemical bonding of the ring molecule which leads to the formation of a 'closed' structure of the type discussed above. The molecular-weight dependence of the dipole moment ratio shown in *Figure 8* points to similarities in the conformational behaviour of PMPS and dimethylsiloxane with maximum dipolar reinforcement for linear PMPS occurring when $n_n \sim 50$. Mark and Ko[20] have examined chain conformations in PMPS from a theoretical viewpoint and have demonstrated a dependency on chain tacticity. In these molecules a low energy state is achieved through phenyl–phenyl interactions. For such interactions to occur in a syndiotactic structure the all-*trans* state is not favoured as this would result in the phenyl groups being on opposite sides of the chain and therefore not ideally placed for close interactions. Phenyl–phenyl interactions in an isotactic structure, on the other hand, would stabilize the all-*trans*-conformation because the phenyl groups would already be on the same side of the chain and would be able to interact strongly. To date, the effects of stereochemistry on the properties of PMPS has received little attention and is an area which requires further investigation. It is interesting to note that the maximum in the dipole moment ratio occurs for a molecule with a molecular weight which places it within region (iii) in *Figure 6*. It is within this region that segmental rotations are the dominant part of the dipolar relaxation.

CONCLUSIONS

The dielectric behaviour, in the region of the glass–rubber relaxation, of a series of undiluted linear MPS oligomers and PMPS shows a systematic variation with changes in molecular weight. The broadness of the relaxation time distribution, as characterized by the empirical HN and KWW functions, increases as the chain length increases, reflecting increases in the degree of cooperativity required for dipolar rotations. The apparent activation energy varies as first the whole molecule, and then segmental rotations, contribute the major part of the total dielectric relaxation. The dipole moment ratio exhibits a maximum at $n_n \sim 50$, which indicates that maximum dipolar reinforcement is occurring at this point. The results for a cyclic MPS oligomer demonstrate (i) the restrictions placed upon dipolar rotations, and (ii) the effectiveness of dipolar cancellations, in siloxane ring structures.

ACKNOWLEDGEMENTS

Acknowledgements are due to Mr A. Stewart for the construction of the dielectric cell. AAG is indebted to Aston University for providing financial support during this study.

REFERENCES

1 Clarson, S. J and Semlyen, J. A. (Eds) 'Siloxane Polymers', Prentice Hall, New Jersey, 1993
2 Fytas, G., Dorfmuller, D. and Chu, B. *J. Polym. Sci. Polym. Phys. Edn* 1984, **22**, 1471
3 Boese, D., Momper, B., Meier, G., Kremer, F., Hagenah, J-U. and Fischer, E. W. *Macromolecules* 1989, **22**, 4416
4 Baird, M. E. and Sengupta, C. R. *J. Chem. Soc. Faraday Trans. 2* 1972, **68**, 1795
5 Baird, M. E. and Sengupta, C. R. *J. Chem. Soc. Faraday Trans. 2* 1974, **70**, 1741
6 Clarson, S. J. and Semlyen, J. A. *Polymer* 1986, **27**, 1633
7 Clarson, S. J., Semlyen, J. A. and Dodgson, K. *Polymer* 1991, **32**, 2823
8 Havriliak, S. and Negami, S. *J. Polym. Sci. (C)* 1966, **14**, 99
9 Davidson, D. W. and Cole, R. H. *J. Chem. Phys.* 1950, **18**, 1417
10 Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1941, **9**, 341
11 Williams, G. W. and Watts, D. C. *Trans. Faraday Soc.* 1970, **66**, 80
12 Moynihan, C. T., Boesch, L. P. and Laberge, N. L. *Phys. Chem. Glasses* 1973, **14**, 122
13 Alvarez, F., Alegria, A. and Colmenero, J. *Phys. Rev. B* 1991, **44**, 7306
14 Dasgupta, S. and Smyth, C. P. *J. Chem. Phys.* 1967, **47**, 2911
15 Onsager, L. J. *J. Am. Chem. Soc.* 1936, **58**, 1488
16 Noll, W. 'Chemistry and Technology of Silicones', Academic, New York, 1968
17 Liao, S. C. and Mark, J. E. *J. Chem. Phys.* 1973, **59**, 3825
18 Salom, C., Freire, J. J. and Hernandez-Fuentes, I. *Polym. J.* 1988, **20**, 1109
19 Mark, J. E. *J. Chem. Phys.* 1968, **49**, 1398
20 Mark, J. E. and Ko, J. H. *J. Polym. Sci. Polym. Phys. Edn* 1975, **13**, 2221