Polymer Vol. 37 No. 13, pp. 2603–2607, 1996

0032-3861/96/$15.00+0.00

Studies of cyclic and linear polydimethylsiloxanes: 32. Dielectric relaxation investigations

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

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

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

The dielectric α-relaxation of a series of narrow-molecular-weight fractions of cyclic and linear polydimethysiloxanes (PDMSs) has been investigated as a function of frequency in the temperature range 140.5–157.5 K. The temperature of the α-transition decreases with increasing chain length for cyclic PDMS and increases with increasing chain length for linear PDMS, in agreement with the previously reported differential scanning calorimetry (d.s.c.) glass transition. The cooperativity of the relaxation process, according to the Kohlrausch–Williams–Watts analysis, is greater in linear PDMS. The activation energy and molecular dipole moment increase with increasing chain length for both cyclic and linear molecular types. Experimental values of the dipole moment ratio are in good agreement with those measured by static dielectric techniques and with the theoretical long-chain value. Copyright © 1996 Elsevier Science Ltd.

(Keywords: dielectric relaxation; polydimethylsiloxanes; dipole moment)

INTRODUCTION

Polymers containing inorganic constituents in the backbone have been recognized as having superior thermal stability when compared with their organic counterparts[1]. Siloxane polymers, $-(\mathrm{RR'SiO})_y-$, are the most common class of inorganic polymer and have been widely studied. This has resulted in a range of commercial products becoming available which encompass liquids, elastomers and crosslinked resins[2]. In particular, polydimethylsiloxane (PDMS) has been extensively studied in both its linear and ring form. Narrow fractions of cyclic and linear PDMS have been synthesized with a range of molecular weights, from small oligomers to cyclic polymers containing hundreds of skeletal bonds. These structures have been found to exhibit distinct differences in their equilibrium properties at low molecular weight levels, which reflect the conformational restrictions and reduced flexibility of the cyclic molecules[3].

Polysiloxanes have long been considered for use as liquid dielectrics because of their low dissipation factors at high temperatures and frequencies. Consequently, there has been much interest in the electrical properties of polysiloxanes and in this present paper we report the dielectric behaviour, as a function of temperature and frequency, of narrow fractions of cyclic and linear PDMSs with varying molecular weights.

The dielectric α-relaxation of linear PDMS has been shown to have a strong dependence on sample thermal history. Baird and Sengupta[4] observed the dielectric loss behaviour of linear PDMS with $M_w = 107\,000$ and found that, on cooling from room temperature, the onset of crystallization occurred at ca. -50°C. The resulting dielectric loss peaks, measured in the α-relaxation region, were broad and asymmetric with a half-height width of ca. 6 decades of frequency. The degree of crystallinity in this sample was not investigated. The apparent activation energy for the α-process was reported to be 100 kJ mol^{-1}. Adachi and coworkers[5] carried out a more systematic study on a linear PDMS with a molecular weight of 8.3×10^6, where amorphous samples were obtained by cooling from room temperature to below the glass transition at a rate of 50 K min^{-1} and crystalline samples were obtained by annealing at -78°C for 24 h. Once again, no information on the degree of crystallinity was presented. In an isochronal scan the amorphous sample exhibited two loss peaks, i.e. a sharp peak centred at 155 K, which was assigned to the

---

* 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

glass transition, and a high-temperature (at 165–185 K), less intense and broader peak, which was associated with dynamic crystallization of the sample during the heating scan. The crystalline sample exhibited a broad glass transition peak at 160 K, with the upward shift in temperature, compared with the amorphous sample, being caused by the crystallites restricting the motions of adjacent amorphous segments. The presence of crystallinity restricting the motions of adjacent amorphous segments. The presence of crystallinity increased the half-width of the absorption curve from 2.2 to 5.6, decades of frequency, reduced the relaxation strength from 0.82 to 0.43, reduced the maximum value of dielectric loss from ~0.2 to ~0.05, and increased the activation energy for the α-relaxation process from 75 to 120 kJ mol^{-1}.

EXPERIMENTAL

Materials

The cyclic PDMS, $[(CH_3)_3SiO]_y$, was prepared by a ring–chain equilibrium reaction in toluene at 110°C, while the trimethylsilyl-terminated linear PDMS, $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$, was obtained from commercial Dow Corning DC200 series fluids. The cyclic and linear PDMS materials were then fractionated by vacuum fractional distillation and preparative gel permeation chromatography, as described in detail previously[6,7]. Values for the molar masses of the siloxanes and the polydispersity (M_w/M_n) were obtained by using a gel permeation chromatograph calibrated using standard siloxane samples, with the chromatograms being corrected for axial broadening effects. The characterization data for the cyclic and linear PDMS samples are summarized in *Tables 1* and *2*, respectively. The cyclic fractions had number-average numbers of skeletal bonds, n_n, in the range 28–99, while the linear fractions had n_n values in the range 28–86. The values of the polydispersity index of the samples were close to unity (M_w/M_n values were in the range 1.01–1.07), indicating very narrow molar-mass distributions. The materials were all clear viscous liquids at room temperature.

Table 1 Relaxation parameters for various cyclic fractions of PDMS: error in values is ±0.02

n_n	$\Delta\epsilon^a$	$\alpha_{hn}{}^a$	$\beta_{hn}{}^a$	$\beta_{kww}{}^b$
28	0.46	0.51	0.84	0.51
35	0.44	0.44	0.87	0.54
50	0.41	0.53	0.89	0.55
66	0.43	0.41	0.85	0.53
99	0.43	0.51	0.90	0.52

[a] Values derived from Havriliak–Negami analysis
[b] Values derived from Kohlrausch–Williams–Watts equation

Table 2 Relaxation parameters for various cyclic fractions of PDMS; error in values is ±0.02

n_n	$\Delta\epsilon^a$	$\alpha_{hn}{}^a$	$\beta_{hn}{}^a$	$\beta_{kww}{}^b$
28	0.54	0.37	0.87	0.52
34	0.50	0.44	0.87	0.45
57	0.51	0.31	0.94	0.44
72	0.47	0.35	0.91	0.47
86	0.43	0.35	0.90	0.53

[a] Values derived from Havriliak–Negami analysis
[b] Values derived from Kohlrausch–Williams–Watts equation

A previous study by Clarson *et al.*[8] has shown that cyclic and linear fractions of the range of molecular weights used here can be rapidly cooled from the liquid state at room temperature to below the glass transition without any crystallization occurring. Therefore, in order to maintain a consistent thermal history for each sample, and to ensure amorphous samples, the cooling unit containing the dielectric cell and sample was cooled from room temperature to −150°C at a rate in excess of 50 K min^{-1} prior to each measurement.

Dielectric measurements

Electrical capacitance (C) and dissipation factor ($\tan\delta$) values for each sample were measured by using a GenRad 1689 Precision RLC Digibridge over the range 12–10^5 Hz, using an average value of 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 ca. 0.1 cm^3. The geometrical capacitance of the dielectric cell, C_0, was 25 pF at 12 Hz. 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 any stray capacitances.

Temperature control was achieved by using a specially constructed double Dewar system 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

The product of the experimental parameters taken from the dielectric bridge, $C\tan\delta$, is equivalent to $C_0\epsilon''$ since $C/C_0 = \epsilon'$ and $\tan\delta = \epsilon''/\epsilon'$, where ϵ' and ϵ'' are the frequency-dependent dielectric constant and dielectric loss, respectively. Therefore, by dividing the values of $C\tan\delta$ by the geometrical cell capacitance values (at each frequency), the dielectric loss, ϵ'', can be obtained. *Figures 1* and *2* show isothermal plots of the frequency dependence of the dielectric loss for cyclic and linear fractions, respectively, of PDMS in the α-relaxation region. Values of the maximum dielectric loss, ϵ''_{max}, remained constant, within experimental error, at 0.12 for both cyclic and linear fractions over the respective molecular-weight ranges. The loss plots are skewed towards the high-frequency side, which is a characteristic response of amorphous polymers. The greater dipolar mobility of linear PDMS is apparent from the relaxation plots shown in *Figure 3* where the latter shows the dielectric loss curves obtained at 148 K for fractions of cyclic and linear PDMS with $n_n = 28$. The cyclic PDMS

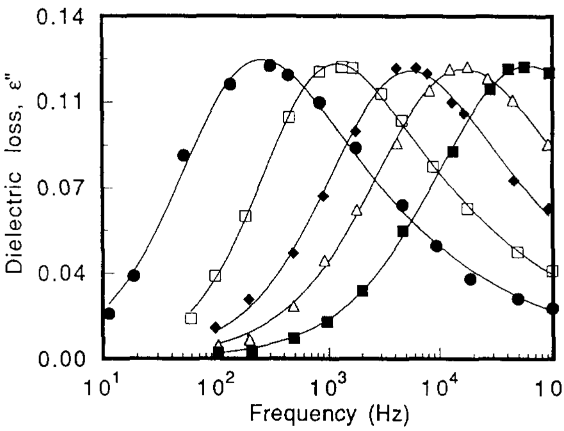

Figure 1 Dielectric loss curves for cyclic PDMS with $n_n = 66$: (●) 148.5; (□) 151.0; (◆) 153.0; (△) 154.5; (■) 156.5 K (solid lines are curve fits to the Havriliak–Negami equation)

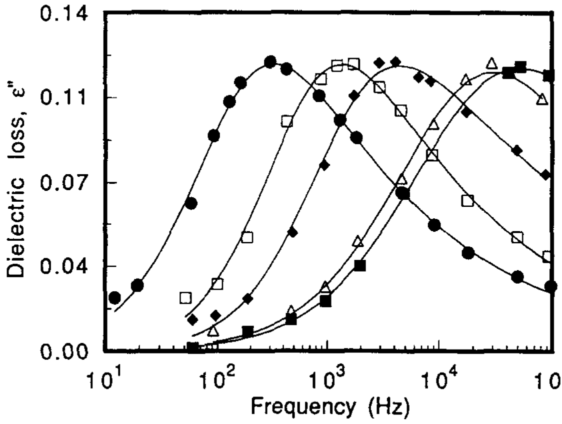

Figure 2 Dielectric loss curves for linear PDMS with $n_n = 28$: (●) 142.0; (□) 143.5; (◆) 145.0; (△) 147.5; (■) 148.0 K (solid lines are curve fits to the Havriliak–Negami equation)

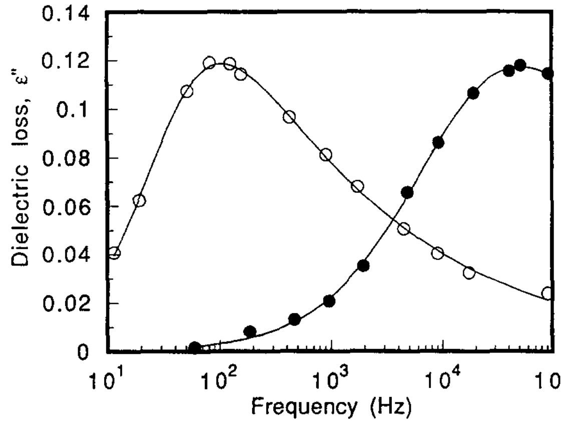

Figure 3 Dielectric loss curves for cyclic (○) and linear (●) PDMS fractions with $n_n = 28$ at 148 K (solid lines are curve fits to the Havriliak–Negami equation)

has a maximum in the dielectric loss at ca. 100 Hz, whereas the linear PDMS exhibits a maximum in the dielectric loss close to 10^5 Hz. For both cyclic and linear fractions the temperature corresponding to the maximum in dielectric loss, ϵ''_{max}, at a particular frequency, was found to be molecular-weight dependent. Relationships have been reported[9,10] which account for the variation of the glass transition temperature, T_g, with chain length for linear polymers, with these taking the following form:

$$T_g = T_\infty - (K/M_n) \qquad (1)$$

where T_∞ is the asymptotic value of the glass transition and K is a constant. A plot of this type, by using dielectric data with T_α, where the latter is the temperature of the dielectric loss peak corresponding to a 1 kHz measuring frequency, plotted against the reciprocal-number-average molecular weight is shown in *Figure 4*. Across the molecular-weight range used here the α-relaxation of cyclic PDMS fractions occurs at higher temperatures when compared with the linear PDMS fractions. Moreover, T_α for the cyclic fractions increases with decreasing M_n, whereas T_α for the linear fractions decreases with decreasing M_n. These trends have previously been reported[8] for the molecular-weight dependence of the d.s.c. glass transition of a similar series of cyclic and linear fractions of PDMS. A linear fit to the cyclic data in *Figure 4* gave a T_∞ value equal to 149 K and a K value equal to -2.5×10^3 K g mol^{-1}. For the linear data, a linear fit gave T_∞ equal to 148 K and K equal to 6.5×10^3 K g mol^{-1}. These values are in good agreement with those reported in ref. 8 and indicate that for high-molecular-weight cyclic and linear PDMS the limiting glass transition temperatures will be equal. According to simple free volume theories the T_g/molecular-weight behaviour for cyclic PDMS was unexpected and was subsequently accounted for in a configurational entropy model developed by Di Marzio and Guttman[11].

Empirical relaxation functions

The dielectric loss curves for all samples were analysed by using the empirical Havriliak–Negami (HN) function[12], as follows:

$$\frac{(\epsilon^*(\omega) - \epsilon_\infty)}{(\epsilon_0 - \epsilon_\infty)} = \frac{1}{[1 + (i\omega\tau)^{\beta_{hn}}]^{\alpha_{hn}}} \qquad (2)$$

where ϵ^* is the complex dielectric constant at angular frequency ω, ϵ_0 and ϵ_∞ are the relaxed and unrelaxed values of the dielectric constant, respectively, τ is the central relaxation time, and β_{hn} and α_{hn} characterize the broadening and skewing, respectively, with $0 < \beta_{hn} \leq 1$ and $0 < \alpha_{hn} \leq 1$. When $\beta_{hn} = 1$ the HN function reduces

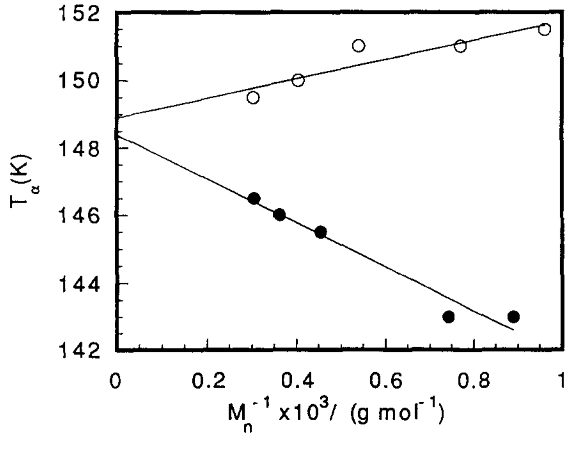

Figure 4 Variation of T_α at 1 kHz with reciprocal molecular weight for cyclic (○) and linear (●) PDMS fractions

to the asymmetric Davidson–Cole function[13], while for $\alpha_{hn} = 1$ a symmetrical Cole–Cole[14] dispersion is obtained. If $\alpha_{hn} = \beta_{hn} = 1$ 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 1–3*.

Dielectric data in the frequency domain can also be satisfactorily represented by the 'stretched exponential' Kohlrausch–Williams–Watts (KWW) function[15], as follows:

$$\phi(t) = \exp[(-t/\tau)^{\beta_{kww}}] \tag{3}$$

where $\phi(t)$ is a relaxation function, τ is a characteristic relaxation time and β_{kww} is a broadening and skewing parameter where $0 < \beta_{kww} \leq 1$. The values of β_{kww} in this study were determined by using the method of Moynihan for evaluating the Fourier transform[16] which requires measurement of the width of the loss peak at $\epsilon''_{max}/2$. The relaxation parameters derived from this analysis are listed in *Tables 1* and *2*. Values of the symmetrical broadness parameter, β_{hn}, tend towards a slight increase with increasing molecular weight for both cyclic and linear PDMS. This behaviour reflects a narrowing of the distribution of the relaxation times, and hence a decrease in the cooperativity of the α-relaxation, as the number of skeletal bonds increases. The small differences in values between the two molecular types are within experimental error. The parameter α_{hn} shows no discernible trend with molecular weight in either case, but the consistently lower values for the linear fractions reflects the greater skew of the relaxation process in linear PDMS, when compared with cyclic PDMS. The parameter β_{kww} shows no discernible trend with changes in molecular weight but average values taken over the range of molecular weights do reveal a difference between cyclics ($\beta_{kww} = 0.53$) and linears ($\beta_{kww} = 0.48$), suggesting that the α-relaxation is more cooperative in linear PDMS. The relaxation strength, $\Delta\epsilon$, which is related to the molecular dipole moment being relaxed, decreases from 0.54 to 0.43 and from 0.46 to 0.41 with increasing chain length, for linear fractions and cyclic fractions, respectively.

Activation energy

The shift in the frequency of the maximum in dielectric loss with isothermal temperature can be used to construct Arrhenius plots for each sample and to obtain values of the apparent activation energy, ΔE_{act}, for the α-relaxation process. The molecular-weight dependence of the activation on energy for cyclic and linear fractions is shown in *Figure 5*, along with the standard error associated with each measurement. Activation energies lie in the range 125–136 kJ mol^{-1} for the cyclic fractions and 121–146 kJ mol^{-1} for the linear fractions (slightly higher values than those reported in ref. 5). Initially, the activation energies for the linear fractions fall below those of the cyclics and then, at $n_n \sim 50$, there begins a much steeper rise in the activation energy of the linears with increasing molecular weight, compared with the cyclic fractions, which leads to a cross-over at $n_n \sim 65$. It is interesting to note that a similar cross-over point has also been reported to occur at $n_n \sim 100$ in a comparison of the viscosities of cyclic and linear fractions over a wide molecular-weight range[17]. The dielectric activation energy behaviour observed in this present study requires further investigation, although it is apparent that it is not due to entanglement effects since the critical molar mass for entanglement, M_c, has been reported at ~17 000 for cyclic PDMS and at ~16 600 for linear PDMS[18], significantly beyond the range of molecular weights studied here.

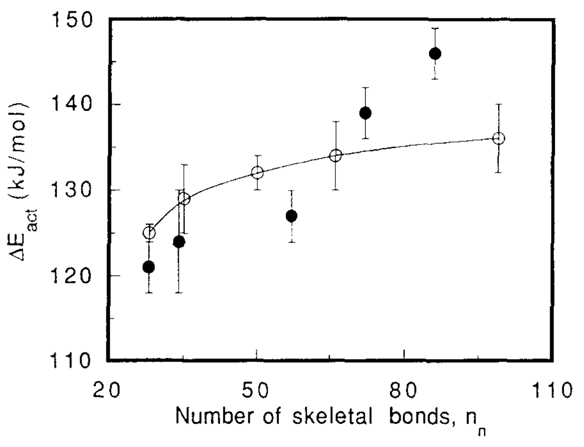

Figure 5 Molecular-weight dependence of the activation energy for cyclic (○) and linear (●) PDMS fractions (solid line is given as a guide to the eye)

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[19], as follows:

$$\Delta\epsilon = \frac{12\pi N_v \epsilon_0}{3kT(2\epsilon_0 + \epsilon_\infty)} \left(\frac{\epsilon_\infty + 2}{3}\right)^2 \mu^2 \tag{4}$$

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 [20] and molecular weight, as well as $\Delta\epsilon$, the mean-square molecular dipole moments were calculated and are plotted in *Figure 6* against the number of skeletal bonds. The molecular dipole moment increases in a linear fashion with increasing chain length, with no

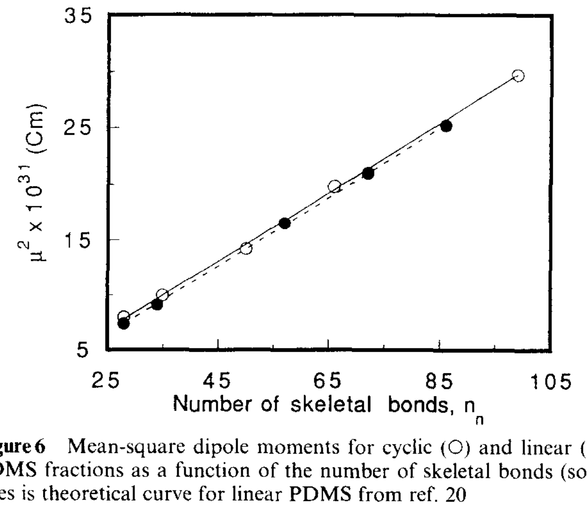

Figure 6 Mean-square dipole moments for cyclic (○) and linear (●) PDMS fractions as a function of the number of skeletal bonds (solid lines is theoretical curve for linear PDMS from ref. 20

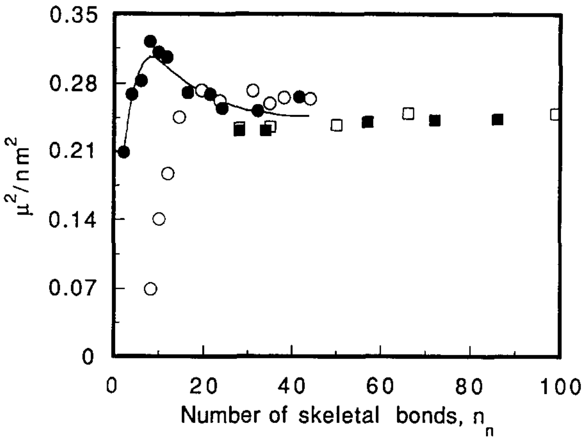

Figure 7 Dipole moment ratios as a function of the number of skeletal bonds for: (□) cyclic PDMS, present study; (○) cyclic PDMS, ref. 20; (■) linear PDMS, present study; (●) linear PDMS, ref. 20 (solid line is the theoretical curve for linear PDMS from ref. 20)

significant differences between the dipole moments of cyclic and linear PDMS over the plotted molecular-weight range. This finding is in agreement with an earlier study by Beevers *et al.*[20] in which static dielectric permittivity data was analysed to give dipole moment values and this revealed significant differences between cyclic and linear fractions only when $n_n < 15$. Furthermore, the μ^2 values reported in ref. 20 are in excellent agreement with those found in this present study. The dipole moment ratio, μ^2/nm^2, where m is the link dipole moment, is dependent upon the conformational properties of flexible polymer molecules and has been experimentally and theoretically analysed for the polysiloxanes[21]. Experimental values of the dipole moment ratio for cyclic and linear fractions of PDMS were calculated by using an m value of 2.0×10^{-30} C m, taken from ref. 20, and are plotted in *Figure 7*. The experimental values from the static dielectric study of Beevers *et al.*[20], are also plotted along with theoretical values, of the dipole moment ratio calculated by the same authors[20], using a rotational isomeric state model for linear PDMS. The maximum in the ratio found for linear PDMS at $n_n \sim 8$ has been attributed to small chains forming a low-energy all-*trans* conformational state as a result of the unequal bond angles at the silicon and oxygen atoms of the polysiloxane chain, which results in an enhancement of the dipole vectors[21]. The range of molecular weights in this study is beyond the point at which this maximum occurs but the resulting experimental dipole moment ratio values are equal, within experimental error, to the theoretical long-chain asymptotic value of 0.23[21].

CONCLUSIONS

Cyclic and linear PDMS, over a narrow molecular weight range (n_n = 28–99 and 28–86, respectively) have been shown to exhibit a number of differences in their relaxation behaviour. Dipolar segments in linear PDMS, which give rise to the dielectric α-relaxation, relax at a significantly faster rate than dipoles in the equivalent cyclic PDMS. The differences in the molecular dynamics between the cyclic and linear PDMS are reflected in the Kohlrausch–Williams–Watts analysis, which suggests that the α-relaxation is broader and thus more cooperative in linear PDMS. The variation of T_α with molecular weight is positive for linear PDMS and negative for cyclic PDMS, in agreement with a trend which was first observed using d.s.c., which confirms the related nature of dielectric and heat flow studies in characterizing glass transition processes. The good agreement between the dipole moment and dipole moment ratio values obtained from this present study and those from earlier studies highlights the usefulness of dynamic dielectric studies for determining dipole moments, which are traditionally calculated from static permittivity and polarization data.

ACKNOWLEDGMENTS

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 Noll, W. 'Chemistry and Technology of Silicones', Academic Press, New York, 1968
2 Clarson, S. J. and Semlyen, J. A. (Eds) 'Siloxane Polymers' Prentice Hall, New Jersey, 1993
3 Semlyen, J. A. in 'Siloxane Polymers' (Eds S. J. Clarson and J. A. Semlyen), Prentice Hall, New Jersey, 1993, Ch. 3, p. 135
4 Baird, M. E. and Sengupta, C. R. *J. Chem. Soc. Faraday Trans. 2*, 1972, **68**, 1795
5 Adachi, H., Adachi, K., Ishida, Y. and Kotaka, T. *J. Polym. Sci. Polym. Phys. Edn* 1979, **17**, 851
6 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
7 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
8 Clarson, S. J., Dodgson, K. and Semlyen, J. A. *Polymer*, 1985, **26**, 930
9 Roe, R. J. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. F. Mark, N. B. Bikales, C. G. Overberger and G. Menges), Vol. 7, 2nd Edn, Wiley, New York, 1986, p. 531
10 Edwards, S. F. *Polymer* 1994, **35**, 3827
11 DiMarzio, E. A. and Guttman, C. M. *Macromolecules* 1987, **20**, 1403
12 Havriliak, S. and Negami, S. *J. Polym. Sci. (C)* 1966, **14**, 99
13 Davidson, D. W. and Cole, R. H. *J. Chem. Phys.* 1950, **18**, 1417
14 Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1941, **9**, 341
15 Williams, G. *J. Non-Cryst. Solids* 1991, **131–133**, 1
16 Moynihan, C. T., Boesch, L. P. and Laberge, N. L. *Phys. Chem. Glasses* 1973, **14**, 122
17 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **22**, 663
18 Orrah, D., Semlyen, J. A. and Ross-Murphy, S. B. *Polymer* 1988, **29**, 1452
19 Onsager, L. J. *J. Am. Chem. Soc.* 1936, **58**, 1488
20 Beevers, M. S., Mumby, S. J., Clarson, S. J. and Semlyen, J. A. *Polymer* 1983, **24**, 1565
21 Mark, J. E. *J. Chem. Phys.* 1968, **49**, 1398