Studies of cyclic and linear poly(dimethylsiloxanes): 19. Glass transition temperatures and crystallization behaviour

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Differential scanning calorimetry (d.s.c.) was used to investigate the thermal behaviour of cyclic and linear poly(dimethylsiloxanes) over the temperature range 103–298 K. Fractions of the polymers studied had number-average molar masses in the range $160 < M_n < 25\,500\,\mathrm{g\,mol^{-1}}$ and heterogeneity indices $M_w/M_n < 1.1$ in most cases. D.s.c. was applied to measure the glass transition temperatures T_g cold crystallization temperatures T_c and polymer crystalline melting temperatures T_m of the oligomer and polymer fractions. Cyclic siloxanes $[(CH_3)_2SiO]_x$ with number-average numbers of skeletal bonds n_n in the range $24 \leqslant n_n \leqslant 79$ and linear siloxanes $(CH_3)SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ with n_n in the range $10 \leqslant n_n \leqslant 40$ were found not to crystallize. The T_g values of the linear siloxanes were found to be in agreement with values in the literature and they increased with increasing M_n. By contrast, the T_g values of the cyclics were found to decrease with increasing M_n.

(Keywords: cyclic poly(dimethylsiloxane); linear poly(dimethylsiloxane); glass transition temperature; crystallization; differential scanning calorimetry)

INTRODUCTION

Cyclic poly(dimethylsiloxanes) PDMS were the first synthetic cyclic polymers to be prepared[1-4] and characterized[5-14]. In this paper, glass transition temperatures and crystalline melting characteristics of cyclic PDMS fractions are determined by differential scanning calorimetry (d.s.c.). They are compared with those of linear PDMS.

EXPERIMENTAL

Preparation of materials

The cyclics $[(CH_3)_2SiO]_x$ were obtained from a PDMS ring-chain equilibration reaction carried out in toluene at 383 K. The linear PDMS materials $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ were obtained by fractionation of Dow Corning D.C. 200 series Dimethicone fluids. Vacuum fractional distillation and preparative gel permeation chromatography (g.p.c.) were used to prepare sharp fractions of the cyclic and linear siloxanes with number-average molar masses and heterogeneity indices shown in *Tables 1* and *2*. They were characterized by gas-liquid chromatography and analytical g.p.c.

Differential scanning calorimetry

The instrument used for this investigation was a Mettler TA 3000 series thermal analyser system. This consisted of a Mettler DSC 30 differential scanning calorimeter, interfaced to a Mettler T.C. 10 TA microprocessor. Effects due to thermal lag in the system were corrected and the temperature scale of the instrument was checked by regular calibration using indium and lead standards.

In order to ensure a consistent thermal history for each of the samples, the following conditions were employed. The d.s.c. cell containing the sample was rapidly cooled to 103 K at a rate of 49 K min^{-1}. It was held at 103 K for 3 min to allow the system to attain thermal equilibrium. The cell was heated to 298 K at a rate of 10 K min^{-1}. The heating and cooling was controlled by a microprocessor. All the exothermal and endothermal events over the temperature range scanned were recorded by the microprocessor.

RESULTS AND DISCUSSION

Glass transition temperatures T_g

The T_g values of the cyclic and linear PDMS fractions are shown in *Tables 1* and *2*. A thermogram of the glass transition for a 394 bond cyclic PDMS fraction is shown in *Figure 1*. The value obtained for T_g may be taken as $T_1 = 146.4\,\mathrm{K}$, $T_2 = 148.2\,\mathrm{K}$ or $T_3 = 150.0\,\mathrm{K}$. This is because the glass transition temperature of a polymer derived from d.s.c.[15] may be defined by three temperatures T_1, T_2 and T_3, as shown in *Figure 1*. Thus T_1

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Table 1 Number-average number of skeletal bonds n_n, number-average molar masses M_n, heterogeneity indices M_w/M_n and glass temperatures T_g for the cyclic dimethylsiloxanes and poly(dimethylsiloxanes)

Fraction	n_n	M_n (g mol^{-1})	M_w/M_n	T_g (K)
R1	10	370	–	–
R2	14	500	1.03	156.8
R3	24	880	1.05	154.6
R4	28	1040	1.04	153.7
R5	31	1160	1.02	152.8
R6	36	1340	1.02	152.3
R7	38	1420	1.02	151.9
R8	44	1630	1.02	152.1
R9	47	1730	1.02	151.9
R10	66	2470	1.04	150.8
R11	68	2520	1.06	151.0
R12	79	2930	1.04	150.8
R13	84	3130	1.05	151.0
R14	88	3270	1.07	150.5
R15	109	4030	1.03	150.4
R16	135	5000	1.05	150.9
R17	154	5720	1.04	150.5
R18	190	7030	1.04	150.3
R19	239	8860	1.05	150.2
R20	311	11 530	1.05	150.1
R21	394	14 600	1.09	150.2
R22	657	24 370	1.10	150.3

Table 2 Number-average number of skeletal bonds n_n, number-average molar masses M_n, heterogeneity indices M_w/M_n and glass transition temperatures T_g for the linear dimethylsiloxanes and poly(dimethylsiloxanes)

Fraction	n_n	M_n (g mol^{-1})	M_w/M_n	T_g (K)
L1	0	160	–	–
L2	2	240	–	123.4
L3	4	310	–	129.1
L4	10	530	1.01	137.4
L5	13	630	1.03	139.4
L6	17	810	1.02	141.2
L7	22	990	1.01	143.3
L8	30	1290	1.02	144.8
L9	40	1630	1.01	146.1
L10	56	2260	1.01	147.5
L11	62	2460	1.02	148.0
L12	74	2920	1.15	148.3
L13	106	4080	1.24	149.2
L14	127	4880	1.23	148.8
L15	166	6330	1.17	149.3
L16	204	7720	1.16	149.5
L17	267	10 060	1.15	149.5
L18	327	12 290	1.14	149.4
L19	393	14 750	1.11	149.7
L20	488	18 250	1.09	149.8
L21	573	21 390	1.09	149.8
L22	682	25 460	1.05	149.7

corresponds to the temperature at which the onset of the endothermal change takes place. T_2 corresponds to the temperature at which the regression line, constructed through the trace below the starting point of the transition, intersects the tangent drawn from the inflection point of the glass transition step. T_3 corresponds to the temperature at which 50% of the transition is complete and was adopted as the T_g value throughout, as it was found to be the most reproducible temperature in this investigation. T_g for each fraction was obtained by taking the average of three independently determined values of T_3 and were consistent to within ± 0.5 K.

A plot of the T_g values of the cyclic and linear PDMS fractions against their number-average number of skeletal bonds n_n is shown in *Figure 2*. A plot of the T_g values against their reciprocal number-average molar masses M_n^{-1} is shown in *Figure 3*. A least mean squares line has been constructed through the data for the linear fractions and is shown in *Figure 3*. It predicts an infinite molar mass $T_g(\infty)$ of 150.2 ± 1.0 K for linear PDMS. The corresponding value $T_g(\infty)$ for cyclic PDMS was determined in a similar way and found to be 149.8 ± 1.0 K. $T_g(\infty)$ for linear PDMS is in close agreement with the literature values of 148 K found by Cowie and McEwen[16] and by Barrie *et al.*[17], 149 K reported by Turdakin *et al.*[18] and 150 K obtained by Lee[19], Adachi[20] and Krause[21]

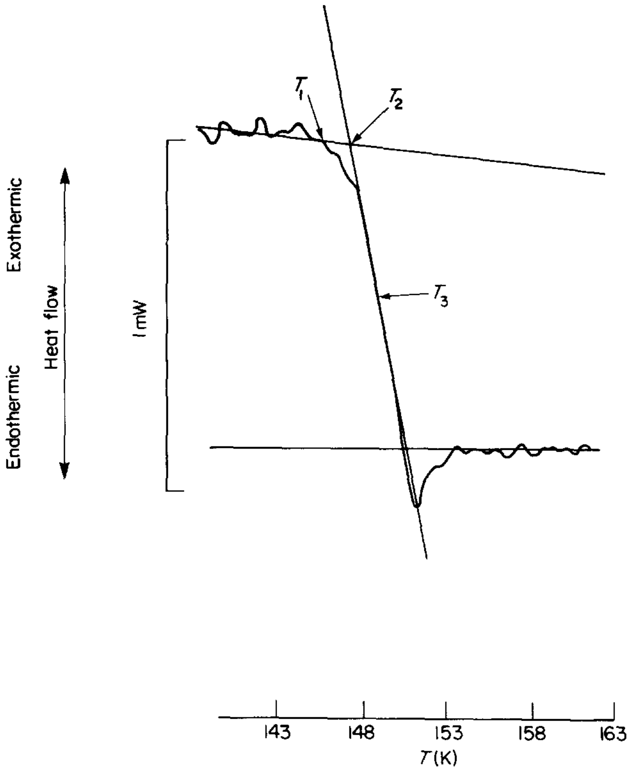

Figure 1 Evaluation of T_g for cyclic poly(dimethylsiloxane) fraction R21 ($n_n = 394$)

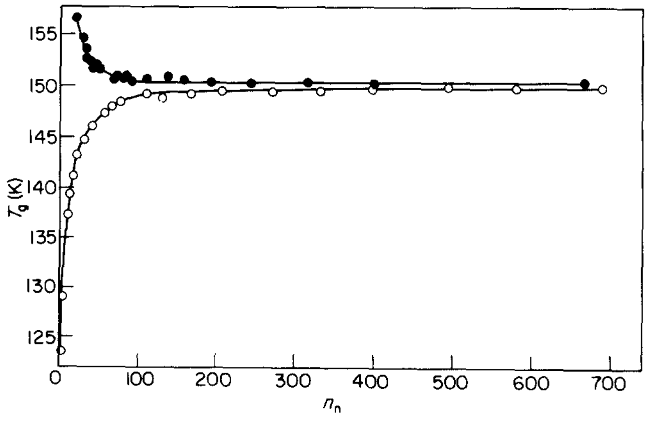

Figure 2 T_g of the cyclic dimethyl siloxanes (●) and linear dimethyl siloxanes (○) plotted against number-average number of skeletal bonds n_n

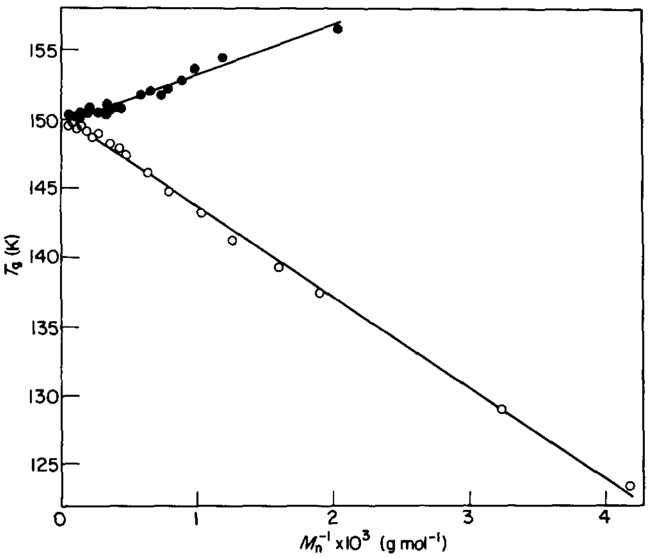

Figure 3 T_g of the cyclic dimethylsiloxanes (●) and linear dimethyl siloxanes (○) plotted against reciprocal number-average molar mass M_n^{-1}

Table 3 Cold crystallization temperatures T_c and molecular crystalline melting temperatures T_m for the cyclic and linear dimethylsiloxanes

Fraction	T_c (K)	T_m (K)
R1	205.9	229.1
R2	179.2	255.0
L1	–	207.1
L2	144.9	188.1
L3	154.6	204.1

and their coworkers. A T_g value of 150 K has also been reported for PDMS networks by Wier *et al.*[22] and Polmanteer and Hunter[23].

The linear relationship between the T_g values of the linear PDMS fractions and their reciprocal number-average molar masses M_n^{-1} has a negative slope of -6.5×10^3 K g mol^{-1}. The linear plot for the corresponding cyclics has a positive slope of 3.6×10^3 K g mol^{-1}.

A number of relationships have been proposed to account for a linear dependence of T_g on reciprocal molar mass for linear polymers[24–26]. They are of the form:

$$T_g = T_g(\infty) - \frac{K}{M_n} \tag{1}$$

$$\frac{1}{T_g} = \frac{1}{T_g(\infty)} + \frac{K'}{M_n} \tag{2}$$

where T_g is in Kelvin, $T_g(\infty)$ is the asymtotic value and K and K' are constants. Incidentally, the linear dependence of T_g on M_n^{-1} for linear PDMS has been reported by Cowie and McEwen[16] with a slope of -5.9×10^3 K g mol^{-1}. In this case, T_g values were derived from T_2 values (see *Figure 1*) rather than T_3 values as reported here.

In our work, we have observed that the T_g values for cyclic PDMS fractions decrease with increasing M_n. This type of behaviour has not been observed previously or predicted theoretically.

Crystallization behaviour

It has been shown that high molar mass linear PDMS polymers are highly crystalline, and do not show a glass transition, when they are cooled at rates of less than about 1 K min^{-1} [27]. It has also been reported that when high molar mass linear PDMS polymers are quenched or rapidly cooled to below T_g, four thermal transitions are detected when the samples are reheated[19]. These transitions are (1) the glass transition, (2) an exothermal crystalline formation (cold crystallization) and the endothermic melting of (3) one crystalline form, and (4) the other crystalline form of the polymer.

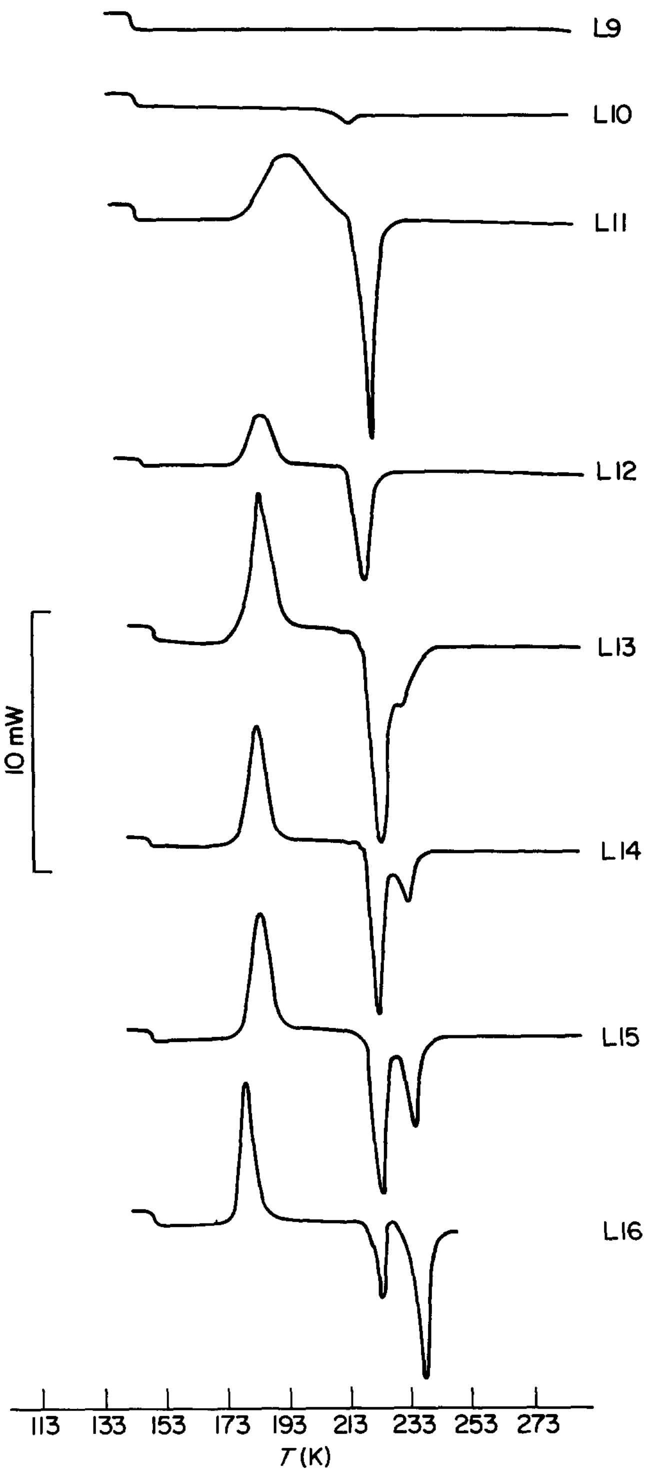

Figure 4 Thermograms of linear poly(dimethylsiloxane) with $40 < n_n < 204$

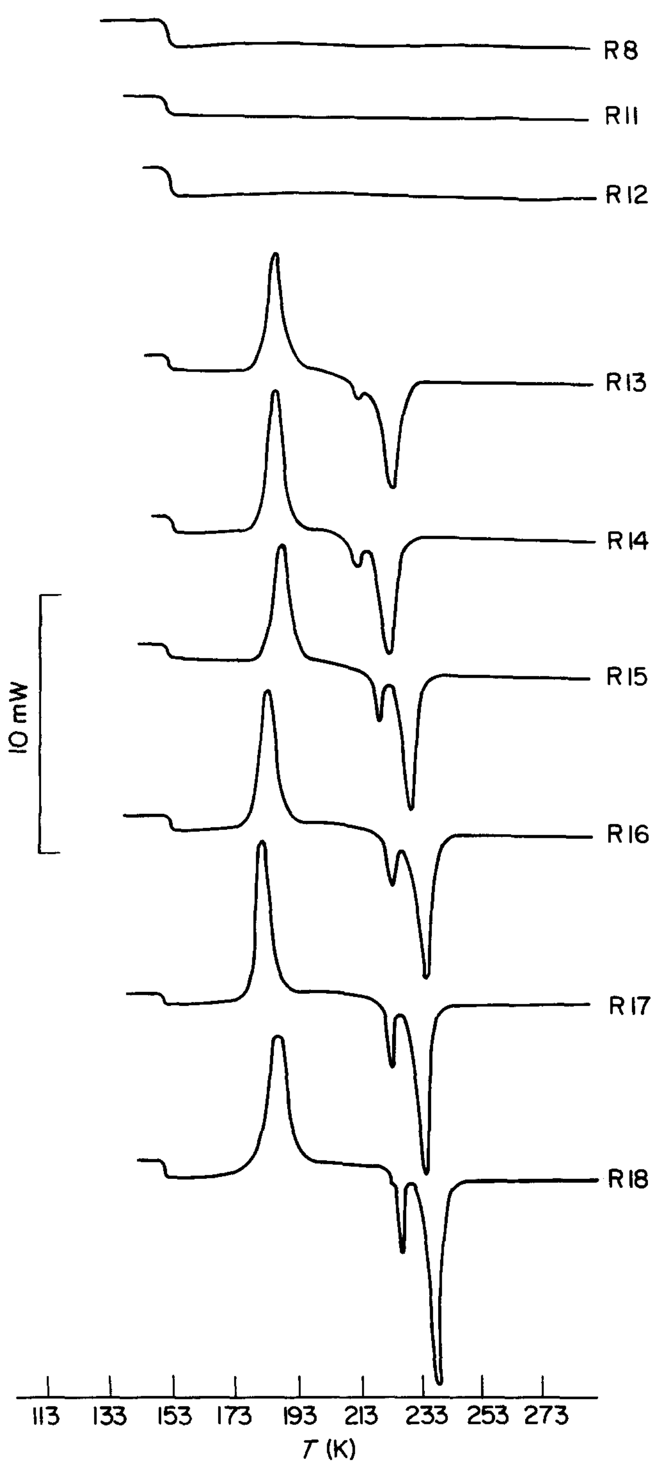

Figure 5 Thermograms of cyclic poly(dimethylsiloxane) with $44 < n_n < 190$

In the present investigation, the samples with the lowest M_n values (R1, R2, L1, L2 and L3) all formed molecular crystals with melting temperatures in overall agreement with literature values[28–30] (see *Table 3*).

The fractions R3–R12 and L4–L9 showed only a glass transition on reheating from 103 K to 298 K. The absence of cold crystallization or polymer crystalline melting peaks shows that the cyclic fractions with n_n in the range $24 \leqslant n_n \leqslant 79$ and the linear fractions with n_n in the range $10 \leqslant n_n \leqslant 40$ are amorphous materials.

The thermograms of R13–R22 and L11–L22 were all seen to show a glass transition, an exothermic cold crystallization peak and polymer crystalline melting

Table 4 Cold crystallization temperatures T_c and polymer crystalline melting temperatures T_{m_1} and T_{m_2} for the cyclic poly(dimethylsiloxanes)

Fraction	T_c (K)	T_{m_1} (K)	T_{m_2} (K)
R13	185.4	211.3	221.5
R14	184.9	210.8	221.0
R15	187.4	218.8	227.4
R16	183.3	221.7	231.4
R17	184.1	223.1	233.0
R18	187.8	225.6	236.4
R19	182.2	226.0	238.0
R20	183.7	224.5	238.2
R21	184.6	226.2	238.1
R22	183.6	227.0	237.8

Table 5 Cold crystallization temperatures T_c and polymer crystalline melting temperatures T_{m_1} and T_{m_2} for the linear poly(dimethylsiloxanes)

Fraction	T_c (K)	T_{m_1} (K)	T_{m_2} (K)
L10	–	217.9	–
L11	196.9	223.8	–
L12	187.8	220.6	–
L13	186.0	223.2	235.4
L14	185.2	223.4	233.7
L15	186.0	223.8	235.0
L16	181.3	223.2	236.8
L17	184.9	223.9	236.5
L18	184.2	224.1	236.3
L19	182.7	224.5	236.4
L20	184.1	224.4	236.3
L21	183.6	225.0	236.2
L22	181.5	225.4	235.7

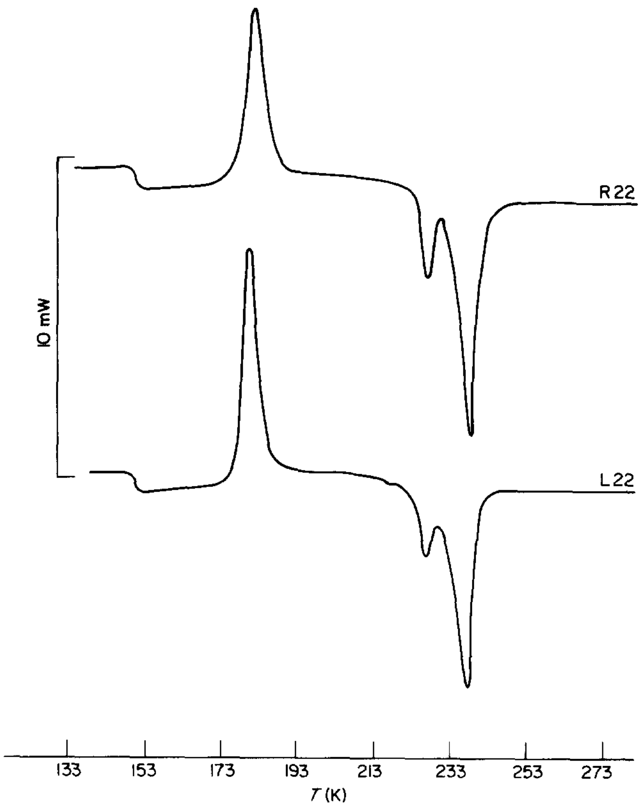

Figure 6 Thermograms of cyclic (R22) and linear (L22) poly(dimethylsiloxanes) with $M_n \simeq 25\,000$ g mol^{-1}

peaks. The cold crystallization temperatures T_c and polymer crystalline melting temperatures T_{m1} and T_{m2} for the fractions are shown in *Tables 4* and *5*. The fractions which exhibit polymer crystalline melting peaks were cyclic R13 ($n_n = 84$) and higher fractions and L11 ($n_n = 56$) and higher fractions. The thermograms showing the onset of polymer crystallization for the cyclic and linear fractions are shown in *Figures 4* and *5*. The cyclic polymers in this study require a higher value of n_n than the corresponding linears for polymer crystallization to occur. It is also noted that the linear PDMS fractions with n_n in the range $56 \leqslant n_n \leqslant 166$ preferentially form crystallites which melt at the lower temperature T_{m1}.

The thermograms for L22 and R22 show very similar thermal behaviour (see *Figure 6*). The glass transition temperatures, cold crystallization temperatures and polymer crystalline melting temperatures for these fractions are in close agreement with values reported previously for high molar mass PDMS[19].

D.s.c. investigations of the T_g values of some other polysiloxane materials with different substituent groups are in progress.

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REFERENCES

1 Semlyen, J. A. and Wright, P. V. *Polymer* 1969, **10**, 543
2 Wright, P. V. *J. Polym. Sci. Polym. Phys. Edn.* 1973, **11**, 51
3 Dogson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
4 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
5 Higgins, J. S., Dodgson, K. and Semlyen, J. A. *Polymer* 1979, **20**, 553
6 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **21**, 663
7 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 869
8 Beevers, M. S., Mumby, S. J., Clarson, S. J. and Semlyen, J. A. *Polymer* 1983, **24**, 1565
9 Burton, D. J., Harris, R. K., Dodgson, K., Pellow, C. J. and Semlyen, J. A. *Polymer* 1983, **24** (*Commun*), 278
10 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1980, **21**, 781
11 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 865
12 Edwards, C. J. C., Bantle, S., Burchard, W., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 873
13 Higgins, J. S., Ma, K., Nicholson, L. K., Hayter, J. B., Dodgson, K. and Semlyen, J. A. *Polymer* 1983, **24**, 793
14 Garrido, L., Mark, J. E., Clarson, S. J. and Semlyen, J. A. *Polymer* 1984, **25** (*Commun.*), 218
15 Griffiths, M. D. and Maisey, L. J. *Polymer* 1976, **17**, 869
16 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1973, **14**, 423
17 Barrie, J. A., Fredrickson, M. J. and Sheppard, R. *Polymer* 1972, **13**, 431
18 Turdakin, V. A., Tarasov, V. V. and Mal'tsev, A. K. *Russ. J. Phys. Chem.* 1976, **50**, 1192
19 Lee, C. L., Johannson, O. K., Flaningam, O. L. and Hahn, P. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1969, **10(2)**, 1311
20 Adachi, H., Adachi, K., Ishida, Y. and Kotaka, T. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 851
21 Krause, S., Iskander, M. and Iqbal, M. *Macromolecules* 1982, **15**, 105
22 Wier, C. F., Leser, W. H. and Wood, L. A. *J. Res. Natl. Bur. Stand.* 1950, **44**, 367
23 Polmanteer, K. E. and Hunter, M. J. *J. Appl. Polym. Sci.* 1959, **1**, 3
24 Fox, T. C. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
25 Ueberreiter, K. and Kanig, G. *J. Colloid. Sci.* 1952, **7**, 569
26 Somcynsky, T. and Patterson, D. *J. Polym. Sci.* 1962, **62**, 151
27 Helmer, J. D. and Polmanteer, K. E. *J. Appl. Polym. Sci.* 1969, **13**, 2113
28 Hunter, M. J., Warrick, E. L., Hyde, J. F. and Currie, C. C. *J. Am. Chem. Soc.* 1946, **68**, 2284
29 Bridgman, P. W. *J. Chem. Phys.* 1951, **19**, 203
30 Patnode, W. J. and Wilcock, D. F. *J. Am. Chem. Soc.* 1946, **68**, 358