Studies of cyclic and linear poly(dimethylsiloxanes): 23. Low temperature behaviour as studied by dynamic oscillatory shear viscometry and differential scanning calorimetry

D. J. Orrah and J. A. Semlyen
Department of Chemistry, University of York, York, YO1 5DD, UK

and K. Dodgson
Department of Chemistry, Sheffield City Polytechnic, Sheffield, S1 1WB, UK

and S. B. Ross-Murphy
Unilever Research, Colworth Laboratory, Colworth House, Sharnbrook, Bedford, MK44 1LQ, UK
(Received 5 August 1986; accepted 23 October 1986)

Fractions of cyclic and linear poly(dimethylsiloxanes) have been investigated by using a differential scanning calorimeter (d.s.c.) and an oscillatory shear rheometer. Different heating and cooling rates were found to have a significant effect on the crystallization behaviour of the materials. The d.s.c. results are compared with those from an earlier study as well as with data from dynamic oscillatory shear viscometry. Cyclics in the range $24 < n_n < 63$ and linears in the range $10 < n_n < 17$ (where n_n is the number average number of bonds) were found to show no propensity to crystallize, whether heated or cooled at slow or fast rates. By contrast, all the siloxane materials outside these ranges have been shown to crystallize readily.

(Keywords: cyclic; linear; poly(dimethylsiloxane); differential scanning calorimetry; oscillatory shear viscometry)

INTRODUCTION

Earlier publications in this series have described the preparation and properties of a homologous sequence of cyclic poly(dimethylsiloxanes) (PDMS) containing up to 1000 skeletal bonds. These have been studied both in the bulk and in solution, using a wide range of techniques including dilute solution viscometry[1], small-angle neutron scattering[2,3], light scattering[4,5] and bulk viscometric[6] and morphological studies[7]. The latter, in particular, have proved of considerable interest. This is because on cooling the transition from pure crystalline to glassy solid behaviour has been followed as a function of the number of skeletal bonds, n_n. This communication furnishes more details about such measurements, using both thermodynamic (differential scanning calorimetry (d.s.c.)) and mechanical (oscillatory shear) probes of the glassy and crystalline states.

In order for polymers to spontaneously crystallize, it is usually required that there is a considerable degree of regularity of the chemical and geometric structure of the macromolecule. Thus, traditionally, crystallizing polymers include linear polycondensates (where regularity is assured by the strictly alternating sequence of main chain atoms) and those simple addition polymers where stereoregularity allows for long geometrically regular sequences of sidechain atoms[8]. For crystallizing polymers, a crystalline melting point T_M can be defined. As long ago as 1947, Flory showed that this crystalline melting point varied inversely with number average degree of polymerization or, for solutions, with the volume fraction of diluent[9].

Amorphous polymers, by contrast, at high temperatures are said to be 'rubbery' (even though not crosslinked), whilst as the system is cooled below the glass transition temperature, T_g occurs when the amount of available free volume is less than is required for movement of whole portions of chain. Both glass transition and crystalline melting behaviour for high molecular weight species can be monitored by thermal and/or thermomechanical techniques. For example, crystalline melting is a first order Ehrenfest transition, and thus corresponds to a discontinuity in exo/endotherms measured by d.s.c.; whereas the glass transition, a second order transition, corresponds to a change in the specific heat of the sample and thus a change in slope of the thermograph. The glass state may just as well be defined in terms of the mechanical behaviour of the glassy and rubbery materials. For high polymers, the glassy material typically has a shear modulus of 10^9 Pa, whereas the rubbery state lies typically 3–4 orders of magnitude lower in modulus. The strain response is quite different because the glassy material fails at 1–2% strain (brittle), whilst in the rubbery state the sample shows substantial liquid-like creep (rather than failure) even at 100% strain. The modulus of the crystalline material is 1–2 orders of magnitude greater than for the glassy state, but

0032-3861/87/060985-06$03.00

in practice this material is much less brittle, because 100% crystallinity is rare. As a result, the overall material behaves as a composite, i.e. the crystalline regions act to reinforce the amorphous matrix.

All the above is well established for high molar mass polymer chains, in this report we discuss the response of both linear and cyclic PDMS samples of medium to low molar mass. These are typically low viscosity oils at ambient temperature, and form glassy or crystalline solids as the temperature is lowered.

Earlier work has suggested that because of the geometry of the dimethyl groups, high molar mass PDMS crystallizes quite readily[10-16]. Further, the rate of crystallization is high because of the comparatively unhindered rotation about backbone bonds, allowing chains to enter the crystal structure and pack together[17]. However preliminary results have also suggested that there is a crystallization 'gap' within the homologous series of oligomeric dimethylsiloxanes[7]. In a previous investigation, d.s.c. was used with cooling (49°C min^{-1}) and heating (10°C min^{-1}) rates that are quite suitable for studying glass transition temperatures but not for investigating crystallization behaviour. Under these thermal conditions cyclic dimethylsiloxanes in the range $24 \leqslant n_n \leqslant 79$ and linear dimethylsiloxanes in the range $10 \leqslant n_n \leqslant 40$ were found not to crystallize[7]. Here, we report the results of d.s.c. measurements using slower heating and cooling rates (for example, 2°C min^{-1}). The data obtained are compared with those obtained previously. In addition, supporting oscillatory shear measurements have been carried out under closely similar temperature profiles.

EXPERIMENTAL

Materials

Cyclic poly(dimethylsiloxanes) (PDMS) $[(CH_3)_2SiO]_x$ were prepared from a ring-chain equilibration reaction, as described previously[18]. Sharp fractions of cyclic and linear PDMS $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ were obtained by using preparative gel permeation chromatography (g.p.c.). The fractions were characterized and details are given in *Table 1*.

D.s.c. measurements

D.s.c. measurements were carried out using a Mettler (Mettler GmbH) TA 3000 series thermal analyser system, consisting of a Mettler DSC 30 differential scanning calorimeter connected to a Mettler TC 10TA microprocessor. Aluminium test pans were used, the sample pan containing ~10 mg of material, against a reference pan of air. Measurements were performed over the temperature range −20°C to −140°C using heating/cooling rates betweeen 2°C min^{-1} and 49°C min^{-1}.*

Thermomechanical measurements

Thermomechanical measurements were carried out using a Rheometrics RMS 605M Mechanical Spectrometer (Rheometrics Inc., N.J. USA), using oscillatory shear (parallel plate) geometry. Measurements were performed over the range −20°C to −140°C, using heating/cooling rates between 0.2 and 50°C min^{-1}.

* Temperatures are expressed in °C in this paper as these are the units of the instruments employed (0°C ≡ 273 K).

Table 1 Number-average number of skeletal bonds n_n, number-average molar masses M_n and heterogeneity indices M_w/M_n for the cyclic PDMS $[(CH_3)_2SiO]_x$ and linear PDMS $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ fractions investigated

Fraction	n_n	M_n	M_w/M_n
Linears			
L 1	10	545	1.01
L 2	17	804	1.02
L 3	22	990	1.01
L 4	24	1064	1.02
L 5	30	1290	1.02
L 6	31	1364	1.02
L 7	40	1630	1.01
L 8	47	1917	1.10
L 9	55	2194	1.11
L10	114	4237	1.01
L11	267	10074	1.10
Cyclics			
R 1	24	880	1.05
R 2	31	1149	1.02
R 3	38	1420	1.02
R 4	47	1730	1.02
R 5	61	2262	1.04
R 6	62	2315	1.06
R 7	63	2343	1.03
R 8	65	2410	1.01
R 9	66	2447	1.05
R10	70	2606	1.03
R11	74	2744	1.02
R12	79	2929	1.03

RESULTS

D.s.c. measurements

The d.s.c. traces obtained were sensitive to heating rate, to n_n and to whether linear or cyclic samples were being examined.

Figure 1 contrasts the effect of fast (49°C min^{-1}) and slow (2°C min^{-1}) rates of heating/cooling ($d\theta/dt$) for two linear PDMS fractions, i.e. $n_n = 55$ and 47 respectively. When $d\theta/dt$ is large, no obvious features are seen, although there is some evidence for a cold crystallization peak on reheating (at 10°C min^{-1}) for the $n_n = 55$ sample. Both samples show small T_M peaks at *ca.* −55°C. By contrast, on subjecting the samples to less extreme thermal histories, there is clear evidence for a broad 'freezing' and sharp melting point trace. The breadth of the former, and its appearance at slightly lower temperatures on cooling than on the subsequent reheating, still suggests a slight reluctance to crystallize and a corresponding tendency to supercool[12]. *Figure* 2(*a*) contrasts this behaviour with the linear sample with $n_n = 267$, already shown to be readily crystallizable[7]. The exotherm ($d\theta/dt = -2$°C min^{-1}) is much more prominent, and occurs at a slightly higher temperature, indicating that less supercooling has occurred. On reheating ($d\theta/dt = 2$°C min^{-1}) no cold crystallization is seen, but there are two endotherms (−45°C and −36°C). *Figure 2*(*b*) illustrates the effect of changing $d\theta/dt$ to −49°C min^{-1} and 10°C min^{-1} respectively. A large exotherm is developed corresponding to a cold crystallization maximum at −90°C, together with three much smaller endotherms.

The above range of experiments was repeated for samples which had previously not been observed to crystallize under the experimental conditions reported in ref. 7. *Figure 3* illustrates the thermogram for a cyclic,

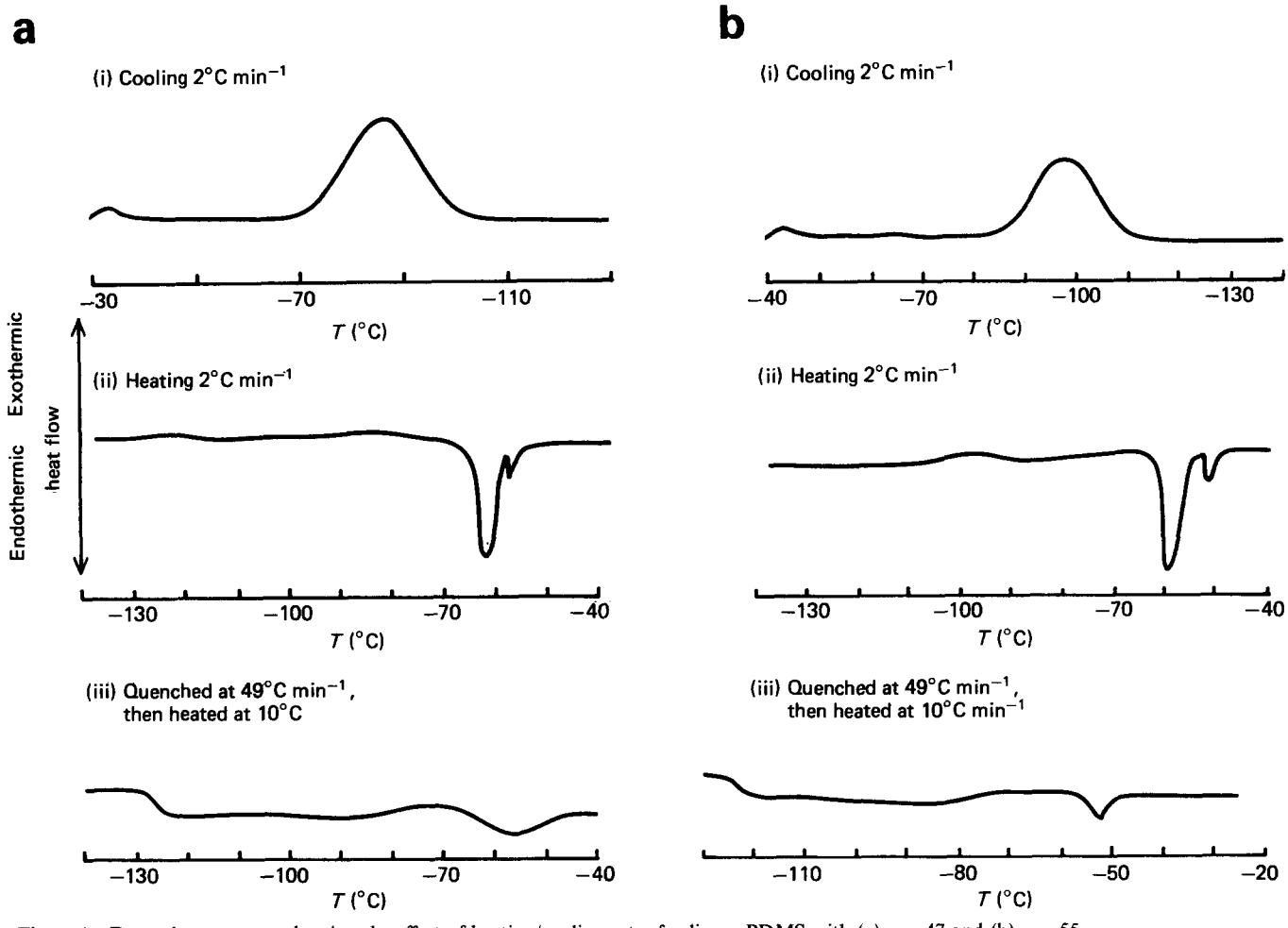

Figure 1 D.s.c. thermograms showing the effect of heating/cooling rates for linear PDMS with (a) $n_n = 47$ and (b) $n_n = 55$

$n_n = 70$, under various heating/cooling rates. Except for that sample which had been heated at 2°C min^{-1} after cooling at the same rate, there is only evidence of a glass transition at ~ -120°C. Only for the former conditions do we see a broad exotherm centred at *ca.* 86°C, and a series of endotherms lying in the range -55°C to -70°C. These latter transitions were critically dependent upon the heating rate, and they were not observable if this was >5°C min^{-1}. To confirm this, the same sample was annealed for 2 h at -85°C and then heated at 2°C min^{-1}. Under the latter conditions the endotherm became much more pronounced and resolved into two peaks. Even for samples which had been cooled extremely fast (49°C min^{-1}) some evidence of endothermal peaks is seen if the samples were subsequently heated at 2°C min^{-1}.

Ring samples with $n_n = 74$ and 79 when subjected to heating rates of 2°C min^{-1} give evidence of crystallization (cf. ref. 7). For cyclics with $n_n = 65$ and 66 there is only a small indication of first order transitions. For the cyclic fractions with $n = 31$ to 63, all evidence of crystallization is absent.

Similar experiments were carried out on linear fractions with $10 \leqslant n_n \leqslant 40$. For the sample with $n_n = 40$, again no crystallization is seen on cooling, but a very broad exotherm is seen centred around -78°C, and sharp double peaked endotherms at -63°C and -57°C for a fraction heated at the slow rate of 2°C min^{-1} (*Figure 4*). Similar results were obtained from chains with $n_n = 31$ and 30, and they are still just noticeable when $n_n = 22$. However, for $n_n = 17$ no such transitions can be seen.

In addition to the above experiments, fractions of rings with $n_n = 63$ and 31 were annealed for 2 h at -85°C and then reheated. As shown in *Figure 5*, there is no evidence of crystallization for these samples, nor was there for linear chains in the range $10 \leqslant n_n \leqslant 17$.

Thermomechanical measurements

By performing small strain oscillatory measurements ($\gamma \simeq 4 \times 10^{-3}$, $\omega = 100$ rad s^{-1}) during heating and cooling cycles, the bulk consequence of the thermal transitions discussed earlier may be followed. This is clearly necessary since a glass transition can only be unequivocally identified by its influence on mechanical properties. For the present samples, the material at room temperature resembles a low viscosity oil, and for small strains, the torque generated in oscillatory shear was too small to give reliable readings. However, on crystallization there is the expected large increase in shear modulus G^*, and 'mechanical spectra' of G^* or G' vs. temperature are charted in *Figures 6–10*, where G' is the storage modulus.

Figure 6 illustrates this for a cyclic fraction, $n_n = 114$, which is known to crystallize readily. Here we see both the very sudden increase in G' on cooling and the effect of cooling rates. At $d\theta/dt = -1$°C min^{-1} the apparent crystalline freezing point is -65°C, whilst for $d\theta/dt = -10$°C min^{-1} it occurs at *ca.* -82°C. On heating, however, the apparent T_m occurs at ~ -48°C, and is effectively independent of the heating rate

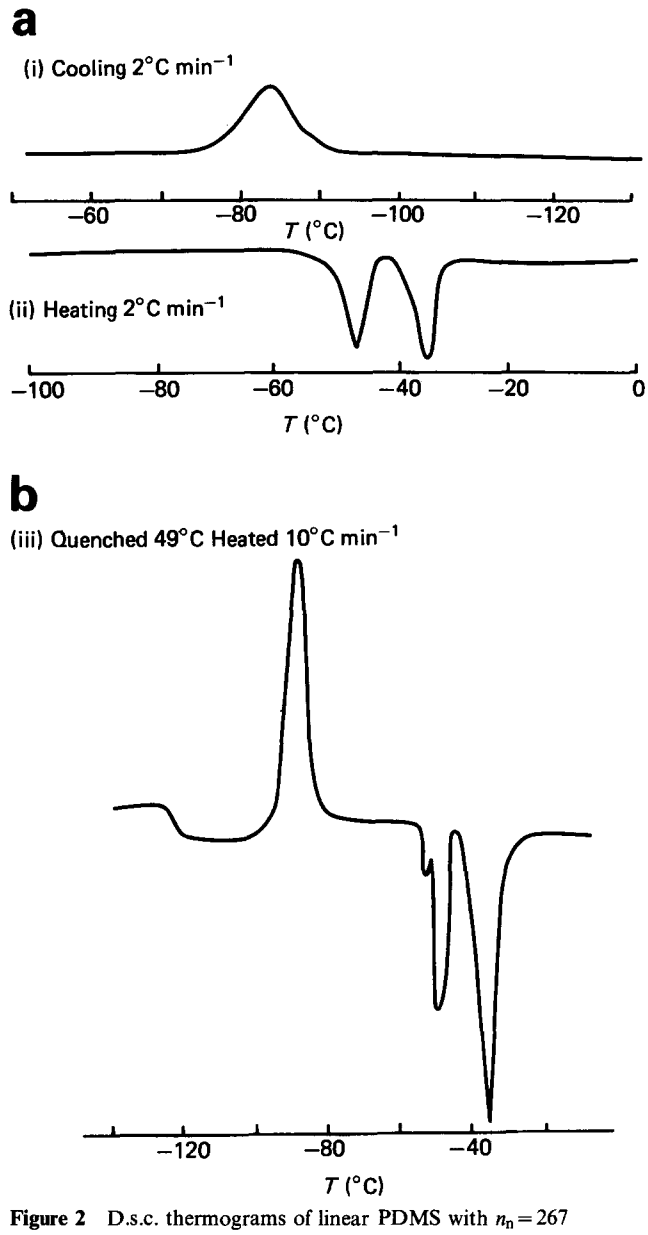

Figure 2 D.s.c. thermograms of linear PDMS with $n_n = 267$

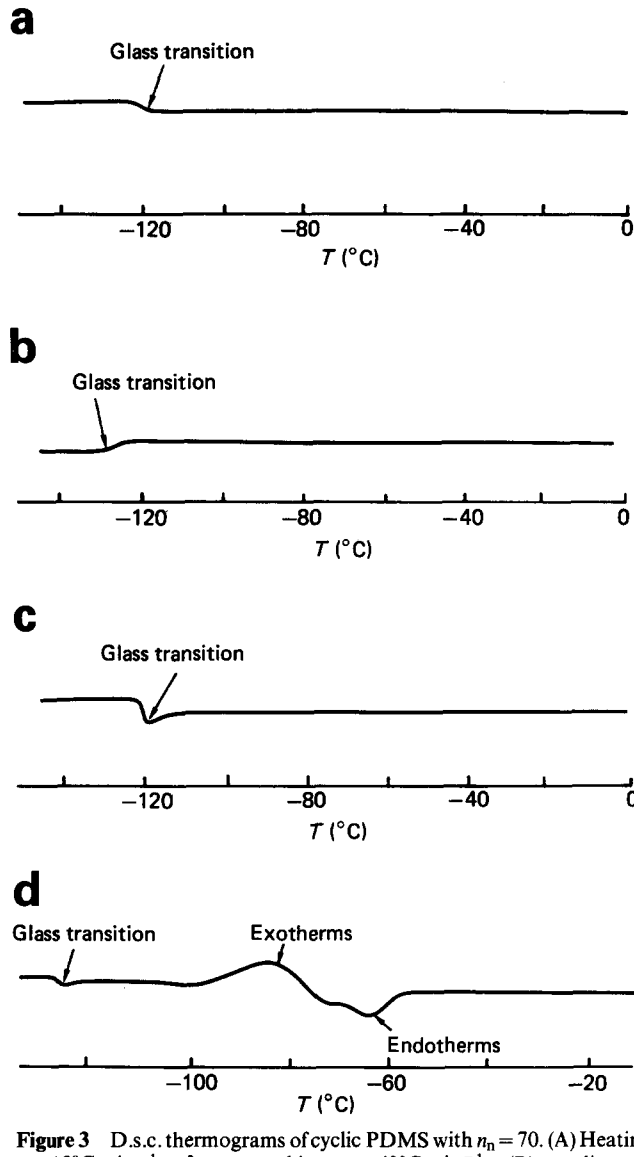

Figure 3 D.s.c. thermograms of cyclic PDMS with $n_n = 70$. (A) Heating at 10°C min^{-1} after quenching at 49°C min^{-1}, (B) cooling at 2°C min^{-1}, (C) heating at 10°C min^{-1} after cooling at 2°C min^{-1} and (D) heating at 2°C min^{-1} after cooling at 2°C min^{-1}

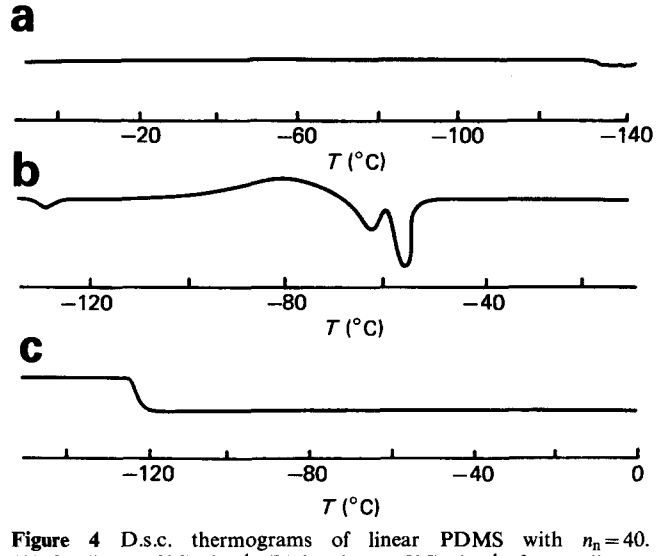

Figure 4 D.s.c. thermograms of linear PDMS with $n_n = 40$. (A) Cooling at 2°C min^{-1}, (B) heating at 2°C min^{-1} after cooling at 2°C min^{-1} and (C) heating at 10°C min^{-1} after cooling at 49°C min^{-1}

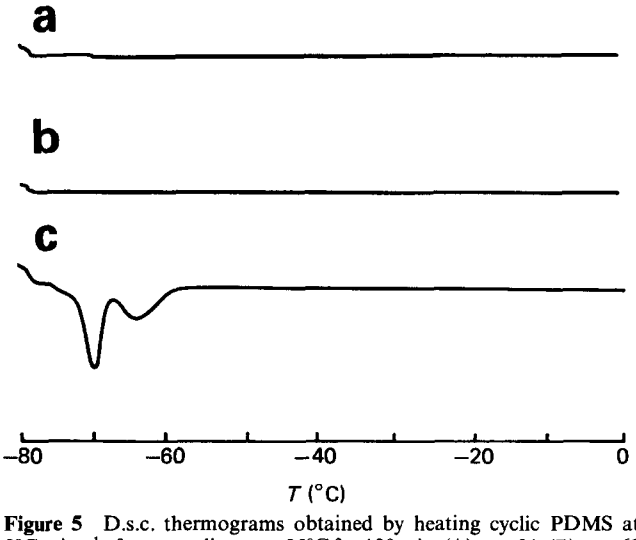

Figure 5 D.s.c. thermograms obtained by heating cyclic PDMS at 2°C min^{-1} after annealing at −85°C for 120 min. (A) $n_n = 31$, (B) $n_n = 63$ and (C) $n_n = 70$

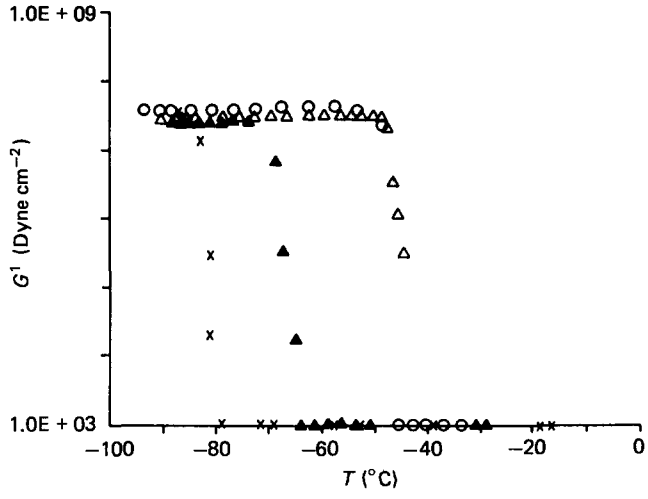

Figure 6 Mechanical spectra of G' vs. temperature for cyclic PDMS with $n_n = 114$. Cooling at 1°C min^{-1} (▲) followed by heating at 1°C min^{-1} (△). Cooling at 10°C min^{-1} (×) followed by heating at 10°C min^{-1} (○)

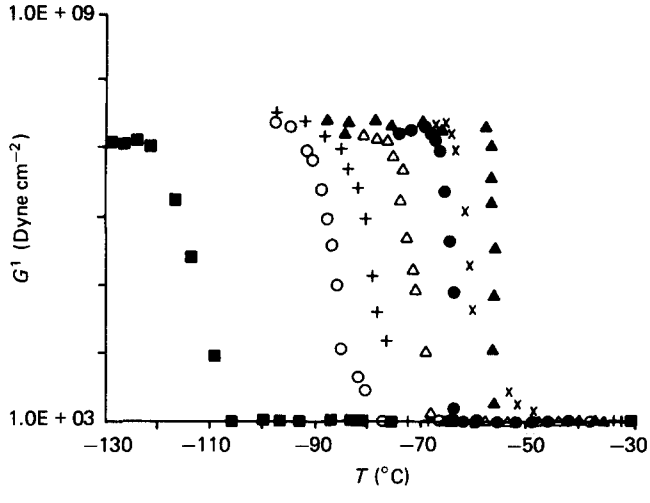

Figure 7 Mechanical spectra of G' vs. temperature for cyclic PDMS with $n_n = 114$ showing the effect of different cooling rates: 0.2°C min^{-1} (▲), 1.0°C min^{-1} (×), 2.0°C min^{-1} (●), 5.0°C min^{-1} (△), 10.0°C min^{-1} (+), 20.0°C min^{-1} (○) and 50.0°C min^{-1} (■)

(1°C min^{-1} and 10°C min^{-1}). This effect is illustrated even more clearly in *Figure 7*, for cooling rates between 0.2°C min^{-1} and 50.0°C min^{-1}. For the former, the hysteresis between the heating and cooling cycles is ~10°C, whereas for the latter it is around 115°C. Whilst at least part of this effect may be due to the much larger thermal equilibration time for the Rheometrics instrument compared to the d.s.c., the final value of $G \sim 2 \times 10^7$ dyne cm^{-2} is, nevertheless, gratifyingly independent of this treatment.

The fractions which had been observed to crystallize under cooling rates > 5°C min^{-1} in d.s.c. experiments all gave qualitatively similar traces to those just described. Subsequent experiments were all performed at 2°C min^{-1} to facilitate direct comparisons with d.s.c. experiments.

Cyclic PDMS fractions in the range $24 \leqslant n_n \leqslant 79$ and linear fractions in the range $10 \leqslant n_n \leqslant 40$ showed different mechanical behaviour to the fractions in *Figures 6* and *7*. The behaviour of a ring with $n_n = 65$ is shown in *Figure 8*. On cooling (−2°C min^{-1}) G^* remains low until ~73°C. On reheating (2°C min^{-1}), the response is almost completely reversible until ~ −95°C when a second peak is detected in G^*; this peak centred at around −78°C is presumably the same as that corresponding to the exothermal/endothermal peaks in the d.s.c. The loss factor $\tan\delta$ ($= G''/G'$) shows two distinct maxima, the lower temperature peak suggesting by its breadth that this corresponds to a true glass transition. The higher temperature peak may still indicate a cold crystallization of the amorphous fluid. Similar but more pronounced effects are seen for the cyclics with $n_n = 70$ and 79 and are illustrated in *Figure 9*. For the cyclic PDMS fraction with $n_n = 65$ cold crystallization is no longer apparent in the mechanical spectrum for heating rates of 2.0°C min^{-1}. Ring fractions with $n_n = 63$ and 31 show no signs of crystallization. The mechanical spectra of these two fractions simply show the thermally reversible glass transition.

Similar experiments were carried out on linear fractions with $10 \leqslant n_n \leqslant 40$. Linear fractions with $n_n = 30$ and 24 show cold crystallization (see *Figure 10*). However, a linear fraction with $n_n = 17$, when heated and cooled at 2°C min^{-1}, yields a mechanical spectrum giving evidence of a glass transition and no sign of any crystallization.

DISCUSSION

The d.s.c. and rheological measurements give thermal transition temperatures (glass transition, cold crystalli-

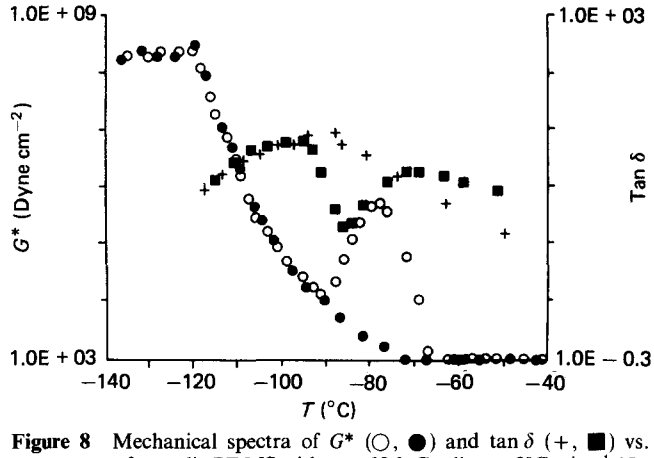

Figure 8 Mechanical spectra of G^* (○, ●) and $\tan\delta$ (+, ■) vs. temperature for cyclic PDMS with $n_n = 65.0$. Cooling at 2°C min^{-1} (○, +) followed by heating at 2°C min^{-1} (●, ■)

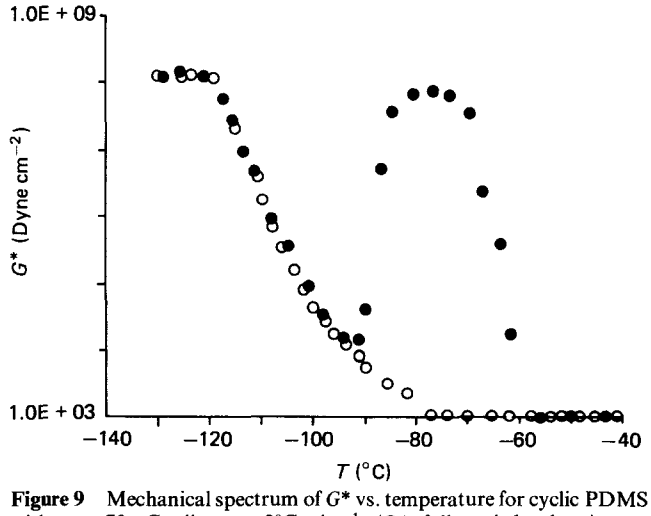

Figure 9 Mechanical spectrum of G^* vs. temperature for cyclic PDMS with $n_n = 70$. Cooling at 2°C min^{-1} (○) followed by heating at 2°C min^{-1} (●)

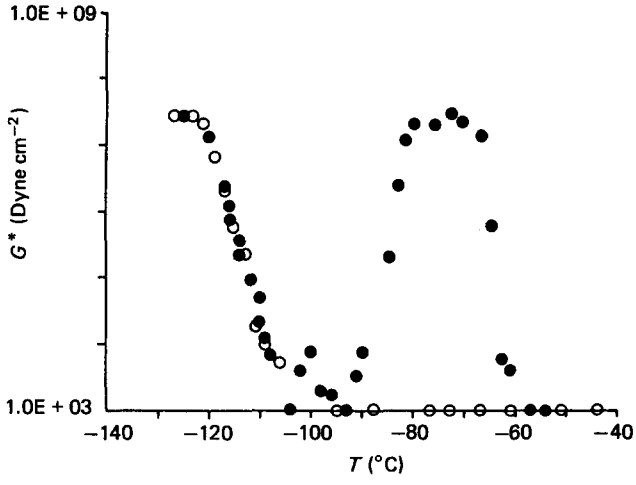

Figure 10 Mechanical spectrum of G^* vs. temperature for linear PDMS with $n_n = 30$. Cooling at 2°C min^{-1} (○) followed by heating at 2°C min^{-1} (●)

zation and melting) that are in good agreement. Previous investigations[7] and this study show that the propensity of ring and chain PDMS fractions to crystallize is dependent on their molar mass. Here it is demonstrated that the rate of thermal scan is an important variable. Previously, when d.s.c. thermograms were obtained at heating rates of 10°C min^{-1}, no crystallization was observed for ring fractions with n_n in the range $24 \leqslant n_n \leqslant 79$ and for linear fractions $10 \leqslant n_n \leqslant 40$. However, the rheological measurements presented in this paper, where thermal scan rates were one fifth of those employed previously, show that materials in the upper extremes of these ranges begin to show evidence of crystallization. The data show that for rings in the range $65 \leqslant n_n \leqslant 79$ and linear in the range $17 \leqslant n_n \leqslant 40$ there is no evidence of crystallization on cooling, whereas the mechanical spectra obtained on heating at 2°C min^{-1} show a maximum value in G^* at ~ -75°C indicative of cold crystallization (*Figure 8*). At thermal scan rates of 2°C min^{-1}, the cyclics in the range $24 \leqslant n_n \leqslant 63$ and linears in the range $10 \leqslant n_n \leqslant 17$ still show no evidence of crystallization. Therefore behaviour dependent on different ranges of degree of polymerization are clearly defined for both ring and chain molecules.

In the intermediate range, i.e. $n_n = 65$ to 79 for ring fractions and $n_n = 17$ to 40 for chains, the results show an increasing reluctance to crystallize as n_n decreases. At heating rates of 10°C min^{-1} and 5°C min^{-1} no evidence of crystallization is shown, whereas with a heating rate of 2°C min^{-1} cold crystallization is apparent. This indicates that the rate of crystallization of these samples is lower than the rate of crystallization of ring and linear fractions, with $n_n > 79$ and $n_n > 40$ respectively.

The annealing experiments establish that there is a range of molar masses for which ring and chain PDMS fractions do not crystallize at all. This is a very limited range for linear PDMS fractions (i.e. $10 \leqslant n_n \leqslant 17$), whereas for the ring fractions the range is considerably larger (i.e. $24 \leqslant n_n \leqslant 63$). These results may be a consequence of the differences between the statistical conformations of ring and chain PDMS. In particular, the cyclics would be expected to have fewer degrees of freedom than chains with similar molar masses[19,20]. Hence, the alignment of the molecular segments of the rings may be expected to be more restricted. This argument is in agreement with the observation that cyclic PDMS have considerably higher glass transition temperatures T_g than their linear counterparts up to quite high molar masses but the T_g values are similar when they are both high polymers[7].

The observation that cyclic and linear silicones have different crystallization behaviour may be of consequence in future low temperature applications.

ACKNOWLEDGEMENTS

We are indebted to the Science and Engineering Research Council for a Research Studentship (to D.J.O). We gratefully acknowledge the contributions of Mr R. Richardson (Unilever Research, Colworth) for his assistance and expertise in obtaining the rheological data, Mr A. Smith (Sheffield City Polytechnic) for his help with the d.s.c. calibration and Mr T. M. Elsworth (University of York) for assistance in the preparation and characterization of the linear PDMS fractions.

REFERENCES

1 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265
2 Dodgson, K., Higgins, J. S. and Semlyen, J. A. *Polymer* 1979, **20**, 553
3 Dodgson, K., Hayter, J. B., Higgins, J. S., Ma, K., Nicholson, L. K. and Semlyen, J. A. *Polymer* 1983, **24**, 793
4 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 869
5 Bantle, S., Burchard, W., Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 873
6 Bannister, D. J., Dodgson, K. and Semlyen, J. A. *Polymer* 1980, **21**, 663
7 Clarson, S. J., Dodgson, K. and Semlyen, J. A. *Polymer* 1985, **26**, 930
8 Mandelkern, L. 'Crystallization of Polymers', McGraw Hill, 1964
9 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953
10 Fischer, D. J. *J. Appl. Polym. Sci.* 1961, **16**, 436
11 Lee, C. L., Johannson, O. K., Flanningham, O. L. and Hahn, P. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* 1969, **10(2)**, 1311
12 Helmer, J. D. and Polmanteer, K. E. *J. Appl. Polym. Sci.* 1969, **13**, 2113
13 Turdakin, V. A., Tarasov, V. V. and Mal'tsev, A. K. *Russ. J. Phys. Chem.* 1976, **50**, 1192
14 Ohlberg, S. M., Alexander, L. E. and Warrick, E. L. *J. Polym. Sci.* 1958, **27**, 1
15 Warrick, E. L. *J. Polym. Sci.* 1958, **27**, 19
16 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
17 Polmanteer, K. E., Servais, P. C. and Konkle, G. M. *Ind. Eng. Chem.* 1952, **44**, 1576
18 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
19 Edwards, C. J. C., Dodgson, K., Rigby, D., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1983, **24**, 391
20 Edwards, C. J. C., Rigby, D., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1983, **24**, 395