Cyclic polysiloxanes: 4. Glass transition temperatures of poly(phenylmethylsiloxanes)

S. J. Clarson*
Department of Chemistry, University of York, York YO1 5DD, UK, and
Department of Chemistry, Sheffield City Polytechnic. Sheffield S1 1WB, UK

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

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The glass transition temperature (T_g) for cyclic and linear poly(phenylmethylsiloxanes) (PPMS) were determined using differential scanning calorimetry. The samples had number-average molar masses in the range $300 \leqslant M_n \leqslant 27\,100$ g mol^{-1}, with heterogeneity indices $1.03 \leqslant M_w/M_n \leqslant 1.16$; they were all found to be amorphous materials, apart from the linear oligomer $(CH_3)_3SiO[(C_6H_5)(CH_3)SiO]Si(CH_3)_3$. The T_g values for the linear PPMS fractions showed a linear dependence upon reciprocal number-average molar mass M_n^{-1}, in agreement with theoretical predictions for linear polymers. The T_g values for the cyclic PPMS fractions, by contrast, were found to show a non-linear dependence upon M_n^{-1}. The asymptotic values of the glass transition temperatures $T_g(\infty)$ for both cyclic PPMS and linear PPMS were found to be in close agreement with the literature value for high-molar-mass linear PPMS. High-resolution ^{1}H nuclear magnetic resonance spectroscopy was used to demonstrate that the cyclic and linear PPMS fractions used in this investigation—and also in a variety of other studies in this series—are stereochemically atactic polymers.

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

INTRODUCTION

A number of simple relationships have been proposed in the literature to account for the observed variation of the glass transition temperatures T_g of linear polymers with chain length, and they predict T_g to show a linear dependence on reciprocal number-average molecular mass M_n^{-1} (ref. 1). These are of the form:

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

$$1/T_g = 1/T_g(\infty) + K'/M_n \qquad (2)$$

where T_g is in kelvins, $T_g(\infty)$ is the asymptotic value and K and K' are constants. Such relationships have also been extended to account successfully for the behaviour reported for the star-branched polymers[2,3].

In a recent publication[4] we reported the glass transition temperatures for the cyclic poly(dimethylsiloxanes) (PDMS) in the molar-mass range $370 \leqslant M_n \leqslant 24\,500$ g mol^{-1}. The cyclic polymers showed remarkable behaviour in that their T_g values were found to increase with decreasing M_n. This was unanticipated, as the T_g values of the cyclic polymers, having no end-groups, would not be expected to show any dependence on molar mass using a simple free-volume theory[1]. Following these experimental findings, the first theoretical model for the glass formation of non-catenated ring polymers was developed by Di Marzio and Guttman[5] and was based on a configurational entropy theory[6,7]. For completely flexible Gaussian linear (l) and ring (r) polymers, the difference in configurational entropy on a per monomer basis is:

$$S_l - S_r = 3\ln(2\pi x/3)/2x \qquad (3)$$

where x is the chain length or ring size, respectively. As the configurational entropy of a ring polymer is always less than that of its linear analogue[8], the ring system will clearly always have a higher T_g. At infinite molar mass, however, the glass transition temperatures $T_g(\infty)$ for cyclic and linear polymers should be the same, as was observed experimentally for cyclic and linear PDMS[4]. The theory was then developed by incorporating the effect of flexes on the configurational entropy of cyclic and linear molecules[5]. The results of this approach are particularly elegant in that the two input parameters—the hole energy E_h and the flex energy $\Delta\varepsilon$—can be selected to fit the T_g data for the linear polymers and the resulting values for the ring analogues are then essentially based on a no-parameter prediction. The Di Marzio and Guttman theory[5] successfully predicts that the glass transition temperature of a ring molecule system increases as the molar mass is lowered, while the glass transition temperature of a linear polymer system

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* To whom correspondence should be sent at permanent address: Department of Materials Science and Engineering, and the Polymer Research Centre, University of Cincinnati, Cincinnati, OH 45221-0012, USA

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decreases with decreasing molar mass, as was observed for the cyclic and linear poly(dimethylsiloxanes)[4]. The synthesis and characterization of cyclic poly(2-vinylpyridine) (P2VP) fractions with molar masses in the range $4000 \leqslant M_w \leqslant 200\,000\ \mathrm{g\,mol^{-1}}$ were described recently by Hogen-Esch and Toreki[9]. An increase in T_g with decreasing molar mass was observed for cyclic P2VP, in agreement with the Di Marzio and Guttman theory—this being the first example of a vinyl polymer to exhibit such behaviour. The T_g values of the cyclic polystyrenes have also been measured by Roovers[10] and were reported to show only a very slight decrease with molar mass down to a M_w value of $6900\ \mathrm{g\,mol^{-1}}$. However, a study of smaller polystyrene rings is clearly needed to test the predictions of the Di Marzio and Guttman theory[5] for this system.

In this publication we will report the T_g values of the cyclic and linear poly(phenylmethylsiloxanes) (PPMS) for the first time as determined by differential scanning calorimetry (d.s.c.).

EXPERIMENTAL

Preparation and characterization of samples

The preparation of the cyclic $[\mathrm{PhMeSiO}]_x$ and linear $\mathrm{Me_3SiO[PhMeSiO]_ySiMe_3}$ poly(phenylmethylsiloxane) (PPMS) sharp fractions have been reported in detail previously[11]. The samples have been characterized using a variety of experimental techniques including gas–liquid chromatography, high-performance liquid chromatography, gel permeation chromatography, low-angle laser light scattering, mass spectrometry and small-angle neutron scattering[11–13]. In this investigation the stereochemical structures of the polymers were determined using high-resolution ^{1}H nuclear magnetic resonance spectroscopy. The n.m.r. spectra were obtained using a Nicolet 300 MHz spectrometer in the Department of Chemistry, University of Cincinnati, USA. Deuterated chloroform at 293 K was used as the solvent and reference.

Differential scanning calorimetry

A Mettler TA 3000 series thermal analyser system, consisting of a Mettler DSC 30 differential scanning calorimeter interfaced to a Mettler TC 10 TA microprocessor, was used for this investigation. The temperature scale of the instrument was checked and effects due to thermal lag in the system were corrected by regular calibration using indium and lead standards[14].

An electrical heater/liquid nitrogen system was used for heating and cooling the d.s.c. cell and was controlled by the microprocessor. To assure a consistent thermal history in each case, the following conditions were employed throughout. The d.s.c. cell containing the sample and reference was rapidly cooled to 140 K at a rate of 49 K min^{-1} and maintained at this temperature for 3 min to allow the system to attain thermal equilibrium. The cell was then heated to 298 K at a rate of 10 K min^{-1}. The thermal events over the temperature range scanned were recorded by the microprocessor and transferred to a plotter. The amount of sample used in each case was $\simeq 15$ mg.

RESULTS AND DISCUSSION

^{1}H n.m.r. and stereochemical structure of the cyclic and linear PPMS fractions

^{1}H n.m.r. spectra of one cyclic PPMS and two linear PPMS fractions were measured in order to determine the stereochemical structure of the polymers. In each case, bands at $d \simeq 7$, corresponding to phenyl protons, and $d \simeq 0$, corresponding to α-methyl protons, were

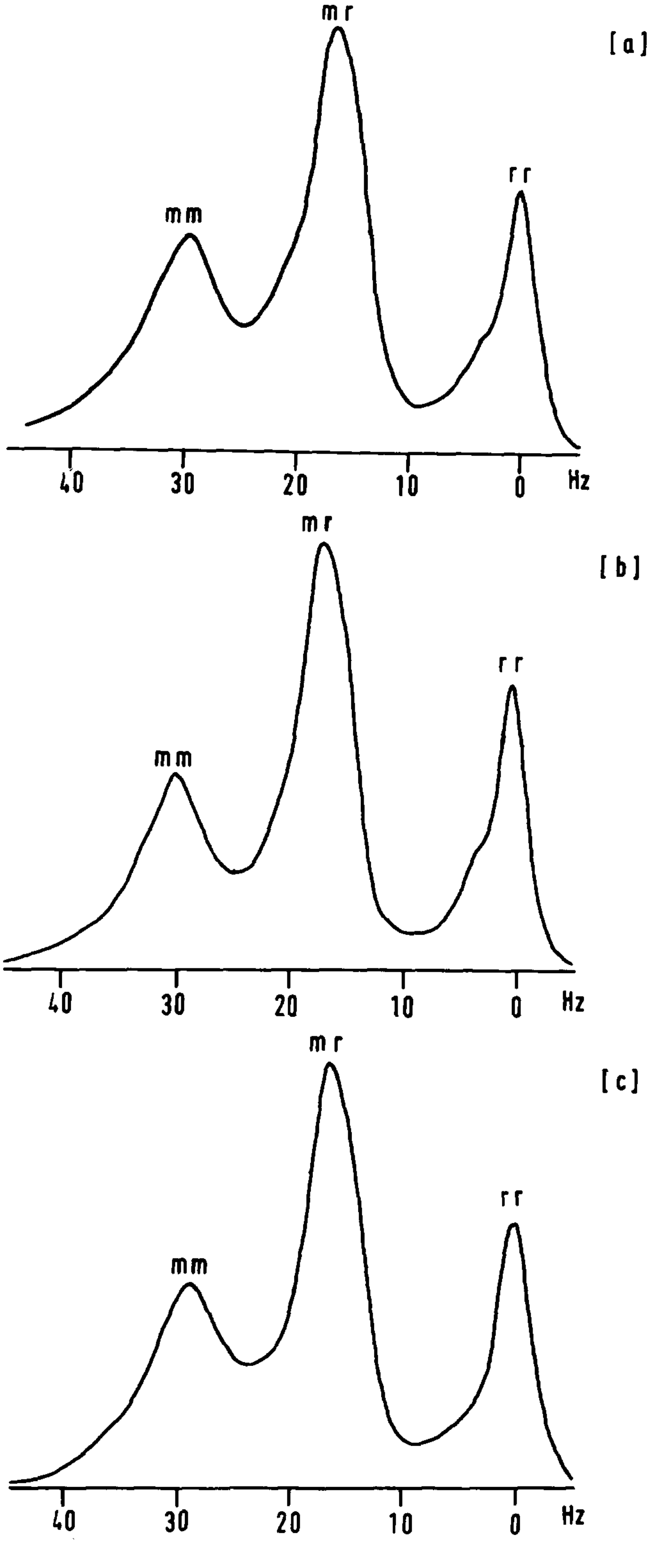

Figure 1 300 MHz ^{1}H n.m.r. spectra corresponding to the α-methyl protons for (a) 122-bond linear, (b) 332-bond linear and (c) 135-bond cyclic poly(phenylmethylsiloxanes)

Table 1 Number-average number of skeletal bonds n_n, fraction of isotactic f_{mm}, heterotactic f_{mr} and syndiotactic f_{rr} triads, fraction of *meso* f_m and racemic f_r diads, average lengths of meso l_m and racemic l_r sequences and persistence ratios p for the cyclic and linear poly(phenylmethylsiloxane) fractions

Sample	n_n	f_{mm}	f_{mr}	f_{rr}	f_m	f_r	l_m	l_r	p
Linear	122	0.34	0.44	0.22	0.56	0.44	2.55	2.00	1.12
Linear	332	0.30	0.46	0.24	0.53	0.47	2.30	2.04	1.08
Cyclic	135	0.32	0.45	0.23	0.54	0.46	2.42	2.02	1.10

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 *cyclic* phenylmethylsiloxanes and poly(phenylmethylsiloxanes)

Fraction	n_n	M_n (g mol^{-1})	M_w/M_n	T_g (K)
R1	8[a]	540	–	237.9
R2	10[a]	680	–	241.3
R3	11[a]	750	–	243.0
R4	20	1 390	1.16	248.0
R5	39	2 620	1.06	247.7
R6	49	3 340	1.04	247.5
R7	66	4 520	1.04	248.0
R8	85	5 790	1.04	247.0
R9	107	7 280	1.05	244.9
R10	135	9 190	1.06	245.5
R11	177	12 020	1.03	245.0
R12	268	18 320	1.04	244.9

[a] Mixture of stereoisomers

Table 3 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* phenylmethylsiloxanes and poly(phenylmethylsiloxanes)

Fraction	n_n	M_n (g mol^{-1})	M_w/M_n	T_g (K)
L1	2[a]	300	–	155.8
L2	4[b]	430	–	177.4
L3	6[b]	570	–	193.0
L4	8[b]	710	–	204.3
L5	25	1 890	1.06	224.9
L6	31	2 240	1.08	228.4
L7	39	2 800	1.08	230.9
L8	51	3 600	1.04	233.5
L9	65	4 620	1.06	236.0
L10	82	5 730	1.05	236.4
L11	97	6 750	1.05	236.8
L12	153	10 560	1.16	238.4
L13	186	12 860	1.15	240.0
L14	235	16 190	1.13	239.4
L15	284	19 510	1.12	239.7
L16	332	22 760	1.10	239.2
L17	396	27 100	1.09	240.1
L18	1360	93 000	2.00	240.5

[a] Pure compound
[b] Mixture of stereoisomers

observed. The band at $d \simeq 0$ was resolved into three peaks for all the samples (see *Figure 1*), and the assignment to isotactic (mm), heterotactic (mr) and syndiotactic (rr) triads was made on the basis of previous investigations[15–17]. From the peak integrations the fractions of the three triads f_{mm}, f_{mr} and f_{rr} were obtained for each polymer, and the results are shown in *Table 1*. These values were then used to calculate the fractions of *meso* f_m and racemic f_r diads as follows:

$$f_m = (2f_{mm} + f_{mr})/2 \qquad (4)$$

$$f_r = (2f_{rr} + f_{mr})/2 \qquad (5)$$

The average lengths of *meso* L_m and racemic L_r sequences and the persistence ratios p were obtained using the relationships:

$$L_m = (2f_{mm} + f_{mr})/f_{mr} \qquad (6)$$

$$L_r = (2f_{rr} + f_{mr})/f_{mr} \qquad (7)$$

$$p = L_m f_r = L_r f_m \qquad (8)$$

For atactic cyclic and linear polymers, the fraction of *meso* f_m and racemic f_r diads should both be 0.5, with persistence ratios p of 1.0 (assuming Bernoullian statistics). The ^{1}H n.m.r. results for the cyclic and linear poly(phenylmethylsiloxane) fractions therefore demonstrate that the polymers are stereochemically atactic within experimental error (see *Table 1*). The anionic ring-opening polymerizations of cyclic phenylmethylsiloxane tetramers $[\mathrm{PhMeSiO}]_4$, using potassium hydroxide as the catalyst, that were utilized to prepare the cyclic and linear PPMS samples used in the present investigation—and have been described in detail in part 1 of this series[11]—give atactic polymers. This is in agreement with the stereochemical structure of PPMS deduced from measurements of the molar cyclization equilibrium constants for this system[11,13,18]. It is worth noting, however, that some degree of stereochemical control of the ring-opening polymerization of the phenylmethylsiloxane cyclic trimers $[\mathrm{PhMeSiO}]_3$ has been reported recently[19–21].

Glass transition temperatures of cyclic and linear PPMS

The linear phenylmethylsiloxane L1 was found to show a glass transition, a cold crystallization exothermic transition at 210 K and a crystalline melting transition at 229 K. All the other cyclic (R1–R12) and linear (L2–L18) PPMS samples were found to be completely amorphous materials and hence showed only a glass transition. The cyclic and linear PPMS samples, being stereochemically atactic, were not complicated by the thermal history effects associated with the symmetrically substituted siloxane polymers[22–24]. The glass transition temperatures for the cyclic and linear samples are shown in *Tables 2* and *3*, respectively. As in our previous studies, the T_g values were determined using the midpoint of the glass transition step[4,24].

In *Figure 2* the T_g values of the linear poly(phenylmethylsiloxanes) and the linear poly(dimethylsiloxanes) are plotted against their reciprocal number-average molar masses M_n^{-1}. In accordance with equations (1) and (2), the T_g values for linear PPMS were found to show a linear dependence on M_n^{-1} with a negative slope ($K = -2.6 \times 10^4$ K g mol^{-1}) and an asymptotic value $T_g(\infty) = 240.7$ K. This is a stronger molar-mass dependence of T_g than that observed for linear PDMS

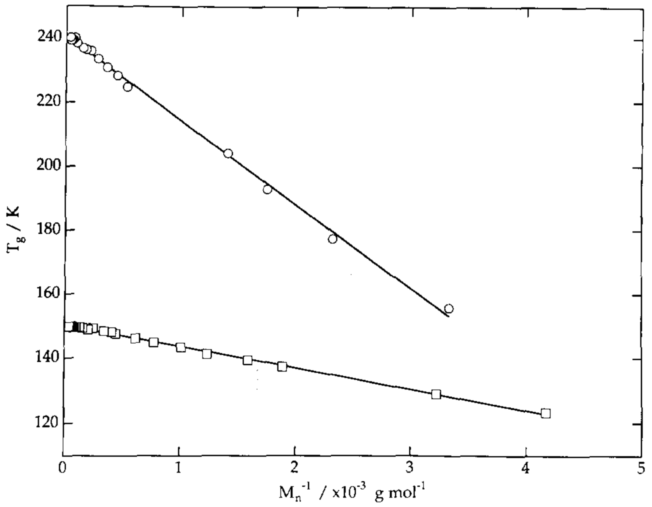

Figure 2 Glass transition temperatures T_g of the linear poly(phenylmethylsiloxanes) (○) and linear poly(dimethylsiloxanes) (□) plotted against their reciprocal number-average molar masses M_n^{-1}

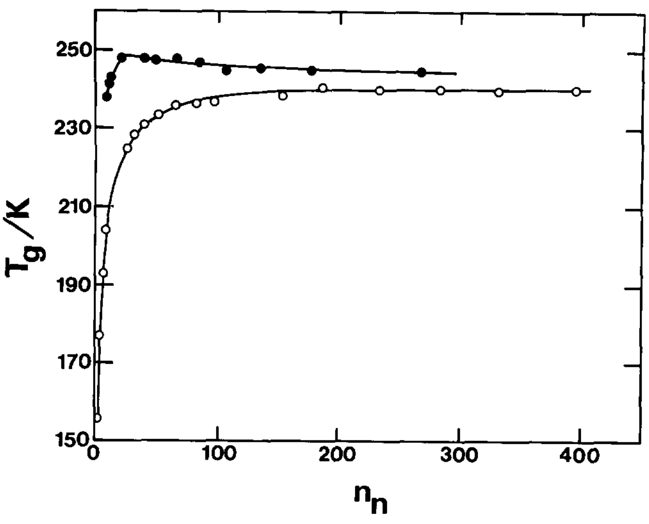

Figure 3 Glass transition temperatures T_g of the cyclic (●) and linear (○) phenylmethylsiloxanes plotted against their number-average number of skeletal bonds n_n

($K = -6.5 \times 10^3$ K g mol^{-1}). Such behaviour is to be expected as both linear PPMS and PDMS are trimethylsilyl-terminated and hence the T_g plots for both polymers as shown in *Figure 2* should extrapolate to intercept at the T_g value of hexamethyldisiloxane—the value for which has not been measured experimentally due to rapid crystallization at its melting point (207 K)[4].

Figure 3 shows the dependence of T_g on the number of skeletal bonds n_n for cyclic and linear PPMS. The T_g values for cyclic PPMS showed a non-linear dependence on M_n^{-1} and an asymptotic value $T_g(\infty) = 244.9$ K was obtained by plotting M_n/T_g against M_n following Ellis[25] and Cowie[26]. The asymptotic values for cyclic and linear PPMS are in good agreement with the T_g value of 244 K reported for a high-molar-mass linear PPMS sample ($M_n = 263\,000$ g mol^{-1}) of uncharacterized stereochemical structure[27]. The T_g values for cyclic PPMS may be contrasted with those reported for the cyclic poly(dimethylsiloxanes), where a linear dependence of T_g on M_n^{-1} was obtained with a positive slope[4].

It is worth considering why the results observed for small cyclic PPMS rings are not in accordance with the Di Marzio and Guttman theory. First, it has been shown theoretically that the T_g values for cyclic polymers show quite a strong ring-size dependence governed by the term $R = zE_h/2\Delta\varepsilon$, where z is the coordination number of the lattice. The T_g values for the corresponding linear polymers have only a weak dependence on R. The origins and consequences of these findings clearly merit closer examination in the context of the variety of ring systems that have now been experimentally studied[4,9,10,28]. Secondly, it is well known from investigations of molar cyclization equilibrium constants[13,18,28,29] that siloxane rings and chains with less than 30 skeletal bonds show deviations from Gaussian statistics. It is noted that a Gaussian correction term is used to account for the reduction in the number of configurations when rings are formed in the Di Marzio and Guttman theory. As the configurational entropy theory of glass formation allows for a general dependence of chain energy on chain shape[30], utilizing the rotational isomeric state models that have been established for both poly(phenylmethylsiloxane)[31] and poly(dimethylsiloxane)[32] instead of the nearest-neighbour model initially used by Di Marzio and Guttman[5] may give further interesting insights into the effect of molecular topology and chain structure on glass formation.

Further studies of the properties of the cyclic and linear poly(phenylmethylsiloxanes) and other polysiloxanes are in progress.

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