

# Thermal properties of poly(tetramethyl-*p*-silphenylene siloxane) and (tetramethyl-*p*-silphenylene siloxane–dimethyl siloxane) copolymers

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Some physical properties of poly(tetramethyl-*p*-silphenylene siloxane) homopolymer and random block copolymers of tetramethyl-*p*-silphenylene siloxane–dimethyl siloxane have been determined and correlated with polymer structure. Differential scanning calorimetry (d.s.c.), differential thermal analysis (d.t.a.), density gradient column measurements and optical hot stage melting point determination and diluent techniques were used. The thermodynamic melting temperature of the homopolymer was estimated to be 160°C and its heat of fusion,  $\Delta H_f$ , found to be 54.4 J/g (13 cal/g or 2710 cal/mol of monomer repeat units). Its limiting glass transition temperature,  $T_g$ , was –20°C.  $T_g$  of the copolymer was found to vary almost monotonically with increasing dimethyl siloxane (DMS) content ranging from –20° (0% DMS) to just above –123°C, for pure DMS polymer. The copolymer melting temperature was found to increase as the fraction of the crystalline (hard) TMPS constituent was increased. Based upon copolymer theory and extrapolated melting point data, it was estimated that the block size of soft DMS component in the copolymer most probably consists of twelve monomer units distributed amongst TMPS sequences of varying length.

## INTRODUCTION

Many characterization parameters are required to define a polymer<sup>1</sup>. Because few of these parameters can be calculated with certainty, physical measurements must be used as a substitute for many theoretical analyses. Among the most simple but important characterizing criteria, which are sometimes overlooked, are melting and glass transition temperatures. In practice, the values normally measured for either one of these parameters are not unique but depend largely upon sample history as well as on the measurement technique(s) used to evaluate them. Only the thermodynamic melting temperature,  $T_m^0$ , and the glass transition temperature at sufficiently long relaxation times,  $T_g^\infty$ , provide a unique description of a given system so that extrapolation methods must always be used to obtain these important parameters. They are frequently required as reference temperatures to relate the fundamental chain chemistry and physics with morphology through the use of other characterizing parameters (some of an engineering nature) such as modulus (tensile, shear, bulk and dynamic), crystallization rates, creep compliance, toughness, extensibility ultimate strength, ductility and so forth<sup>1</sup>. Many methods have been employed in the literature to obtain thermodynamic properties<sup>1,2</sup>. The proper use of measured parameters in regard to theory relevant to both  $T_m^0$  and heat of fusion of the perfect crystal,  $\Delta H_\mu$ , are required to arrive at meaningful results that can be used successfully to obtain other characterizing parameters<sup>1,2</sup>.

In the present investigation the equilibrium melting temperature and heat of fusion of poly(tetramethyl-*p*-silphenylene

siloxane) [poly(TMPS)] have been re-examined along with new work on tetramethyl-*p*-silphenylene siloxane–dimethyl siloxane (TMPS–DMS) block copolymers. The effect of molecular weight and low molecular weight diluent on the crystallization behaviour of poly(TMPS) has been studied and the dependence of glass transition and melting temperature on copolymer composition has been assessed.

## EXPERIMENTAL

### Materials

The samples of homopolymer TMPS and block copolymer TMPS–DMS used in this work are listed in *Table 1*. Other

*Table 1* Equilibrium melting temperatures and glass transition temperatures for TMPS homopolymers and TMPS–DMS copolymers

Sample	Molecular weight	TMPS (wt %)	$T_m^*$ (°C)	$T_g$ (°C)
Homopolymer (TMPS)	$8.7 \times 10^3$	100	137 <sup>a</sup>	—
	$1.27 \times 10^4$	100	151 <sup>a</sup>	—
	$2.7 \times 10^4$	100	159 <sup>a</sup>	—
	$6.03 \times 10^4$	100	158 <sup>a</sup>	—
	$3.8 \times 10^5$	100	158.3 <sup>a</sup>	– 21 <sup>a</sup>
Copolymer	—	90	153.6 <sup>b</sup>	– 39 <sup>a</sup>
	—	80	145.6 <sup>b</sup>	– 53 <sup>a</sup>
	—	50	127.3 <sup>b</sup>	—
	—	40	122.1 <sup>b</sup>	–110 <sup>c</sup>
	—	30	110.5 <sup>b</sup>	–120 <sup>c</sup>
Homopolymer (DMS)	—	0	—	–123 <sup>d</sup>

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<sup>a</sup> Obtained by d.s.c.; <sup>b</sup> obtained by optical microscope; <sup>c</sup> obtained by d.t.a.; <sup>d</sup> data from Magill (1964)

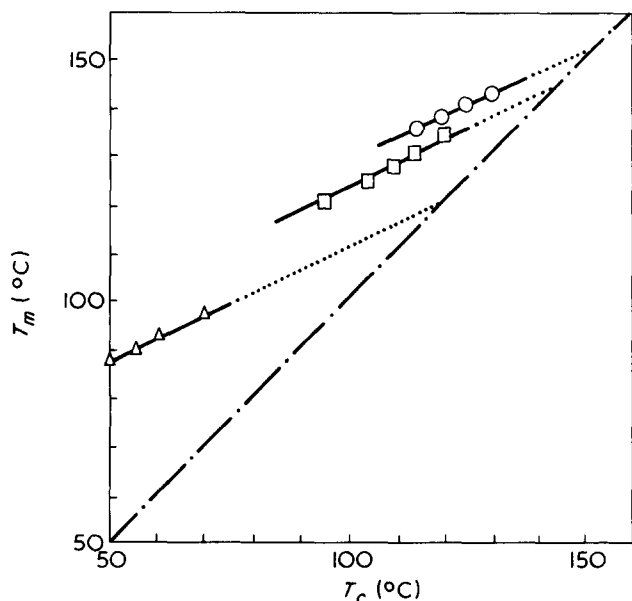


Figure 1 Melting temperature ( $T_m$ ) plotted against the crystallization temperature ( $T_c$ ) of TMPS homopolymer:  $\circ$  ( $M_v$ ,  $1.27 \times 10^4$ ); TMPS-DMS copolymers:  $\square$ , (80/20),  $\triangle$ , (40/60) crystallized from the melt

details are also given in previous papers<sup>3-5</sup>. Specimens for density and differential scanning calorimetry (d.s.c.) studies were carefully fabricated by hot pressing into shapes. All materials were carefully wrapped in aluminium foil and kept at 200°C for 5 min and then subsequently crystallized isothermally at different temperature for various selected times dictated by previous knowledge of crystallization behaviour<sup>4,5</sup>.

#### Melting point determinations

Two methods were used, namely (a) thermal analysis (Perkin-Elmer DSC-1B/DTA) and (b) programmed heating with Mettler optical hot stage microscopy for both homo- and copolymer systems. However, method (a) was used primarily for the homopolymer. Various heating rates were employed in both techniques although 10°C/min and 20°C/min were preferred. In method (b) the temperature at which the spherulitic birefringence completely disappeared was taken as the observed melting temperature of each polymer specimen. Good agreement was obtained when comparisons were made between melting temperatures determined by d.s.c. and the optical technique.

#### Glass transition measurements

Glass transition temperatures were made on all specimens that had been melted at 200°C for 5 min followed by rapid quenching in liquid nitrogen and transfer to the precooled sample pan of the d.s.c. or d.t.a. apparatus in a nitrogen environment. This uniform heat treatment minimized or eliminated effects of sample history. Samples were subsequently scanned mostly at a heating rate of 10°C/min. Allowance was made for the effect of heating rate on  $T_g$ .

#### Heat of fusion measurements

Again two techniques were used to obtain such information, namely (i) d.s.c. and (ii) polymer-diluent melting point depression techniques. From (i) the heat of fusion measurements as a function of  $T_c$  were obtained by integration of the Perkin-Elmer DSC-1B melting curves. Copolymer melting peaks were found to be noticeably broader

than those of the homopolymer specimens. Benzoic acid, naphthalene, indium and tin of high purity were used as calibration standards for d.s.c. heat of fusion and melting point determinations. In (ii) various samples of suitable concentrations of poly(TMPS) homopolymer of  $M_v = 4.31 \times 10^5$  were dissolved in benzene containing dibutylphthalate as a diluent. The benzene was carefully evaporated from each polymer solution and then dried *in vacuo* in the conventional manner, taking care to minimize any removal of diluent. Melting points were determined by both d.s.c. and also with the Mettler hot stage.

#### Density measurements

All sample densities were determined at 25°C in a thermostatically controlled density gradient column containing ethylene glycol-methyl alcohol mixture. The column was calibrated with standard floats reputed to have fourth decimal accuracy but we conservatively estimated our sample accuracy at approximately  $\pm 0.001 \text{ g/cm}^3$ .

## RESULTS AND DISCUSSION

#### Determination of equilibrium melting temperature

Figure 1 shows plots of d.s.c. melting peak temperature for a TMPS homopolymer ( $M_v = 1.27 \times 10^4$ ) along with the optical melting temperatures obtained for 80/20 copolymer and 40/60 copolymer as a function of crystallization temperatures. The equilibrium melting temperature for each of the polymers was determined by the Hoffman<sup>6</sup> extrapolation method (based upon earlier discoveries of Wood and Bekkadahl<sup>7</sup>). Equation (1) which relates the observed melting point of the polymer,  $T_m$ , and with its crystallization temperature  $T_c$ , for a homopolymer is easily applied<sup>8</sup> to copolymers<sup>6</sup>.

$$[T_m^*(X_a) - T_m] = \Phi [T_m^*(X_a) - T_c] \quad (1)$$

In this equation  $T_m^*(X_a)$  is the equilibrium melting temperature for the copolymer with the composition ( $X_a$ ) and  $\Phi$  is a constant dictated by the crystallization kinetics and thermodynamics of the system(s). According to Hoffman-Weeks<sup>6</sup> the slope  $\Phi$  described should be 0.5 for ideally chain-folded lamellar crystals. For bundle-like crystal, a  $\Phi$  of unity is anticipated<sup>8,9</sup>. In practice, values for  $\Phi$  are found to lie in the range of 0.25 to 0.5<sup>10</sup> for the chain-folded lamellar crystals and to exhibit a value of unity for the bundle-like crystals<sup>8,9</sup>. Various factors affecting  $\Phi$  have been discussed in detail by many workers<sup>8,11</sup>. Note that all the plots (Figure 1) are approximately linear with slopes between 0.48 and 0.5. Extrapolated equilibrium melting temperatures for both homopolymers and random block copolymers are listed in Table 1.

According to Flory<sup>12</sup>, the polymer melting temperature has a dependence on molecular weight given by:

$$1/T_m - 1/T_m^0 = K/M_n \quad (2)$$

In this equation,  $T_m$  should be the extrapolated melting temperature  $T_m^*$  for the homopolymer of given molecular weight  $M_n$ , and  $T_m^0$  the thermodynamical equilibrium melting temperature for the homopolymer of infinite molecular weight.  $K$  is a constant for a given system. Figure 2 shows the plots of the extrapolated equilibrium melting temperatures  $T_m^*$  from Figure 1 for the TMPS homopolymer plotted

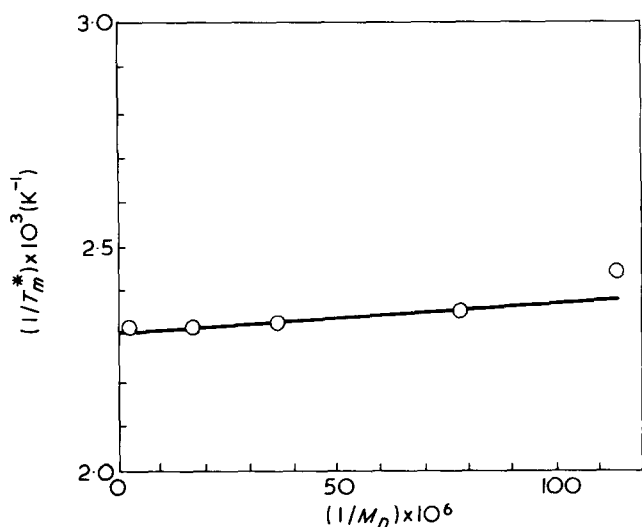


Figure 2 Dependence of the reciprocal of the extrapolated equilibrium melting temperature  $T_m^*$  ( $K^{-1}$ ) on number-average molecular weight

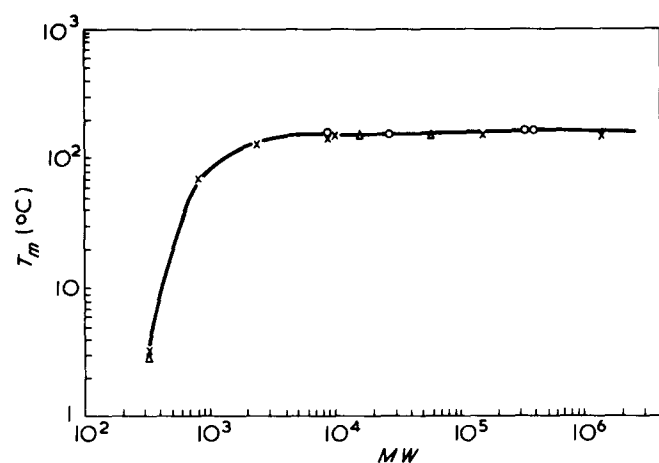


Figure 3 Equilibrium melting point ( $^{\circ}C$ ) – molecular weight curve for poly(TMPS). Data:  $\Delta$ , computer fitting crystallization kinetic data;  $\circ$ , kinetic theory using small-angle X-ray crystallite size – crystallization temperature data and  $\times$ , extrapolated melting point – crystallization data for a wide range of molecular weight homopolymers (Magill unpublished results).

against the molecular weight. From Figure 2, the equilibrium melting temperature for poly(TMPS) of infinite molecular weight was found to be  $160^{\circ}C$ . This point is well illustrated in Figure 3 which shows how a limiting melting point, dependent upon morphology, exists for each molecular weight after equation (2) and these data in the limit of very high molecular weight provide  $T_m^0$  in good agreement with the value of  $160^{\circ}C$  obtained in Figure 2. There is sometimes confusion in the literature concerning the usage of the equation (2) (as well as equations 4 and 5).  $T_m$  (in equation 2), and  $T_m^*$  (in equations 4 and 5) should be used only with the appropriately extrapolated value for each polymer (as in Figure 1) and not the actual observed melting temperature(s), for a single crystallization temperature, which exhibits a crystallite size dependence related to its sample history. When equations (2), (4) and (5) are applied using the directly observed melting temperature, the  $T_m^0$  value obtained is too low<sup>13</sup>.

#### Heat of fusion

In our work the heat of fusion for perfectly crystalline poly(TMPS) was determined by two methods. One of these

used the extrapolation method to 100% crystallinity; the other was obtained by studying the effect of diluent (melting point depression) on the melting point of the polymer. The degree of crystallinity of all samples was estimated from the density studies using the equation:

$$X_c = (V_a - V)/(V_a - V_c) \quad (3)$$

where  $V$  is the specific volume of any sample;  $V_a$ , the specific volume of amorphous poly(TMPS), was found to be  $1.015 \text{ cm}^3/\text{g}^{14}$ .  $V_c$ , the specific volume of perfectly crystalline poly(TMPS) was taken as  $0.9074 \text{ cm}^3/\text{g}^{14}$ . Heats of fusion obtained by d.s.c. were plotted against crystallinity obtained from density measurements for poly(TMPS) in the molecular weight range  $M_v = 6.03 \times 10^4$  to  $5.7 \times 10^5$ . These results are shown in Figure 4. The extrapolated value of the limiting heat of fusion to 100% crystallinity (by density) was found to be  $54.4 \text{ J/g}$  ( $13 \text{ cal/g}$ ). Other more extensive results which extend along the dotted line also support this claim<sup>15</sup>.

Melting temperature is found to decrease continuously as diluent concentration is increased. The relation describing this behaviour is given by the following<sup>16,12</sup> equation:

$$(1/T_m^* - 1/T_m^0)/v_1 = (R/\Delta H_\mu)(V_2/V_1)(1 - BV_1v_1/RT_m^*) \quad (4)$$

where  $\Delta H_\mu$  is the heat of fusion per polymer unit;  $T_m^0$  is the equilibrium melting temperature of the pure polymer and  $T_m^*$  is the extrapolated melting temperature of the polymer-diluent mixture.  $V_1$  and  $V_2$  represent the molar volumes of diluent and polymer, respectively;  $v_1$  is the volume fraction of diluent;  $R$  is the gas constant and  $B$  is the diluent-polymer interaction parameter<sup>17</sup>. From Figure 5 a plot of  $(1/T_m^* - 1/T_m^0)/v_1$  against  $v_1/T_m^*$  (from equation 4),  $\Delta H_\mu$  is found from the intercept on the ordinate axis to be  $54.4 \text{ J/g}$  ( $13 \text{ cal/g}$ ) and the value of  $B$  is estimated as  $0.25 \text{ J/cm}^3$  ( $0.06 \text{ cal/cm}^3$ ). The magnitude and sign of  $B$  suggests that dibutylphthalate is a borderline solvent<sup>17</sup> for poly(TMPS). It must be emphasized that the extrapolated or limiting melting temperature,  $T_m^*$ , must be used in equation (4) for each polymer-diluent mixture. Again, it should be pointed

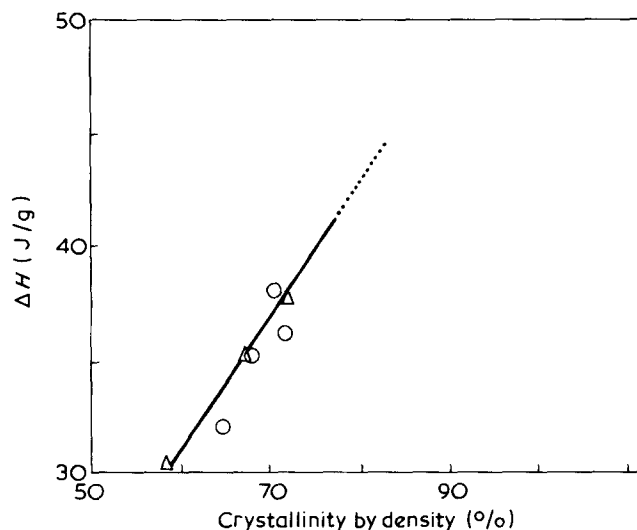


Figure 4 Correlation of the heat of fusion  $\Delta H$  ( $J/g$ ) by d.s.c. with the crystallinity by density (%);  $\circ$ ,  $M_v = 5.7 \times 10^5$ ;  $\Delta$ ,  $M_v = 6.03 \times 10^4$

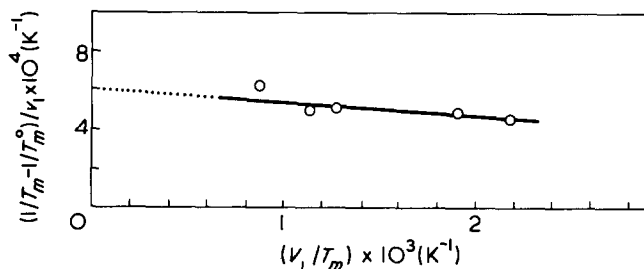


Figure 5 Plots of the melting temperature depression ( $K^{-1}$ ) of poly(TMPS) with volume fraction dibutylphthalate diluent ( $K^{-1}$ )

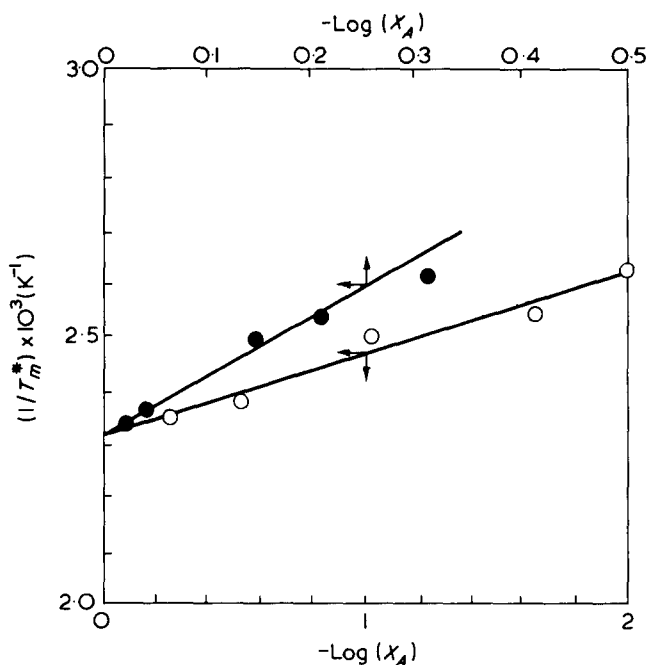


Figure 6 Plots of the copolymer extrapolated equilibrium melting temperature ( $K^{-1}$ ), from Figure 1, against the copolymer composition based on DMS segment sizes of 1 (○) and 18 (●) units, respectively

out that care must always be exercised to ensure that ideal or close to ideal crystallization requirements are adhered to in these experiments (i.e. no phase separation between polymer and diluent is allowed). Unfortunately this conditions is seldom realized in practice in diluent systems so that one is forced to use  $T_m$  instead of  $T_m^*$  in the hope that  $\Delta H_u$  will not be affected significantly by this approximation if the crystallinity of the crystals formed is fairly high.

#### Copolymer system

Both  $T_m^0$  and  $\Delta H_u$  were also obtained from the copolymer melting point depression measurements. The decrease of the melting point for the copolymer was given by the equation<sup>16,18,19</sup>:

$$1/T_m^* - 1/T_m^0 = -(R/\Delta H_u) \log(X_a) \quad (5)$$

where  $T_m^0$  is the thermodynamic melting temperature of the crystallizable homopolymer component A;  $T_m^*$  is the extrapolated melting temperature of the copolymer with composition (mole fraction)  $X_a$ ,  $R$  is the gas constant and  $\Delta H_u$  is the heat of fusion per chain unit of the crystallizable component A in the copolymer. Plots of  $(1/T_m)$  against  $\log(X_a)$  for the copolymer (Figure 6) based upon a single unit of DMS and on a block of 18 DMS segments, respectively, as the

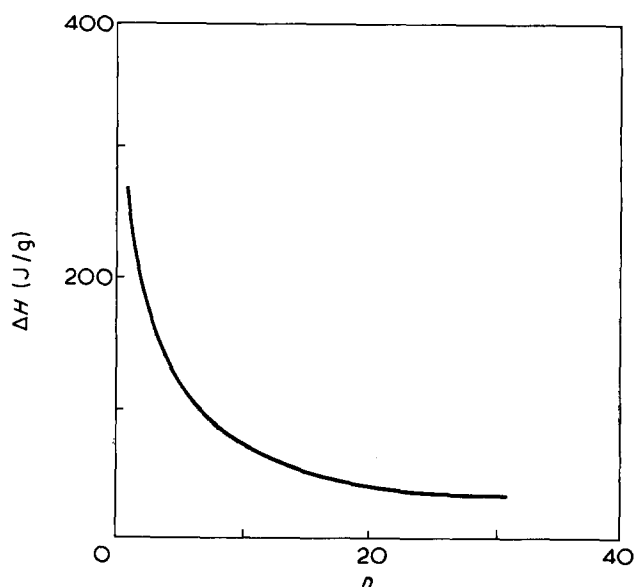
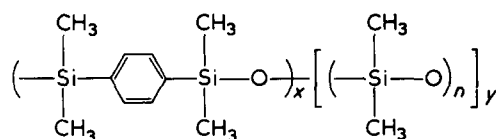


Figure 7 Heat of fusion (J/g) calculated from the random copolymer theory as a function of DMS block size,  $n$

comonomer unit in the polymer chain. It is found from the slopes and the intercepts of these plots that  $T_m^0$  is  $160^\circ C$  in both instances and that  $\Delta H_u$  is  $37.7 J/g$  ( $9 cal/g$ ) for a copolymer comprised of 18 unit blocks of DMS and  $263.6 J/g$  ( $63 cal/g$ ) for one having single units of DMS randomly distributed within the copolymer schematically illustrated:



Based upon theory, Figure 7 shows how  $\Delta H_u$  varies with DMS block size in our TMPS/DMS system. From this graph a block size of 12 DMS units corresponds to a value of  $\Delta H_u = 54.4 J/g$  ( $13 cal/g$ ) obtained from density and diluent studies. Based upon melting point data the agreement between the extrapolated experimental melting data (Figure 1), the calculated and theoretical curve corresponding to these results are illustrated in Figure 8. As expected, the curve for  $n = 1$  lies far below that for  $n = 18$  which falls above the extrapolated  $T_m$  values. The dotted curve for  $n = 14$  lies fairly close to the  $T_m$  values obtained from Figure 1. The value that best fits the data,  $n = 12$  lies below the block size average of 18 units previously anticipated from the co-condensation reaction for the hydroxy end-blocked dimethyl siloxane oligomer of 18 units ( $n = 18$ ) with *p*-bis(dimethyl-hydroxylsilyl) benzene<sup>3,13</sup>. It is interesting that the block value of the DMS does not influence the limiting melting temperature  $T_m^0$  since both  $n = 1$  and  $n = 18$  gave the same value of  $160^\circ C$ . However,  $\Delta H_u$  is strongly influenced by the DMS block size as Figure 7 illustrates.

#### Glass transition temperature

Poly(TMPS) is readily quenchable from the molten state to a glassy polymer in which it can be kept almost indefinitely in liquid nitrogen†. It is well known that  $T_g$  is influenced by

† Normally liquid nitrogen is not a good quenching medium unless the polymer nucleates and crystallizes slowly as is the case for these materials.

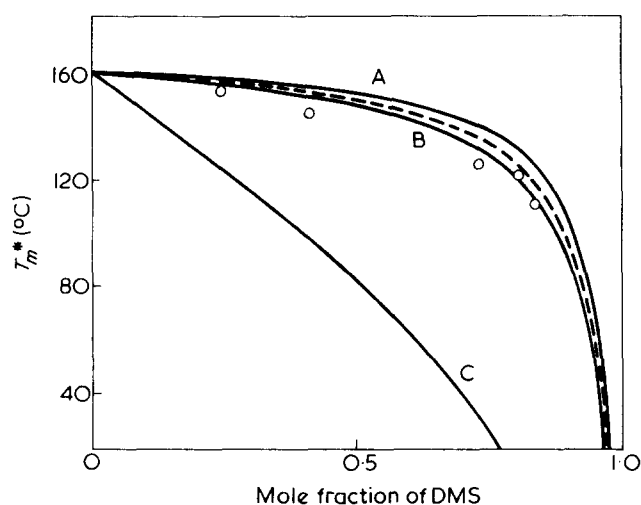


Figure 8 Plots of melting point ( $^{\circ}\text{C}$ ) of TMPS/DMS copolymers against DMS content of different block sizes  $n = 1$ ,  $n = 12$ ,  $n = 14$  (---) and 18, respectively, calculated from random copolymer theory. The experimentally extrapolated  $T_m^*$  values are plotted as (O). A,  $n = 18$ ; B,  $n = 12$ ; C,  $n = 1$

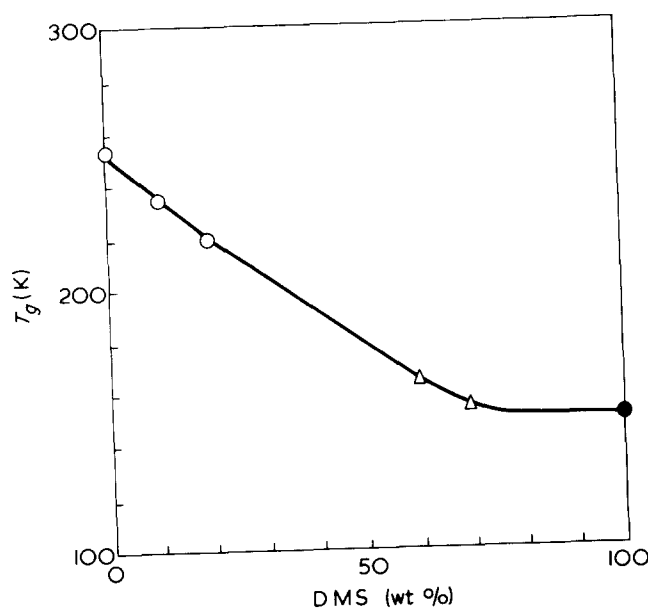


Figure 9 Glass transition temperature  $T_g$  (K) of TMPS-DMS copolymers measured by O, d.s.c.;  $\Delta$ , d.t.a.;  $\bullet$ , data from Magill (1964)

many factors such as chemical structures<sup>20</sup>, extent of copolymerization<sup>21</sup>, degree of crosslinking<sup>22</sup>, degree of crystallinity<sup>23</sup>, diluent content<sup>26</sup> and applied stress<sup>27</sup> amongst others<sup>28-30</sup>. Only the influence of copolymerization, crystallinity<sup>25</sup>, time scale<sup>24</sup> and molecular weight are considered in this study. To a first approximation, crystallinity, time scale and molecular weight can be neglected since all the specimens having comparable molecular weight were quenched under similar conditions to form completely amorphous materials. The effect of chain ends was insignificant in this study. Measurements made at the same heating rate using d.s.c. or d.t.a. methods are shown in Figure 9.  $T_g$  decreases almost linearly with composition up to 70 wt % of DMS. Beyond this point relatively small changes ensue as the limiting 100% DMS level is reached. This is not surprising because in the co-condensation reaction it is anticipated that longer than average DMS sequences may build up along the copolymer chain beyond this 70 wt % DMS content. Naturally, oligomers of DMS segments of varying size have a molecular weight dependence as recent experiments have shown<sup>31,32</sup>. Depending upon the influence of chemical or more especially physical architecture on properties, two  $T_g$  values are sometimes recorded for block copolymers. In the poly(TMPS-DMS) system studied here this is noted in the range of 10-30 wt % of DMS but above the 50 wt % range of DMS only one  $T_g$  is obtained by the Rheo-Vibron viscoelastometer<sup>15</sup>. It appears that the d.s.c. technique which did not detect two  $T_g$  transitions is the less sensitive or discriminating than the Rheo-Vibron viscoelastometer method. A detailed report on the dynamic mechanical behaviour of these polymers will be the subject of a later communication.

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#### REFERENCES

- 1 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 2nd Edn, Wiley, New York, 1975
- 2 Magill, J. H. in 'Properties of Solid Polymeric Materials' (Ed. J. M. Schultz) Academic Press, 1977, vol. 10A, pp 1-368
- 3 Merker, R. L., Scott, M. J. and Haberland, G. G. *J. Polym. Sci. (A)* 1964, 2, 31
- 4 Magill, J. H. *J. Appl. Phys.* 1964, 35, 3249
- 5 Haller, M. N. and Magill, J. H. *J. Appl. Phys.* 1969, 40, 4261
- 6 Hoffman, H. J. and Weeks, J. J. *J. Res. Nat. Bur. Stand. (A)* 1962, 66, 13
- 7 Wood, L. A. and Bekkedahl, H. 'High Polymer Physics' (Ed. H. A. Robinson) Remsen Press, Division Chem. Publ., New York, 1948, p. 258
- 8 Okui, N. and Kawai, T. *Kobunshi Ronbunshu* 1974, 31, 190
- 9 Okui, N. and Kawai, T. *Makromol. Chem.* 1972, 154, 161
- 10 Hoffman, J. D. *SPE Trans.* 1964, 4, 315
- 11 Mandelkern, L. and Baker, C. H. *Polymer* 1966, 7, 7
- 12 Flory, P. J. *J. Chem. Phys.* 1949, 17, 223
- 13 Merker, R. L. and Scott, M. J. *J. Polym. Sci. (A)* 1964, 2, 15
- 14 Gardner, K. H., Magill, J. H. and Atkins, E. D. T. *Polymer* 1978, 19, 370
- 15 Li, H. M. *PhD Thesis* University of Pittsburgh (1977)
- 16 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, New York, 1953, p.568
- 17 Flory, P. J. and Krigbaum, W. R. *Ann. Rev. Phys. Chem.* 1951, 2, 383
- 18 Flory, P. J. *J. Chem. Phys.* 1947, 15, 684
- 19 Mandelkern, L. *Rubber Chem. Technol.* 1959, 32, 1392
- 20 Boyer, R. F. *J. Appl. Phys.* 1954, 25, 825
- 21 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, 2, 493
- 22 Fox, T. G. and Loshaek, S. *J. Polym. Sci.* 1955, 15, 371
- 23 Thompson, A. B. and Woods, D. W. *Trans. Faraday Soc.* 1956, 52, 1383
- 24 Alfrey, T., Goldinger, G. and Mark, H. *J. Appl. Phys.* 1943, 14, 700
- 25 Fox, T. G. and Flory, P. J. *J. Polym. Sci.* 1954, 14, 315
- 26 Nielsen, L. E., Pollard, R. E. and McIntyre, E. J. *J. Polym. Sci.* 1951, 6, 661
- 27 Wall, F. T. and Miller, D. G. *J. Polym. Sci.* 1954, 13, 157
- 28 Uematsu, I., Honda, K. and Koiwa, Y. *Rep. Prog. Polym. Phys. Jpn.* 1966, 9, 249
- 29 Uematsu, I. and Uematsu, T. *Kobunshi Ronbunshu* 1960, 17, 222
- 30 Berry, G. C. and Fox, T. G. *Adv. Polym. Sci.* 1968, 5, 261
- 31 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1973, 14, 423
- 32 Godovskii, Y. K., Levin, V. Y., Slonimskii, G. L., Zhdanov, A. A. and Andrianov, K. A. *Polym. Sci. USSR* 1969, 11, 2778