

# Crystallinity of poly(tetramethyl-*p*-silphenylenesiloxane) and (tetramethyl-*p*-silphenylenesiloxane)-(dimethyl siloxane) copolymers

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An X-ray method is described for determining the degree of crystallinity of poly(tetramethyl-*p*-silphenylenesiloxane) (TMPS) homopolymers and copolymers of tetramethyl-*p*-silphenylenesiloxane (TMPS-DMS) of wt % TMPS-DMS ratio of 48/52, 65/35 and 85/15, respectively. The specimens had an average DMS block size of 30 monomeric units. Polymers ranging from 100 wt % TMPS to approximately 50 wt % of TMPS were studied. Over this composition range the crystallinities varied from 75 to 30% approximately. Crystallinity determinations were also made using a density gradient column and differential scanning calorimetric methods for comparison purposes to check the validity of the X-ray procedure described herein. The results of the three techniques were in satisfactory agreement although some refinements are still in order.

## INTRODUCTION

One of the most useful and practical concepts in the characterization of semicrystalline polymer is that of the degree of crystallinity. The degree of crystallinity is very important particularly in considerations of the physical and/or mechanical properties which are also dependent upon polymer morphology. Many methods have been developed to ascertain crystallinity index. These techniques have aroused considerable debate and even the meaning of polymer crystallinity has been questioned<sup>1</sup>. Determination has been made by X-ray diffraction analysis<sup>2-6</sup>, density methods<sup>7-9</sup>, thermal analysis<sup>10,11</sup> infra-red method<sup>12,13</sup> among others<sup>14,15</sup>.

In the present work, three methods (X-ray diffraction analysis, heat of fusion measurement by d.s.c. and density measurement by density gradient column) are employed to determine the crystallinity of polyTMPS and TMPS-DMS copolymers. Specimens are used over a range of compositions ranging from TMPS homopolymer to approximately 50 wt % TMPS copolymer and covering values of crystallinity ranging from ~ 75 to 30% crystallinity approximately.

## EXPERIMENTAL

### Materials

The samples of block copolymers TMPS-DMS had wt % ratios of 85/15, 65/35 and 48/52, respectively. Details are given in a previous paper<sup>17</sup>. Two specimens of TMPS homopolymer of  $5.7 \times 10^5$  and  $6.03 \times 10^4$  molecular weight were also used. All samples were carefully moulded by hot pressing into shapes suitable for X-ray and density studies. Specimens approximately 0.5 mm thick were carefully wrap-

ped in aluminium foil and annealed for seven days at temperatures in the range 50° to 130°C approximately. Previous studies have indicated that these siloxane polymers are stable under these conditions. Precise details are given in tabular form later in the paper. Considerable care was taken to ensure that specimens were unoriented because of the requirements for X-ray crystallinity determinations.

### Measurements

Heat of fusion measurements were made using a Perkin-Elmer DSC-1B calorimeter at a heating rate of 20°C/min. Benzoic acid and indium of high purity were used as calibration standards for heat of fusion determinations. All density measurements were made at 25°C in a thermostatically controlled density gradient column containing ethylene glycol-methyl alcohol. X-ray measurements were carried out using a General Electric XRD 700 unit in the angular  $2\theta$  range, 5° to 30°. All measurements were made in the conventional manner.

### Determination of degree of crystallinity of density method

In order to calculate crystallinity from the density values, it was assumed that a two phase system exists and that the contribution to the specific volume from the amorphous and crystalline phases were additive. The specific volume  $V_c$ , of perfectly crystalline polyTMPS that relates inversely to the density  $\rho_c$  was calculated by equation (1):

$$V_c = \frac{1}{\rho_c} = \frac{NV}{ZM_w} = 0.9162 \quad (1)$$

where  $Z$  (number of monomeric units per units cell) is 4,  $M_w$  (unit molecular weight) is 208.44,  $N$  is Avogadro's number,  $V$  (volume of unit cell) is<sup>18</sup>  $1.268 \times 10^{21}$ . The specific

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volume of amorphous polyTMPS was determined by a dilatometric method to be<sup>19</sup> 1.015 cm<sup>3</sup>/g at 25°C. The amorphous density of polyDMS obtained by the density gradient column was found to be 0.975 g/cm<sup>3</sup>, in good agreement with Damaschum<sup>20</sup>. It should be pointed out that the volume of the unit cell of a copolymer usually increases as the concentration of comonomer units increases<sup>21,22</sup>. However, the unit cell dimensions for the TMPS–DMS system was found to be invariant with increasing concentration of comonomer units (DMS)<sup>18</sup>. Assuming that a two phase model adequately describes the specific volume of the system comprised of contributions from the polyTMPS amorphous regions and the polyDMS amorphous regions in proportion to their weight fraction of the copolymer composition. Because of polymer incompatibility, the following equation was proposed:

$$v_a = v_{a1}X_1 + v_{a2}X_2 \quad (2)$$

where the specific volume of the amorphous phase for the copolymer is  $v_a$  and  $v_{a1}$  and  $v_{a2}$  refer to the specific volume of the amorphous polyDMS and polyTMPS components, respectively.  $X_1$  and  $X_2$  are the weight fraction of DMS and TMPS in the copolymer, respectively. Total weight of the copolymer ( $W$ ) is given by equation (3):

$$W = W_1 + W_2 + W_3 \quad (3)$$

where  $W_1$ ,  $W_2$  and  $W_3$  are the weight of DMS, amorphous TMPS and crystalline TMPS in the copolymer, respectively. And the total volume of the copolymer is given by the following equation:

$$\frac{W}{\rho} = \frac{W_1}{\rho_1} + \frac{W_2}{\rho_2} + \frac{W_3}{\rho_3} \quad (4)$$

where  $\rho_1$ ,  $\rho_2$ ,  $\rho_3$ , and  $\rho$  are the density of DMS, amorphous polyTMPS, crystalline polyTMPS and the sample, respectively. The crystallinity can now be obtained from the density data by equation (5):

$$X_c = (v_a - v)/(v_{a2} - v_c) \quad (5)$$

In this relation  $X_c$  is the weight fraction crystallinity ( $W_3/W$ ),  $v_a$  is the specific volume of the amorphous phase (given by equation 2),  $v$  is the value of sample,  $v_{a2}$  is the value of the amorphous polyTMPS and  $v_c$  is the value of the crystalline phase.

#### Degree of crystallinity from the heat of fusion

The percent crystallinity of all samples was calculated according to equation (6):

$$\text{Percent crystallinity} = (\Delta H_f / \Delta H_f^*) \times 100 \quad (6)$$

where  $\Delta H_f$  denotes the sample heat of fusion by d.s.c. and  $\Delta H_f^*$  is the heat of fusion for perfectly crystalline polyTMPS where the value is 13.0 cal/g<sup>23</sup>. Note that this value is much less than that previously obtained by Merker and Scott<sup>24</sup>. This simplified expression tends to neglect contributions from the polymer outside of the crystalline core of the two phase system.

#### Crystallinity index from X-ray

According to Weidinger and Hermans<sup>25,26</sup> the weight fraction  $X_c$  of the polymer in the crystalline phase is pro-

portional to the crystalline peak area  $A_c$  and the fraction  $X_a$  in the amorphous phase is proportional to the amorphous reflection area  $A_a$ . The equations can be written as:

$$X_c = K_c A_c \quad (7)$$

and

$$X_a = K_a A_a \quad (8)$$

where  $K_c$  and  $K_a$  are respective proportionality factors. It follows that the degree of crystallinity can be expressed by equation (9):

$$X_c = (1 + A_a K_a / A_c K_c)^{-1} \quad (9)$$

Generally the X-ray pattern of the 100% amorphous phase can only be measured above the melting point of the sample, but 100% crystalline polymer material is never accessible directly.

Figure 1 shows the X-ray diffraction patterns observed for polyTMPS at room temperature (A) and at 200°C (B). Patterns for the TMPS–DMS copolymers; 65/35 (C) and 48/52 (D) at 200°C, along with that of the polyDMS homopolymer (E) at room temperature are illustrated. The amorphous peak positions ( $2\theta$ ) occur at 13.5 for the TMPS homopolymer, at 13.2 and 11.3 for copolymer C and 12.0 for copolymer D. For the amorphous DMS homopolymer, the  $2\theta$  value is 11.6. Figure 1 illustrates that two amorphous diffraction peaks are generally found depending upon the copolymer composition. It is a problem in the crystallinity analysis to estimate precisely how TMPS and DMS amorphous phases contribute to the X-ray diffraction pattern of the copolymer, and to determine how the amorphous area of TMPS and DMS may be subtracted from the actual X-ray pattern seen in Figure 2. If the TMPS crystalline core in the polymer is presumed to be perfect and not affected by the amorphous phase in any of the specimens, then it can be assumed that the intensity  $I_{hkl}$  from a crystal is proportional to any other intensity  $I_{h'k'l'}$ . That is, the peak area  $A_{c1}$ , is proportional to  $A_2$  in Figure 2. The area of  $A_2$  (above  $2\theta = 19^\circ$  area) may consist only of the crystalline phase since amorphous diffraction patterns do not appear beyond  $2\theta = 19^\circ$ . Bearing this in mind, the following relation may be written:

$$A_1 = A_{c1} + A_a \quad (10)$$

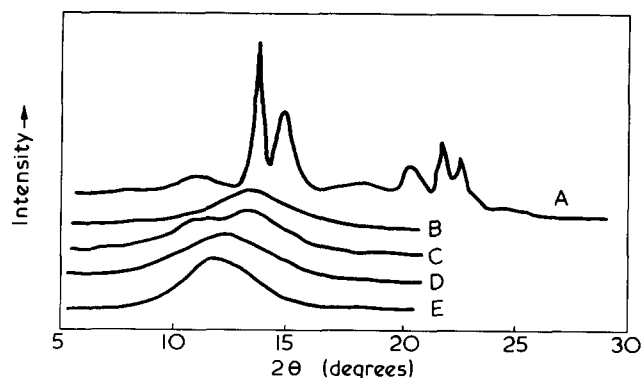


Figure 1 Typical X-ray diffraction of TMPS homopolymer at room temperature (A) and at 200°C (B), TMPS–DMS copolymer 63/35 at 200°C (C), TMPS–DMS copolymer 48/52 at 200°C (D) and DMS homopolymer at room temperature (E)

where

$$A_{c1} = CA_2 \quad (11)$$

Hence it follows that the total crystalline area is given by:

$$A_c = A_{c1} + A_2(1+C)A_2 \quad (12)$$

and the amorphous area is expressed as

$$A_a = A_1 - A_{c1} = A_1 - CA_2 \quad (13)$$

From equation (9), (12) and (13), one obtains

$$X_c = [K_1(A_t/A_2) + K_2]^{-1} \quad (14)$$

where

$$A_t = A_1 + A_2 \quad (15)$$

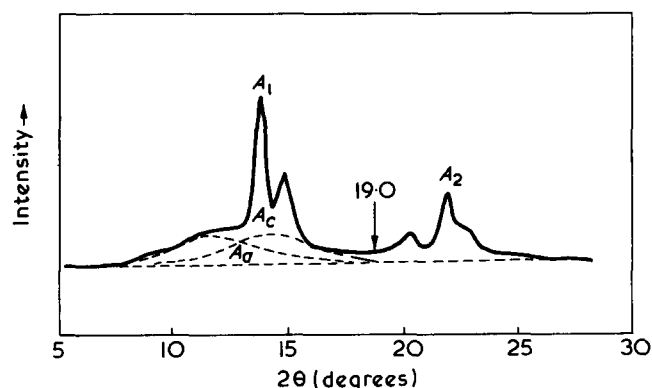


Figure 2 Resolution of X-ray diffraction pattern of TMPS-DMS copolymer. Peak areas for amorphous and crystalline peaks are denoted by  $A_a$  and  $A_c$  for crystalline TMPS by areas  $A_1$  and  $A_2$ , respectively

$A_t$  is the total X-ray reflection area between  $2\theta = 5^\circ$  and  $30^\circ$  respectively.

$$K_1 = K_a/[K_c(1+C)] \quad (16)$$

$$K_2 = 1 - K_a/K_c$$

$A_t$  and  $A_2$  can be obtained experimentally without much difficulty. The peak or area ratio of  $A_t/A_2$  can be compared with values for the degree of crystallinity determined by the other methods such as density or d.s.c. Note that all the base lines for the X-ray diffraction patterns are drawn for  $5^\circ \leq 2\theta \leq 30^\circ$ , although scouting runs were made beyond these extremes. In this investigation all scattering intensities were corrected for Lorentz polarization at each angle, but the absorption correction was neglected since all sample thickness were similar.

## RESULTS AND DISCUSSION

In the present study the sample crystallinity ranged from 75 to 30% and scanned a composition range from the homopolymer (100% TMPS) to copolymers with only 50 wt % of TMPS (see Table 1). Crystallinity values obtained from d.s.c. and from density gradient column measurements are tabulated in Figure 3 for these polymer specimens. Systematic deviations are noted among crystallinity obtained by d.s.c. and density methods. The d.s.c. crystallinity for polyTMPS generally give lower values than are found by the density method for the same samples. Other deviations also exist depending upon the copolymer composition. Significant crystallinity variations are found by d.s.c. measurement for changing copolymer compositions and annealing temperatures. However, density crystallinities are found to depend mainly upon copolymer compositions and to a much less degree on annealing temperature. At first it may seem that these apparent discrepancies may be attributed to contributions to the

Table 1 Crystallinity determined by d.s.c., X-ray and density and for polysiloxane homo- and block copolymers

| Sample        | TMPS (wt %) | $T_a^*$ (°C) | From d.s.c.          |                   | From density                              |                   | From X-ray area ratio $A_t/A_2$ |      |
|---------------|-------------|--------------|----------------------|-------------------|---|-------------------|---------------------------------|------|
|               |             |              | $\Delta H_f$ (Cal/g) | Crystallinity (%) | Density (g/cm <sup>3</sup> ) <sup>†</sup> | Crystallinity (%) |                                 |      |
| Homopolymer A | 100         | 111          | 7.7                  | 59.2              | 1.058                                     | 70.7              | 6.02                            |      |
|               |             | 120          | 8.6                  | 66.2              | 1.066                                     | 78.1              | 6.04                            |      |
|               |             | 124          | 9.1                  | 70.2              | 1.064                                     | 76.0              | —                               |      |
|               |             | 131          | 8.4                  | 64.8              | 1.062                                     | 74.4              | 5.93                            |      |
| B             | 100         | 116          | 8.9                  | 68.5              | 1.067                                     | 78.5              | —                               |      |
|               |             | 120          | 7.3                  | 55.8              | 1.050                                     | 62.9              | —                               |      |
|               |             | 124          | 8.4                  | 64.8              | 1.061                                     | 73.6              | —                               |      |
|               |             | 124          | 9.9                  | 76.2              | 1.043                                     | 58.5              | —                               |      |
| Copolymer A   | 85          | 100          | 7.8                  | 70.5              | 1.044                                     | 59.5              | 7.35                            |      |
|               |             | 111          | 7.7                  | 70.2              | 1.045                                     | 60.4              | 7.54                            |      |
|               |             | 116          | 9.6                  | 73.5              | 1.048                                     | 63.2              | —                               |      |
|               |             | 120          | 9.8                  | 75.0              | 1.045                                     | 60.4              | 7.42                            |      |
|               |             | 124          | 9.4                  | 71.9              | 1.045                                     | 60.4              | —                               |      |
|               |             | 131          | 7.8                  | 59.6              | 1.045                                     | 60.4              | 6.78                            |      |
|               | B           | 65           | 50                   | 5.7               | 43.5                                      | 1.032             | 50.3                            | 9.40 |
|               |             |              | 60                   | 6.1               | 46.5                                      | 1.031             | 49.4                            | 8.60 |
|               |             |              | 70                   | 7.9               | 60.5                                      | 1.032             | 50.3                            | 8.07 |
|               |             |              | 80                   | 6.7               | 51.6                                      | 1.028             | 46.5                            | 8.77 |
|               |             |              | 89                   | 7.0               | 53.6                                      | 1.031             | 49.4                            | —    |
|               |             |              | 96                   | 6.9               | 53.2                                      | 1.032             | 50.3                            | —    |
| C             | 48          | 116          | 5.9                  | 45.2              | 1.034                                     | 52.2              | —                               |      |
|               |             | 50           | 3.0                  | 22.6              | 1.010                                     | 30.3              | 11.20                           |      |
|               |             | 60           | 3.6                  | 27.4              | 1.009                                     | 29.3              | 11.98                           |      |

\* Annealing temperature for seven days; † measured at 25°C

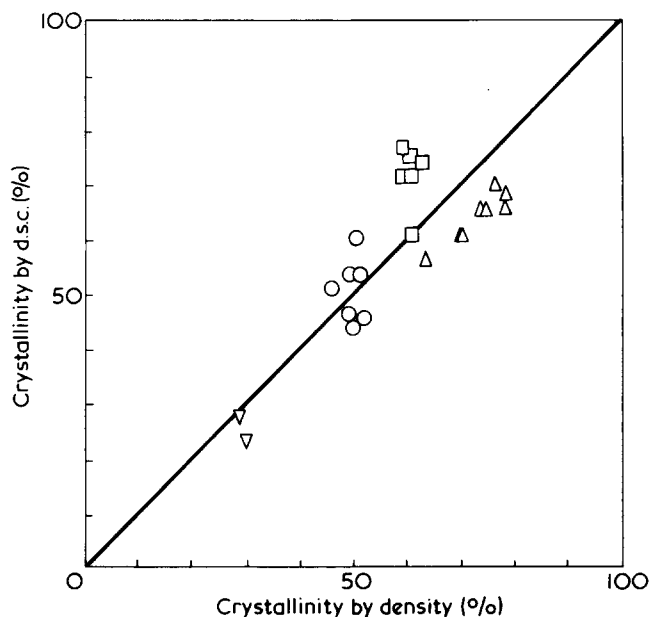


Figure 3 Correlation of density crystallinity with d.s.c. crystallinity, copolymer 48/52 ( $\nabla$ ); copolymer 65/35 ( $\circ$ ); copolymer 85/15 ( $\square$ ); TMPS homopolymer, ( $\Delta$ )

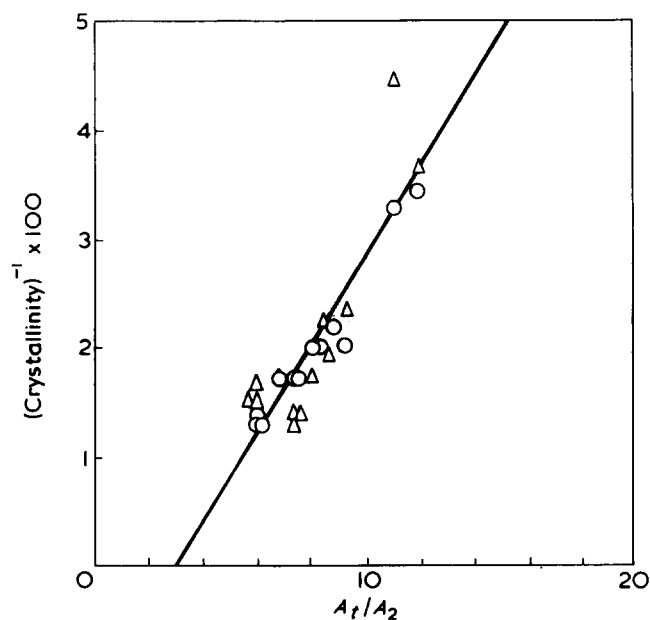


Figure 4 Comparison of degree of crystallinity obtained by the density method ( $\circ$ ) or d.s.c. method ( $\Delta$ ) with the crystallinity index obtained by the X-ray method

density from voids inherent in the specimens as well as to enthalpic contributions from the interfacial regions, plus some degree of experimental error among other causes. It must be pointed out that the crystallinity variations derived from d.s.c. and density methods are outside the limits of experimental error of the techniques. Contributions from voids should lower the density crystallinity but leave the d.s.c. crystallinity unaffected since the heat of fusion determination is mass based. The enthalpy contribution\* due to the morphology of crystal fold surfaces of the crystallites must

\* Estimates of this correction amount to an additional 8% for TMPS homopolymer and 5% approximately for the lowest crystallinity copolymer in Table 1. This tends to bring the d.s.c. values more closely in line with the density results.

be significant (undoubtedly) because of the defect nature of the crystal interfacial regions. Defects in the TMPS crystalline core are unlikely to have a significant affect upon the density crystallinity because the unit cell dimensions appear to be the same for all our samples<sup>18</sup>. When the density crystallinity is compared with the X-ray crystallinity ( $\circ$ , Figure 4) a better correlation is obtained than in the case of the d.s.c. crystallinity vs. X-ray crystallinity illustrated in Figure 4 ( $\Delta$ ). The variations noted in comparing these three different crystallinity values might be ascribed to the affect of diverse aspects of sample morphology<sup>27</sup> on the heat of fusion, particularly for the copolymer materials. At this point we do not have a satisfactory explanation for the discrepancies between crystallinity values derived from d.s.c. and density measurements. However, enthalpic, among other contributions to the d.s.c. crystallinity, will be examined in more detail in later work. At the present time, however, plots of the crystallinities by d.s.c. and/or density methods when compared with X-ray crystallinity expressed in terms of the ratio  $A_1/A_2$ , provide the X-ray constants ( $K_1 = 0.403$  and  $K_2 = -1.21$ ) for a useful crystallinity analysis of block copolymers. From these values of  $K_1$  and  $K_2$  it follows that  $K_d/K_c$  and  $C$  are found to be 2.21 and 4.48 respectively. The value of  $K_d/K_c$  is quite reasonable when compared with results obtained for other polymers<sup>6,28</sup>. Although the method of determining X-ray crystallinity as outlined in this paper is rather simple, it does merit comparison with other conventionally accepted X-ray methods. It seems that the crystallinity method just outlined correlates reasonably well with values determined by other experimental means. However, refinements to this procedure are in order and these will follow in later work dealing with these and other siloxane homo- and block copolymers.

In conclusion it may be added that the X-ray method developed here may also have general validity for block copolymer systems containing one crystalline component.

#### ACKNOWLEDGEMENT

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