Mechanical properties of polysiloxanes:
1. Poly(tetramethyl-*p*-silphenylene siloxane) homopolymer and tetramethyl-*p*-silphenylene siloxane/dimethyl siloxane block copolymers

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The mechanical behaviour of poly(tetramethyl-*p*-silphenylene siloxane) [poly(TMPS)] homopolymer and random block copolymers of tetramethyl-*p*-silphenylene siloxane–dimethyl siloxane [poly(TMPS–DMS)] of mean DMS block of 12 monomer units have been investigated over a wide range of composition and temperature using a Rheovibron viscoelastometer. The compositions ranged from TMPS/DMS wt % ratio of 100/0 to 30/70. The temperature intervals spanned from just above −120°C to the point where melting became evident as dictated by the molecular architecture of each system. Two amorphous relaxation transitions, corresponding to DMS and TMPS phases, were found for copolymers with high TMPS content (⩾80 wt %). At lower TMPS compositions (⩽50 wt %) these transitions merge together. All dynamic transitions are a function of composition and crystallinity. The 'hard' TMPS phase provides crosslinks and acts as filler for the rubbery amorphous phase. The percentage elongation under tensile loading increases with the DMS amorphous content, which parallels an increase in clarity and decrease in density and crystallinity. A morphological model which depends on composition is proposed for these polysiloxanes. The model advanced is consistent with other physical evidence derived from other techniques. Changes in mechanical behaviour parallel changes in specimen morphology.

INTRODUCTION

According to Huggins *et al.*[1] a block copolymer is defined as 'composed of molecules in which two or more polymeric segments of different chemical compositions are attached end-to-end'. Such a definition allows many variations in molecular architecture depending upon the polymerization method used. A material can be tailored, within limitations, to meet certain mechanical property requirements based upon a knowledge of the characteristics of its components. In turn, the copolymer solid state morphology can be correlated with its physical and mechanical behaviour which can provide insights into the fundamental behaviour of such systems[2–5]. A thermodynamic description of phase separation based upon solubility and entropic considerations of copolymer components has been enunciated by Meier and others[6,7] to account for their physical properties. Meier calculated the most stable domain shape for an AB type system (styrene–butadiene) where A and B refer to the two constituents. He showed that a range of morphologies and stabilities was practicable depending upon the molecular ratios M_A/M_B within the copolymer, in which microphase separation occurs into spheres, cylinders or lamellae depending upon composition. Of course, there are several simplifying assumptions in his analysis (e.g. that all copolymer molecules have the same molecular weight, copolymer composition and sequence distribution). Such stringent restrictions seldom hold in practice. A case in point is that of the polysiloxane copolymers[8] presented in this paper, which materials were among the earliest thermoplastic block type elastomers of their class to be synthesized[9] by co-condensation polymerization in the early 1960s. Since that time, however, considerable interest and expertise has developed[10] in making block copolymers of diverse kinds. Physical methods have been applied to gain understanding and check on the synthesis, and in some instances it has been found that complete phase microphase separation does not occur[11,12] because of intervening kinetic factors during sample preparation. An example of this behaviour is found in the poly(bis-phenol-A-carbonate–dimethyl siloxane)[11] in which small-angle X-ray scattering suggests that the boundaries between the polycarbonate hard domains and DMS matrix are not sharp. Other examples have also been cited[13,14]. The reader is referred to the literature for detailed descriptions of other systems since the main thrust of the present paper is on the mechanical property–morphology behaviour of poly(TMPS-DMS) and the changes in its mechanical response with temperature and composition.

EXPERIMENTAL

Materials

The polymers used in this study have been reported in previous papers[8,9,15]. They may be represented chemically as:

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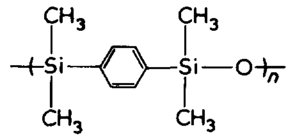

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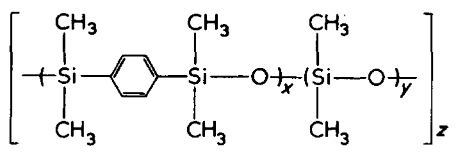

corresponding respectively to TMPS homopolymer and TMPS/DMS copolymers. The latter copolymers studied in this work ranged in wt % compositions from 90/10 to 30/70 with a mean 'soft' DMS block size of twelve monomer units and variable TMPS sequence length. The mean amorphous sequence size deduced from recent physical measurements[17] is shorter than that anticipated from earlier synthesis formulations[9] where an 18 DMS monomer block length was expected. Molecular weights of all polymers by g.p.c. were in the range 10^5 to 10^6 so that chain end effects could be ignored. Many other physical measurements using electron microscopy, small-angle X-ray scattering, density, thermal n.m.r. and g.p.c. analysis, selective chemical degradation, wide-angle X-ray (structure) methods, optical microscopy crystallinity measurements and crystallization kinetic techniques feature among the ways of studying homo- and copolymers. Reference is made here to the many techniques that have been used to characterize our materials, however, the main thrust of the current paper centres on aspects of mechanical behaviour as they relate to morphology.

Dynamic mechanical measurements

These measurements were made with a Dynamic Viscoelastometer Rheovibron Model DDV–II with a low temperature chamber manufactured by the Toyo Measuring Instruments Company Ltd, Japan. Experiments were conducted over all available frequency ranges, namely, 3.5, 11, 35 and 110 Hz, using a range of test lengths for each polymer specimen in order to obtain a correction factor for the measured value of the dynamic force. The correction procedure[17] as detailed in the literature proved to be important in the case of our materials which range from the fairly tough opaque poly(TMPS) homopolymer to translucent elastomeric poly(TMPS–DMS) copolymers as high as 30/70 wt % ratio composition.

For the dynamic mechanical studies, the homopolymer and the copolymers were carefully melt-moulded at 200°C for 5 min in a hot press into bubble-free sheets varying in thickness from 0.014 cm for the 90/10 to 0.032 cm for the 30/70 wt % copolymers. All specimens were quenched to room temperature and allowed to crystallize for several days. Samples were then cut into rectangular strips varying in length from 2.5 to 3.5 cm and width 2 to 5 mm to provide a range of dimensions suitable for the modulus of elasticity measurements. Measurements were made on (a) materials which were cooled in the Rheovibron to approximately −100°C or lower and subsequently heated slowly during measurements to a temperature where incipient melting was indicated by the instrument and (b) crystallized samples which were also investigated during cooling from room temperature to as low as −120°C in a few instances.

Samples used in the Rheovibron instrument were characterized by density gradient measurements, optical microscopic examination of sections, differential scanning calorimetry (d.s.c.) and differential thermal analysis (d.t.a.) and wide- and small-angle X-ray scattering. Crystallinity indices were estimated from both density and d.s.c. melting curves.

RESULTS AND DISCUSSION

Sample morphology

All copolymer specimens were spherulitic in nature. They contained negatively birefringent, finely banded entities with a typical Maltese extinction cross in the polarizer and analyser directions. The poly(TMPS) contained fibrillar negative spherulites. Typical patterns are illustrated in *Figure 1*. In all samples the crystalline TMPS phase coexisting with amorphous DMS was tetragonal. The small-angle X-ray spacing depicted in *Figure 2*, which covered more than a three-fold span in spacing, is consistent with a two phase morphological model of a lamellar nature[8,18], the hard (crystalline) TMPS phase alternating or interdispersed with the 'soft' (non-crystalline) DMS one. Observed T_m and equilibrium melting point, T_m^*, data are recorded in *Table 1* along with calculated values from random copolymer theory, using 12 monomer units as the average DMS sequence length for all polymers investigated. *Table 2* lists a wide range of crystallinity indices ranging from 0.13 to 0.60 for the same polymers. The lower the crystallinity the more elastomeric and clear the specimens, in line with the change in crystallinity. Samples such as the homopolymer and copolymers with high TMPS contents are opaque. The sample clarity improved as the elastomeric nature of the copolymers increased. Furthermore, the elongation (%) at 3000 p.s.i. after prestressing under tensile loading (plotted from Merker *et al.*, *Figure 3*) rises markedly with wt % DMS in the copolymers.

The correlation between the two sets of crystallinity results over the entire composition range in *Table 2* is surprisingly good considering the complex nature of these polysiloxane systems.

Dynamic mechanical properties

It is well known[19] that the dynamic Young's modulus is a linear viscoelastic function which is represented by a complex function, E^*:

$$E^* = E' + iE''$$

with a loss factor $\tan \delta = E''/E$, where the storage modulus $E' = (E^*) \cos \delta$ and loss modulus $E'' = |E^*| \sin \delta$. These quantities are of physical interest in characterization of the mechanical behaviour of the polymer(s). Tan δ provides an important measure of the internal fraction in the system and this is a thermodynamically irreversible process providing information on the conversion of mechanical to thermal energy and consequently on the nature of internal molecular motions under applied stress. The position of the so-called primary transition in amorphous or semicrystalline polymers is determined by its glass transition, the magnitude of the modulus plateau depending on composition, crystallinity index or degree of crosslinking. The results obtained in *Figure 3* for polysiloxanes in this work are no exception to this generalization and the interesting changes that occur can be correlated with morphological observations as described below.

Rheovibron measurements were made on different test lengths of each polymer sample, except for the 50/50 speci-

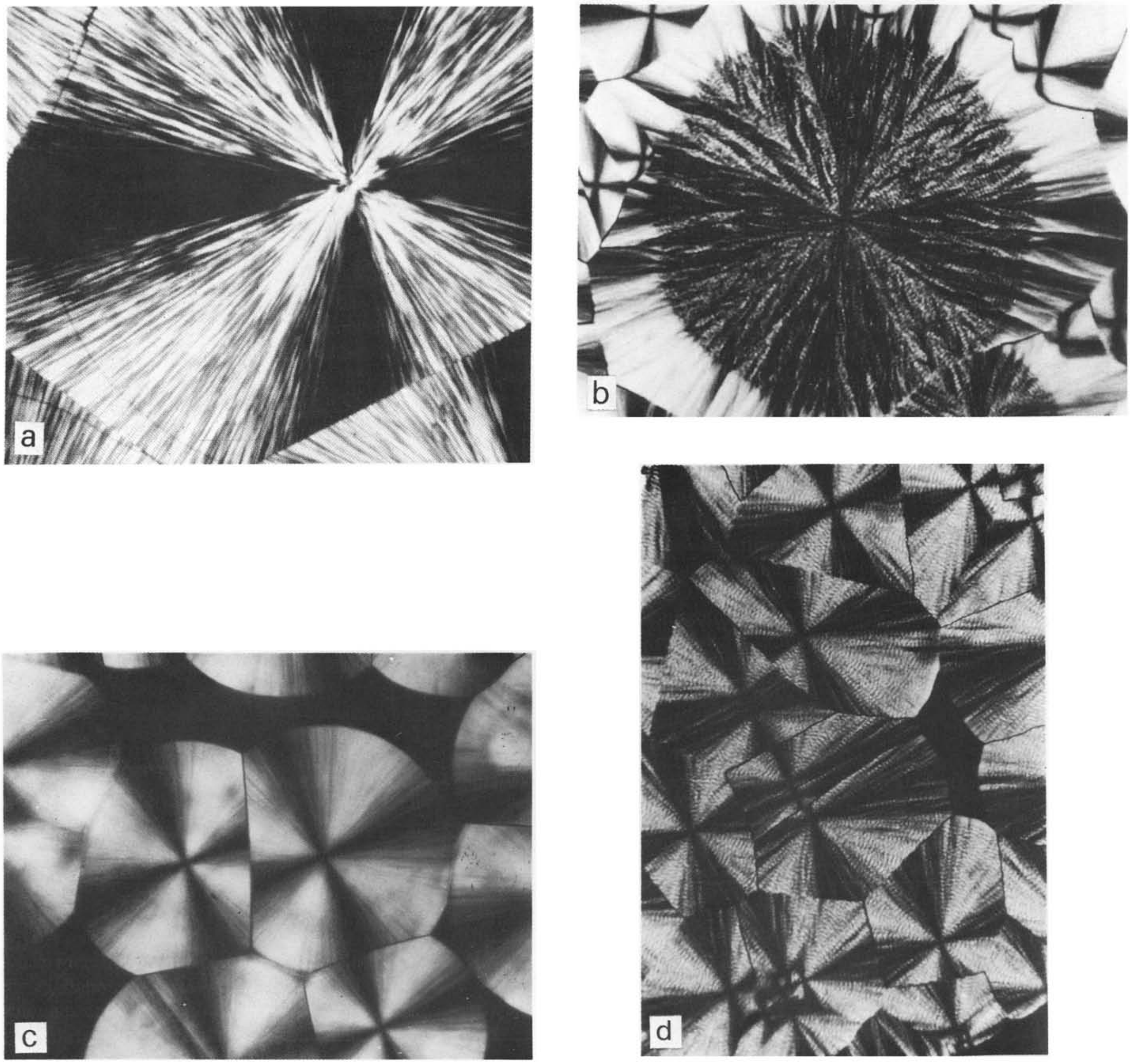

Figure 1 Spherulites of poly(TMPS) and TMPS–DMS copolymers. Samples shown are: (a) poly(TMPS) crystallized at 90°C (x380); (b) TMPS/DMS (30/70 wt %) copolymer stepwise crystallized at 62.5° and 25°C, respectively (x375); (c) TMPS/DMS (50/50 wt %) copolymer crystallized at 30°C (x400); (d) TMPS/DMS (50/50 wt %) copolymer crystallized at 60°C (x400)

men where material was limited. This approach was essential in order to apply clamping corrections which proved to be very important in this work. There are a number of instrument and sample factors that can cause significant errors in these measurements. These have been documented in detail elsewhere[17,20]. Suffice it to point out here the magnitude of these effects and to illustrate them. Generally, the total correction factor is usually greater on the low temperature modulus end of the relaxation spectrum. Typically the errors in E^* and tan δ as a function of temperature are shown in *Figure 4* for the 90/10 composition copolymer. In summary, the correction errors in E^* for the homopolymer, 90/10 and 80/20 copolymers are about 10–15% at room temperature and 45–50% at −110°C. For the 50/50, 40/60 and 30/70 copolymers the error is approximately 25–30% at room temperature and 65–70% in the −110°C region. Since poly(TMPS) is included in this copolymer series, for reference it is appropriate to illustrate (*Figure 5*) how its E', E'' and tan δ at a constant frequency of 110 Hz varies as a function temperature. Note that two major transitions are observed; one in the region of 0° and the other around 130°C for this frequency. The high temperature one is the primary amorphous (glassy) relaxation of TMPS homopolymer which has a crystallinity index around 0.6. This relaxation peak agrees closely with that found by Murray and Markovitz[21] for this particular homopolymer. Using d.s.c. and dilatometry the glass transition[22] for poly(TMPS) of high molecular weight is found to be −20°C, since these techniques normally cor-

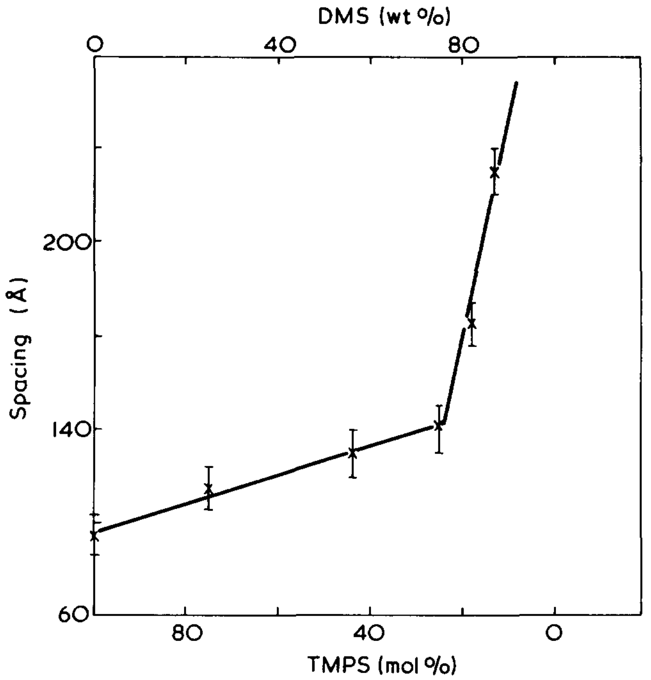

Figure 2 Small-angle X-ray spacing of typical melt formed polysiloxanes of wt % composition ratios of 100/0, 90/10, 80/20, 50/50, 40/60 and 30/70 (after McManus and Magill, unpublished)

Table 1 Melting temperature of polysiloxanes

Ratio of TMPS and DMS (wt %)	Observed* T_m (°C)	Equilibrium† T_m^* (°C)	Melting temperatures‡ (°C)
100/0	–	160	160
90/10	139	153.6	156.4
80/20	–	145.6	152.1
50/50	100	127.3	132.8
40/60	69.5	122.2	122.0
30/70	–	110.5	92.0

* After Merker and coworkers[9];

† equilibrium T_m^* values were obtained by the Hoffman–Weeks extrapolation method. Plots given in ref 20;

‡ calculated from theory with 12 monomer unit DMS sequences, by the method of Mandelkern

respond to a lower frequency of measurement (e.g. 1°C/min T_g in dilatometry).

Undoubtedly, the high temperature transition reflects the onset of melting via a rapid drop in the storage modulus, E', and a strong rise in the damping, tan δ. Measurements were terminated in all samples at the onset of melting because softening and sample distortion usually occurred in the grip holders of the Rheovibron. The d.s.c. and optical hot stage melting behaviour of TMPS is about 140°C for this sample moulded as already described. The Rheovibron proved to be insensitive to several other smaller secondary transitions detected by Murray and Markovitz[21] using a very sensitive computerized instrument which covered a frequency range from 0.002 to 500 Hz and temperature span of –190° to 100°C. In their detailed classification of the mechanical transitions the corresponding morphological features were assigned: β, primary amorphous transition; γ_1, non-crystalline relaxation; γ_2, crystalline relaxation unaffected by spherulite size; γ_3, low temperature relaxation of unknown origin; α_1, associated with non-crystalline regions increasing in intensity as the temperature is raised above 20°C; and α_2, the crystalline relaxation.

These details are introduced almost parenthetically here, to indicate the limited nature of Rheovibron measurements in pursuing detailed mechanisms. However, it is still a useful instrument, especially for comparing the dynamic mechanical behaviour of related polymers and their major 'loss peaks' which are related to molecular architecture and morphological texture, as well as to the mechanical property differences that are associated with sample fabrication[23–25]. *Figure 5* shows how E', E'' and tan δ vary with composition and temperature for poly(TMPS) at 110 Hz. Similar trends are noted at other frequencies in the 3.5–110 Hz interval with small shifts occurring towards higher temperatures at the higher frequencies. This behaviour happens to hold for all the polymers examined.

For the copolymers the trends in behaviour are illustrated in composite graphs (*Figures 6, 7* and *8*) for E', E'' and tan δ, respectively.

Note that 90/10 and 80/20 have two transitions with peaks in the loss tangent (tan δ) and loss modulus, E'', plus

Table 2 Crystallinity indices of poly(TMPS) homopolymer and poly(TMPS–DMS) copolymers

Sample	Density (g/cm^3)	Crystallinity* index (density)	Crystallinity index†(d.s.c.)
100/0	1.046	0.59	0.60
90/10	1.036	0.51	0.53
80/20	1.028	0.44	0.50
50/50	1.009	0.28	0.29
40/60	0.999	0.18	0.17
30/70	0.994	0.13	0.13

* Calculation assumes additivity of copolymer phases for the derived relation X_c (density) = $(\bar{v} - \bar{v}_{a1}) + c(\bar{v}_{a1} - \bar{v}_{a2})/(\bar{v}_c - \bar{v}_{a1}) = \bar{w}_c$, where $\bar{v}$, $\bar{v}_{a1}$, $\bar{v}_{a2}$, and $\bar{v}_c$ represent the mean specific volume of sample, amorphous TMPS, amorphous DMS and crystalline TMPS, respectively. c denotes the DMS composition in the system and w_c is the weight fraction of crystalline TMPS.

† Calculated from the relation X_c(d.s.c.) = $(\Delta H_f + 2\sigma_e/l)\Delta h_f$ where ΔH_f is the measured heat of fusion, Δh_f is the value for the perfect crystal (13 cal/g) and σ_e is the interfacial crystal surface energy

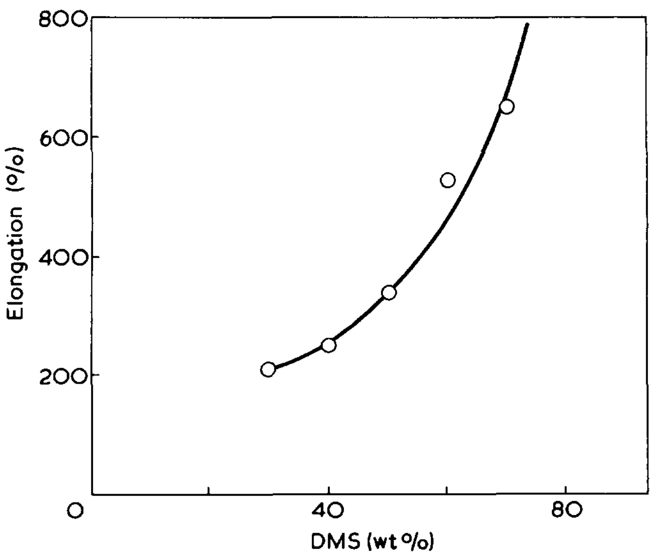

Figure 3 Elongation at 3000 p.s.i. as a function of non-crystalline DMS content (wt %) after prestressing at 3000 p.s.i.

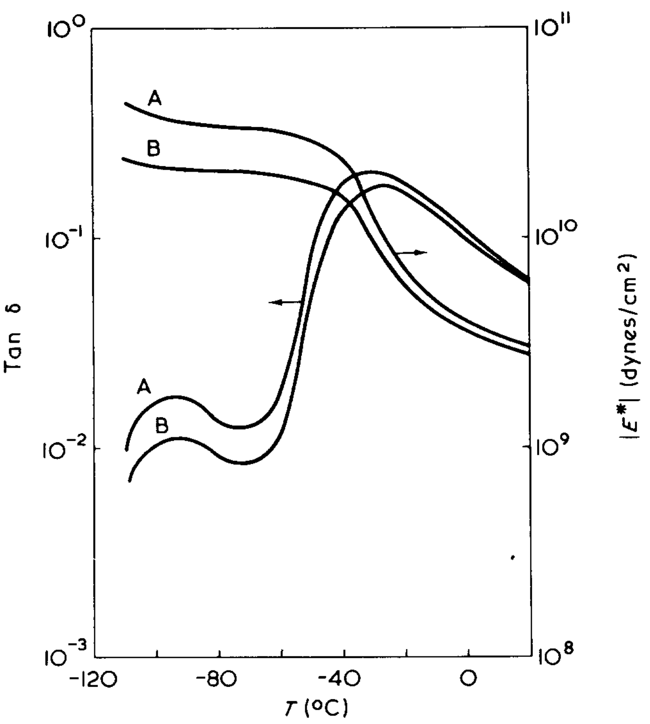

Figure 4 A, Uncorrected and B, corrected (E^*) and tan δ of 90/10 copolymer plotted against temperature at 110 Hz

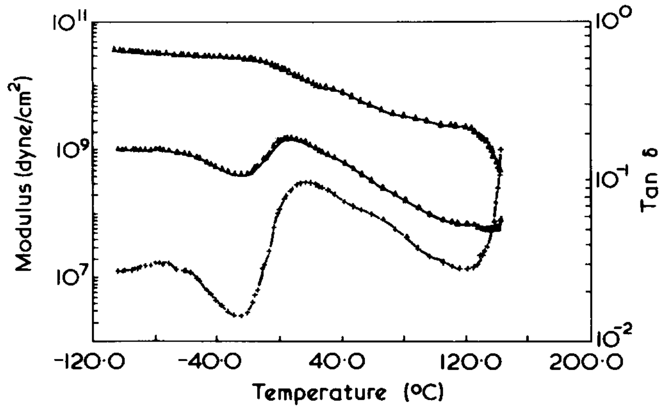

Figure 5 A, E', B, E'' and C, tan δ of the TMPS homopolymer plotted against temperature at 110 Hz

one melting transition in the 120°–130°C range. The transitions in the copolymers fall below the poly(TMPS) values. The tan δ transition in the –40° to –50°C region for 90/10 and 80/20 is associated with the relaxation of the amorphous TMPS and with randomly distributed DMS. The E'' peaks occur at –42°C for 90/10 and –48°C for 80/20 in accordance with a shift of the relaxation behaviour to lower temperatures due to shorter 'sequence' lengths of TMPS in the main chain plus the presence of more flexible DMS component. The tan δ damping for the amorphous TMPS β relaxation first increases in 90/10 relative to poly(TMPS) before it decreases again on going to the 80/20 specimen. This trend is attributed to the lower sample crystallinity which allows greater energy dissipation. The intensity of the amorphous TMPS relaxation decreases even though the crystallinity does not change very much (see *Table 2*).

In the –100° to –90°C region the observed relaxation is believed to correspond to the DMS component of the copolymer. This assignment is based on the fact that the relaxation peaks increase as the DMS content is raised. Furthermore, it is found that the position of the peak for short DMS sequences corresponds closely to the transition found[26] in oligomeric DMS. It is important to realize that the measurement of damping is the summation of the responses of all components in a given sample. The melting temperatures of 90/10 and 80/20 are relatively close (*Table 1*) since their crystallinities and lamellar thickness are comparable (see *Figure 2*).

On going to the 50/50 polymer the trend is similar except that there is only one damping peak apart from a small shoulder due to TMPS in the low frequency results. For 40/60 and 30/70 the two relaxations are combined, moving to lower temperatures. Summarizing the behaviour at constant frequency it can be concluded that:

(i) the relaxation temperature due to the amorphous TMPS component moves to lower temperatures as the DMS content increases;

(ii) the relaxation temperatures due to the DMS component first move up scale and then back down to lower temperatures as the DMS content becomes larger, causing the two relaxation peaks to merge;

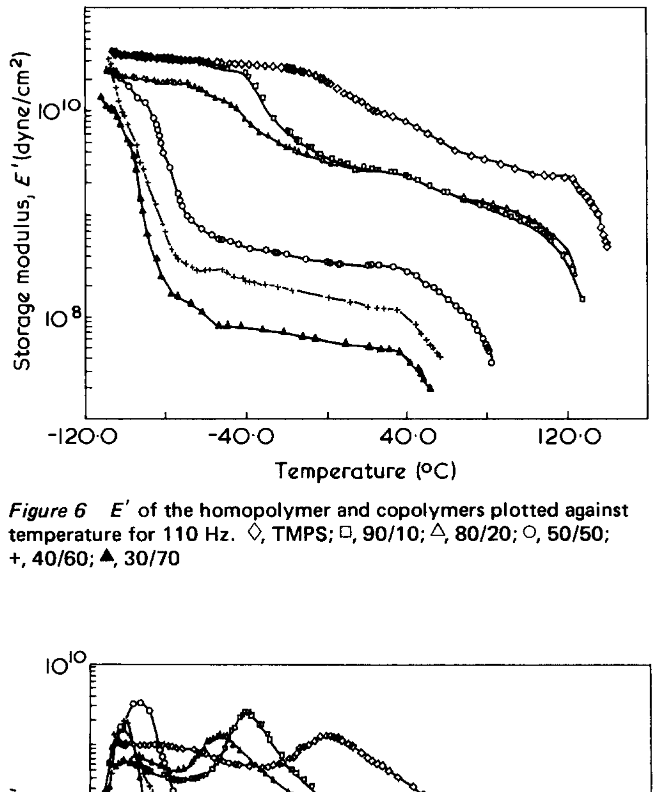

Figure 6 E' of the homopolymer and copolymers plotted against temperature for 110 Hz. ◇, TMPS; □, 90/10; △, 80/20; ○, 50/50; +, 40/60; ▲, 30/70

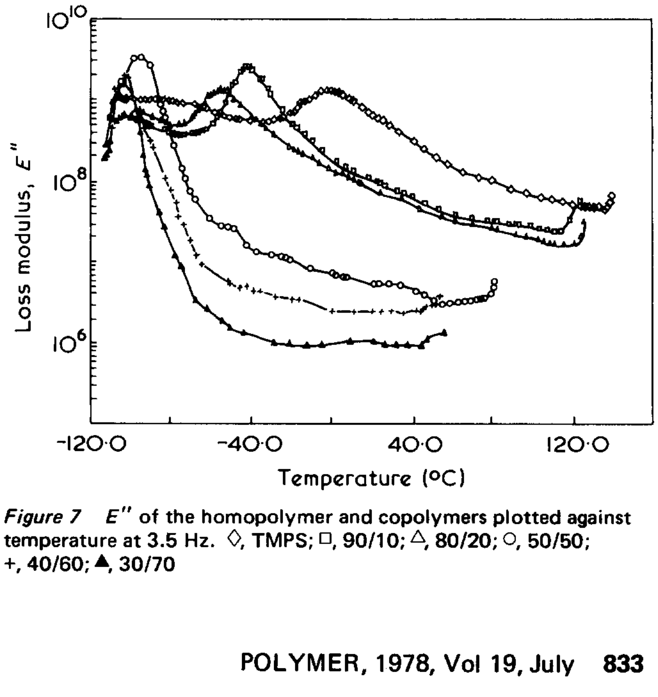

Figure 7 E'' of the homopolymer and copolymers plotted against temperature at 3.5 Hz. ◇, TMPS; □, 90/10; △, 80/20; ○, 50/50; +, 40/60; ▲, 30/70

(iii) at the higher temperature end of the spectrum, the rapid rise in the loss tangent due to the onset of melting moves to lower temperatures as the amorphous (DMS) content of the copolymer is raised.

Based on these results and the morphological results cited here and elsewhere, the models (*Figure 9*) provide a rational explanation for the observed behaviour. Selective chemical degradation work coupled with small-angle X-ray scattering indicates that all copolymers[18] have a common crystalline core of about 60 Å.

(iv) the shift in tan δ with increasing frequency between 3.5 and 110 Hz only amounts to about a 10°C movement (maximum) to higher temperatures for the TMPS β relaxation.

Storage moduli and correlation with crystallinity and composition

In the glassy state E' is about 4×10^{10} dynes/cm^2 and it gradually decreases with increasing temperature before abruptly passing into a rubbery condition about 20° above the transition region (see *Figure 5* or *6*). Beyond this temperature the storage modulus decreases until a steep drop occurs at the onset of melting. Changes with copolymer composition follow a pattern that indicates a shift from plastic to elastomeric behaviour on going from poly(TMPS) to the 30/70 copolymer. Note that E' drops from 10^{10}–10^{11} to 10^7–10^8 dynes/cm^2 in the rubbery region. The microphase morphology can account for this behaviour. As the amorphous content is increased, the copolymer texture changes from a crystalline TMPS continuous phase of lamellae alternating with a small amount of amorphous material to a situation where the amorphous phase is the major component as supported by selective chemical degradation and X-ray long period results[18]. In the plateau region typical rubberlike behaviour is observed for all copolymers. At room temperature deformation occurs affinely. At break, these materials are reported to exhibit high elongation[9] (see *Figure 3*). For sufficiently high temperatures, the effective crystalline TMPS crosslinks are melted permitting the ends of the rubbery segments to move freely as in a typical thermoplastic.

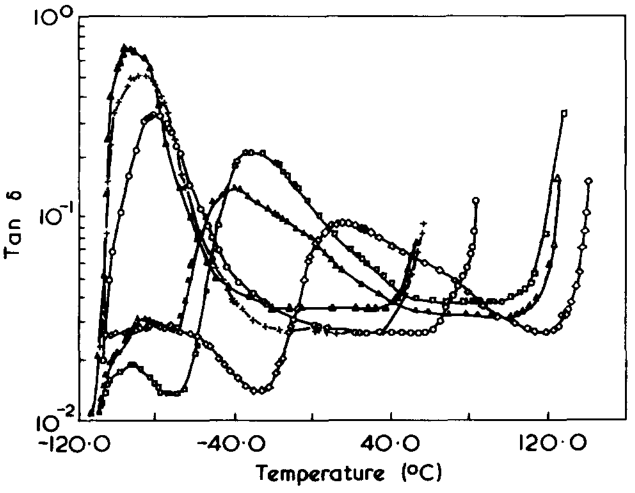

Figure 8 Tan δ of the homopolymer and copolymers plotted against temperature at 110 Hz. ◇, TMPS; □, 90/10; △, 80/20; ○, 50/50; +, 40/60; ▲, 30/70

The behaviour of the dispersed TMPS crystalline phase with a modulus far in excess of the DMS amorphous constituent can be analysed in terms of the morphology. Relevant data is found in *Table 3*. Treating the system as being comprised of filled material of modulus E, and matrix material of E_0, a modified Mooney expression[27] can be written to show the effect of particle (crystallite filler) shape on mechanical behaviour. If P is the aspect ratio of the particle and ϕ_2 is the volume fraction filler:

$$\ln E/E_0 = \left(\frac{1}{1 - 1.4\phi_2}\right) \times \{2.5\phi_2 + [32(1/P - 1)\phi_2/15\pi]$$

$$[0.628(1/P - 1)\phi_2/1/P - 0.075]\}$$

When $P = 1$ the equation describes the reinforcement of spherical or cube-like particles or crystallites. For values of P less

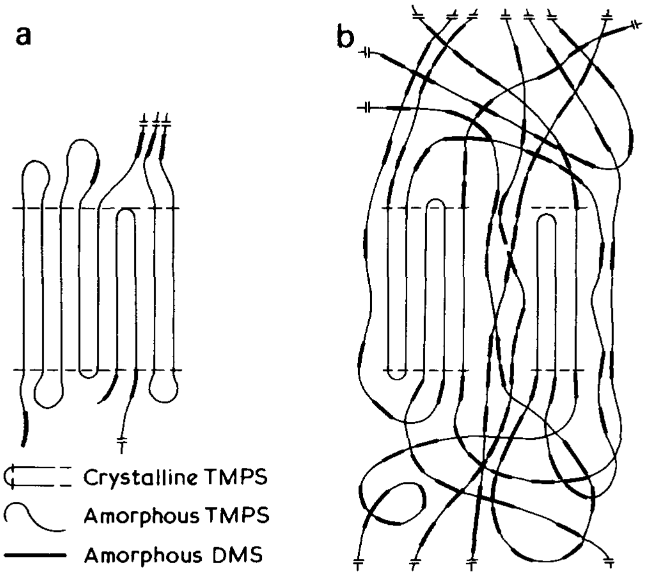

Figure 9 Morphological model of the crystalline lamellae in poly(TMPS/DMS) melt crystallized copolymers for (a) 90/10 and (b) 30/70 which cover high and low crystallinity, respectively

Table 3 Degree of crystallinity and storage Young's modulus ratio

Composition TMPS/DMS	X_c* by weight (%)	X_c by volume (%)	$\frac{\phi_2}{2.303\ (1 - 1.4\phi_2)}$	E' (dynes/cm^2)	Storage Young's modulus ratio, E'/E'_0
100/0	59	56	1.127	8.4×10^9	420
90/10	51	47	0;598	3.5×10^9	175
80/20	44	41	0.418	3.0×10^9	150
50/50	27	25	0.167	4.0×10^8	20
40/60	18	16.5	0.093	1.2×10^8	6.0
30/70	13	12	0.063	5.8×10^7	2.9

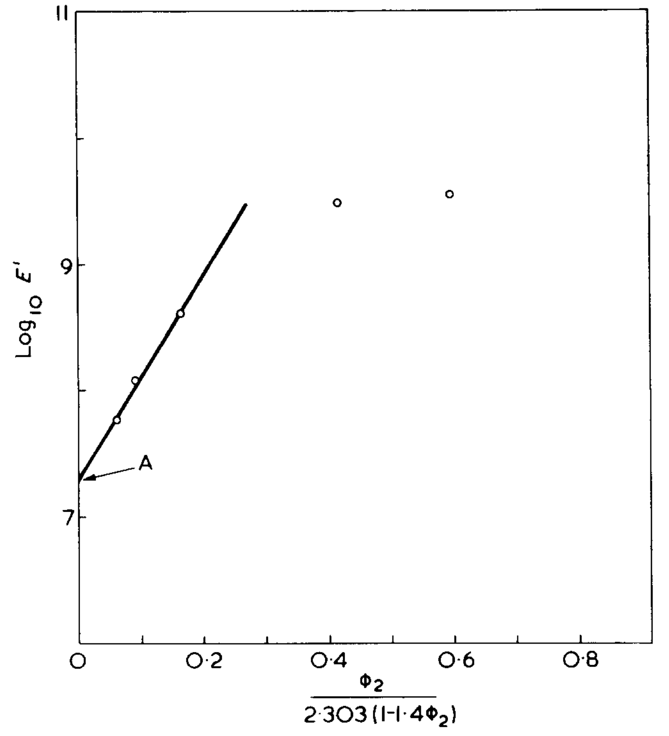

Figure 10 Modified Mooney equation showing the storage Young's modulus ratio E'/E'_0 against volume fraction of (TMPS) filler (TMPS are the crystalline regions) for various crystallite aspect ratios, P. A, $\text{Log}_{10}E'_0 = 7.3$. Slope = 8.0

than unity the equation should be valid for plate-like or disc-shaped fillers. This can be tested for by rearranging the above equation to give:

$$\log_{10}E = \log_{10}E_0 + N_p\phi_2/[2.303(1 - 1.4\phi_2)]$$

where

$$N_p = 2.5 + 32(1/P - 1)/15\pi - \left[\frac{0.628(1/P - 1)}{1/P - 0.075}\right]$$

where $\log_{10}E'$ plotted against $\phi_2/2.303(1 - 1.4\phi_2)$ should give a straight line. The more elastomeric copolymers of 30/70, 40/60, and 50/50 compositions exhibit this behaviour giving $N_p = 8.0$, corresponding to a P value of 1/10 and a log $E' = 7.3$, giving $E' = 2 \times 10^7$ dynes/cm^2 in fair agreement with the result found for unfilled poly(DMS) of 0.9×10^7 dynes/cm^3. *Table 3* contains data appropriate to this analysis. Storage Young's moduli ratio E'/E'_0 as a function of filler volume fractions are tabulated as well as plotted in *Figure 10* for different filler anisotropies. Here it is again clear that deviations from linearity for $P = 1/10$, which best fits the data, move toward even smaller P ratios as the TMPS/DMS content is increased. Based on the validity of the modified Mooney equation, values of the Young's modulus ratios E'/E'_0 are in fair agreement with experiment for 30/70, 40/60, and 50/50 copolymers. At higher filler contents ($\phi > 0.4$) these deviations are not unexpected, for example in the case of 80/20 and 90/10 copolymers, since there are changes in sample internal morphology. Such behaviour noted elsewhere, give results for highly filled polymers that are lower than predicted by the modified Mooney relationship.

CONCLUSIONS

(a) Two amorphous relaxation transitions corresponding to DMS and TMPS components were found for copolymers with TMPS contents ⩾ 80 wt %. A morphological model consisting of lamellae alternating with less ordered amorphous polymer explains these results.

(b) For polymers of lower TMPS content (⩽50 wt %) the two relaxations merge when the TMPS crystalline phase becomes dispersed in the larger rubbery DMS matrix.

(c) Typical thermoelastic elastomeric behaviour is displayed by these polysiloxane copolymers especially at the 50 wt % to the 70 wt % DMS levels where samples of relatively high clarity exist.

(d) All dynamic mechanical properties are functions of composition and crystallinity. On the rubbery plateau the storage Young's moduli of the copolymers of DMS content between 50 and 70 wt % can be accounted for by the reinforcement effect of plate-like crystalline filler in a rubbery DMS matrix with an aspect ratio $P = 1/10$.

(e) All copolymers are spherulitic with the crystallinity index decreasing from 0.53 to 0.13 approximately, as the DMS block content increases from 10 to 70% with some dependence on thermal history. This decrease is explained in terms of the number of TMPS segments with long sequence lengths, well in excess of 60 Å, the minimum lamella thickness is deduced from small-angle X-ray results on chemically degraded polymer using 48% HF solution. The small-angle period in untreated copolymers is strongly dependent upon the amorphous DMS component that is excluded from the crystalline TMPS phase.

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