Thermal and mechanical properties of tetramethyl-*p*-silphenylenesiloxane/dimethylsiloxane block copolymer

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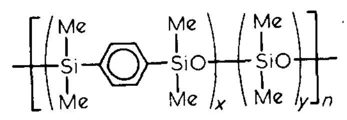
Several kinds of tetramethyl-*p*-silphenylenesiloxane/dimethylsiloxane (TMPS/DMS) block copolymers having various compositions and segment lengths were synthesized by the polycondensation of *p*-bis(dimethylhydroxysilyl)benzene and silanol-terminated DMS oligomers of different degrees of polymerization, which were 19, 43, 300, 380 and 540 DMS monomer units. The compositions ranged from TMPS/DMS wt% ratio of 100/0 to 24/76. For these copolymers, differential scanning calorimetry was carried out to determine the melting temperatures, the heat of fusion and the crystallinities. The melting temperatures and the crystallinities of the block copolymers were found to decrease as DMS contents were increased from 11 to 76 wt% and as DMS segment lengths were decreased from 540 to 19. The crystalline parts of TMPS segment would be increased according to the long TMPS sequences which were obtained from the copolymerizations by using DMS oligomers with high degrees of polymerization such as 300, 380 and 540. The stress–strain behaviour and the dynamic mechanical behaviour were also investigated for these copolymers. The tensile strength was decreased and the percentage elongation was increased with increasing DMS content and segment length. In the case of the copolymers for which the DMS contents remained constant at 26 wt%, two major transitions were observed at around −120° and −10°C for the copolymers having DMS block sizes of 300, 380 and 540. But for the copolymers having those of 19 and 43 the two transitions merged together at −50°C. The relaxations at −120°C corresponding to the glass transition of DMS component and those at −10°C are due to the amorphous TMPS phase which is separated from the DMS phase owing to the longer sequence length. The relaxation observed around −50°C is due to the shorter sequence length of TMPS in the main chain plus the presence of more flexible DMS component. It may be suggested that the long sequence length causes large domains of hard and soft phases which consist of TMPS and DMS blocks respectively.

Keywords Polysilphenylene; polysiloxane; block copolymer; thermal analysis; stress–strain; dynamic mechanical behaviour

INTRODUCTION

High molecular weight tetramethyl-*p*-silphenylenesiloxane/dimethylsiloxane (TMPS/DMS) block copolymer having the general structure:



$$\left[\left(-\mathrm{Si(Me)_2}-\mathrm{C_6H_4}-\mathrm{Si(Me)_2O}- \right)_x \left(-\mathrm{Si(Me)_2O}- \right)_y \right]_n$$

has been prepared from the copolymerization of silanol-terminated polydimethylsiloxane (poly-DMS) and *p*-bis(dimethylhydroxysilyl)benzene (TMPS monomer) by use of essentially non-equilibrating catalyst[1]. The values of *x* and *y* above can be altered by employing silanol-terminated poly-DMS of different degrees of polymerization or by changing the ratio of the starting materials, silanol-terminated poly-DMS and TMPS monomer. This block copolymer is regarded as comprising two segments; one is poly-TMPS as the hard segment and the other is poly-DMS as the soft segment. Magill *et al.* have investigated in detail the chemical degradations[2,3], crystallization kinetics[4,5], thermal properties[6], mechanical properties[7] and morphology[8–10] of these block copolymers having the various compositions. It is found that the copolymer has interesting characteristics as a thermoplastic elastomer. The thermal degradation of poly-TMPS and TMPS/DMS copolymers has also been reported in our previous paper[11].

Okui *et al.* have studied the thermal properties of TMPS homopolymer and block copolymers of TMPS/DMS with mean DMS block size of 12 monomer units over a wide range of composition[6]. The copolymer melting temperature was found to increase as the fraction of the crystalline (hard) TMPS constituent was increased, and it was estimated that the block size of soft DMS component in the copolymer consisted of 12 monomer units distributed amongst TMPS sequences of varying length. On the other hand, Li and Magill have investigated the dynamic mechanical behaviour of the same kinds of copolymers[7]. Two amorphous relaxation transitions, corresponding to DMS and TMPS phases, were found for copolymers with high TMPS content

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($\geqslant 80$ wt%) and these transitions merged together at lower TMPS compositions ($\leqslant 50$ wt%).

However, as they have only examined block copolymers containing a DMS block of 12 monomer units, the influence of DMS block size on thermal and mechanical properties of the copolymers could not be elucidated sufficiently. Here, in order to clarify the effects of TMPS and DMS segment length on the thermal and mechanical properties in further detail, the syntheses of several kinds of TMPS/DMS block copolymers were carried out by using silanol-terminated DMS oligomers of different degrees of polymerization (19, 43, 300, 380 and 540 DMS monomer units) and by changing the ratio of TMPS monomer and DMS oligomer. Furthermore, differential scanning calorimetry (d.s.c.), tensile strength and dynamic mechanical measurements were investigated for TMPS homopolymer and TMPS/DMS block copolymers.

EXPERIMENTAL

Materials

Poly-TMPS. The method of Merker and Scott[12] was used. 5 g of *p*-bis(dimethylhydroxysilyl)benzene was polymerized by refluxing in 20 ml of benzene for 15 h with 0.1 g of tetramethylguanidine di-2-ethylhexoate as catalyst, using an azeotrope trap. Poly-TMPS thus obtained was reprecipitated in excess ethanol and then dried *in vacuo* at 60°C for 24 h.

TMPS/DMS block copolymers. High molecular weight copolymers were conveniently prepared from TMPS monomer and silanol-terminated DMS oligomers with degrees of polymerization of 19, 43, 300, 380 and 540[1]. Into a flask equipped with a reflux condenser and a benzene-filled azeotrope trap was placed a mixture of TMPS monomer, DMS oligomer and few drops of tetramethylguanidine di-2-ethylhexoate in benzene. After refluxing for 15–20 h, the copolymers obtained were reprecipitated in ethanol to remove the catalyst and unreacted starting materials. The composition of TMPS and DMS units could be varied by changing the ratio of TMPS monomer and the DMS oligomers. The structures and compositions of the copolymers were confirmed by ^{1}H n.m.r. spectra. In the spectra of the copolymers the signals of the methyl and phenylene protons of TMPS unit were 0.30 and 7.40 ppm respectively, and that of methyl proton of DMS unit was 0.11 ppm. The compositions were determined by the ratio of the integrated peaks of the methyl groups of TMPS and DMS units.

Thermal analysis

Melting temperature and heat of fusion measurements were carried out by using a Shimadzu SC-20 differential scanning calorimeter at a heating rate of 5°C min^{-1} in a He stream. Potassium nitrate and indium of high purity were used as calibration standards. Before heat of fusion measurements, all samples were melted at 160°C for 5 min and cooled constantly at a cooling rate of 5°C min^{-1} towards room temperature.

The percentage crystallinities of all the samples were calculated according to:

$$\text{crystallinity}\,(\%) = (\Delta H_f/\Delta H_f^*) \times 100 \qquad (1)$$

where ΔH_f denotes the sample's heat of fusion and ΔH_f^* the heat of fusion for perfectly crystalline poly-TMPS (13.0 cal g^{-1} [5]).

Stress–strain measurement

Films of the copolymers were made by casting from 10 wt% of chloroform solutions in thickness from 0.2 to 0.3 mm. The film samples were dried *in vacuo* for 24 h at room temperature. These samples were then cut into rectangular strips of length 10 mm and width 2 mm. Load–elongation curves were obtained with the following settings on a Rheovibron DDV-1: gauge length, 10 mm; crosshead speed, 10 mm min^{-1}; full-scale load, 2 kg.

Dynamic mechanical measurement

Dynamic mechanical measurements were made by using Iwamoto Instruments' dynamic viscoelastometer with a low-temperature chamber for the temperature range from −150°C to ~100°C. Experiments were conducted over all available frequency ranges, 11, 35, 70 and 100 Hz.

For the dynamic mechanical studies, the samples were carefully melt-moulded at 200°C for 5 min in a hot press in thickness from 0.1 to 0.4 mm. All specimens were quenched to room temperature and then cut into rectangular strips varying in length about 50 mm and width 5 mm to provide a range of dimensions suitable for modulus of elasticity measurements. The measurements were made on materials which were cooled in the dynamic viscoelastometer to approximately −150°C and subsequently heated slowly during measurements to about 100°C.

RESULTS AND DISCUSSION

Results of copolymerization

The observed compositions, intrinsic viscosity values and melting temperature of synthesized TMPS homopolymer and TMPS/DMS block copolymers are summarized in *Table 1*. The compositions of the block copolymers agreed with the predicted values from the mole ratio of TMPS monomer and DMS oligomers and from the degrees of polymerization of DMS oligomer. The compositions ranged from TMPS/DMS mole per cent ratio of 75/25 to 16/84 for the copolymers prepared from silanol-terminated DMS oligomers with degrees of polymerization $\bar{y}$ of 19 and 43, and from 75/25 to 10/90 for the copolymers prepared from DMS oligomers with $\bar{y} = 300$, 380 and 540. The average segment length of TMPS segment $\bar{x}$ of the copolymers was calculated from the molecular weights of DMS oligomers and the mole fractions of TMPS/DMS compositions based upon the equation $\bar{x} = \bar{y} \times a/b$, wher a and b denote the TMPS and DMS mole fractions, respectively. The average segment lengths ranged from 4 for copolymer I-4 to 1620 for copolymer V-1, and would be important factors in the physical properties of the copolymers as described below. From the intrinsic viscosity of poly-TMPS, 3.34 dl g^{-1}, the molecular weight of poly-TMPS was calculated to be 9.24×10^5 by the Mark–Houwink relationship[12] $[\eta] = 1.12 \times 10^{-5} M_w^{0.75}$. For the copolymers, the intrinsic viscosity ranged from 0.66 dl g^{-1} for copolymer II-3 to 2.33 dl g^{-1} for copolymer I-2. The postulated molecular weights from these values would be more than 10^5.

Table 1 Characterizations of synthesized poly-TMPS and TMPS/DMS copolymers

Sample no.	TMPS/DMS (mol%)	(wt%)	$\bar{y}^a$	$\bar{x}^b$	$[\eta]^c$ (dl g^{-1})	$T_m{}^d$ (°C)
poly-TMPS	100/0	100/0	–	–	3.34	140
I-1	75/25	89/11	19	57	1.90	126
I-2	50/50	74/26	19	19	2.33	107
I-3	25/75	48/52	19	6	2.01	83
I-4	16/84	36/64	19	4	2.20	71
II-1	75/25	89/11	43	129	0.88	135
II-2	50/50	74/26	43	43	1.04	114
II-3	25/75	48/52	43	14	0.66	94
II-4	16/84	36/64	43	9	0.67	85
III-1	75/25	89/11	300	900	1.10	139
III-2	50/50	74/26	300	300	1.14	138
III-3	25/75	48/52	300	100	0.68	131
III-4	16/84	36/64	300	60	0.87	122
III-5	13/87	29/71	300	43	0.96	117
III-6	10/90	24/76	300	33	0.84	112
IV-1	75/25	89/11	380	1140	1.11	139
IV-2	50/50	74/26	380	380	0.88	138
IV-3	25/75	48/52	380	127	1.69	136
IV-4	16/84	36/64	380	76	1.07	128
IV-5	13/87	29/71	380	54	0.90	119
IV-6	10/90	24/76	380	42	1.03	114
V-1	75/25	89/11	540	1620	1.00	140
V-2	50/50	74/26	540	540	1.33	139
V-3	25/75	48/52	540	180	0.75	138
V-4	16/84	36/64	540	108	0.72	133
V-5	13/87	29/71	540	77	0.98	127
V-6	10/90	24/76	540	60	0.88	120

[a] The average degree of polymerization of DMS oligomer used
[b] The average degree of polymerization of TMPS sequences
[c] Measured in toluene at 25°C
[d] Observed by d.s.c. curves

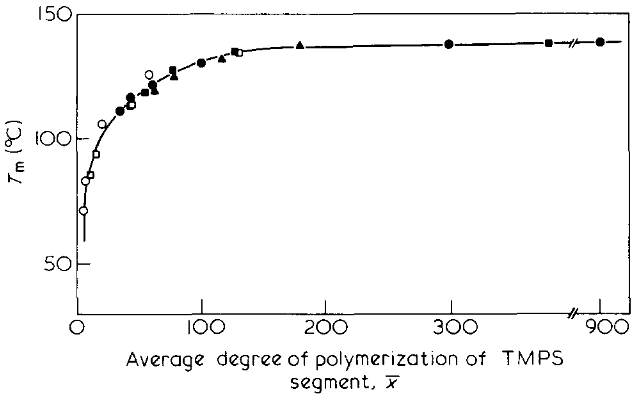

Figure 1 Effect of average degree of polymerization of TMPS segment on the melting temperature of TMPS/DMS block copolymer: ○, $\bar{y}$ = 19; □, $\bar{y}$ = 43; ●, $\bar{y}$ = 300; ■, $\bar{y}$ = 380; ▲, $\bar{y}$ = 540

Thermal properties

D.s.c. measurements could elucidate the dependence of compositions and each segment length on the thermal properties of these copolymers. As shown in *Table 1*, the melting temperature T_m of poly-TMPS was 140°C and T_m of block copolymers, of which DMS average segment lengths $\bar{y}$ were 19 and 43, was lowered remarkably as DMS contents were increased. Especially for copolymers I-3, I-4, II-3 and II-4 the melting temperatures were lower than 100°C because their TMPS average segment length $\bar{x}$ calculated was very short, ranging from 4 to 14. On the other hand, the melting temperatures of copolymers prepared from DMS oligomers of $\bar{y} = 300$, 380 and 540 are considerably higher than those of $\bar{y} = 19$ and 43. Furthermore, for the copolymers of which the compositions are the same, it can be said that the melting temperatures become higher as the DMS segment lengths are increased from 19 to 540. In *Figure 1*, the melting temperatures of all the copolymers synthesized were plotted against the calculated average degrees of polymerization of TMPS segment $\bar{x}$. As can be seen in *Figure 1*, it is obvious that the copolymer melting temperatures are influenced by the average degrees of polymerization of TMPS segment because all the plots fall on one curve. These effects are undoubtedly due to the increase in the thickness of chain-folded lamellae, which occurs as the segment lengths of TMPS crystalline units are increased. It is concluded that higher degrees of polymerization of the silanol-terminated DMS oligomers yield not only longer DMS segment but also TMPS segments in the resulting block copolymers. In other words, while $\bar{x}/\bar{y}$ remains constant, as $\bar{y}$ increases $\bar{x}$ must increase to satisfy the constancy of $\bar{x}/\bar{y}$ and repeating sequences of TMPS in the copolymer chain each become longer.

Heat of fusion measurements by d.s.c. were carried out to determine the percentage crystallinities of TMPS/DMS copolymers of which TMPS mole contents were over 50 mol%. The results are shown in *Table 2*. The crystallinities also depend upon TMPS content and segment length. That is to say, the crystallinities of samples I-1, IV-1 and V-1, of which TMPS contents are

Table 2 Results of heat of fusion and crystallinity of TMPS/DMS block copolymers measured by d.s.c.

Sample no.	TMPS/DMS (mol%)	ΔH_f (cal g^{-1})	Crystallinity (%)
I-1	75/25	5.06	38.9
I-2	50/50	4.23	32.5
IV-1	75/25	6.23	47.9
IV-2	50/50	4.99	38.4
V-1	75/25	6.64	51.1
V-2	50/50	5.58	42.9

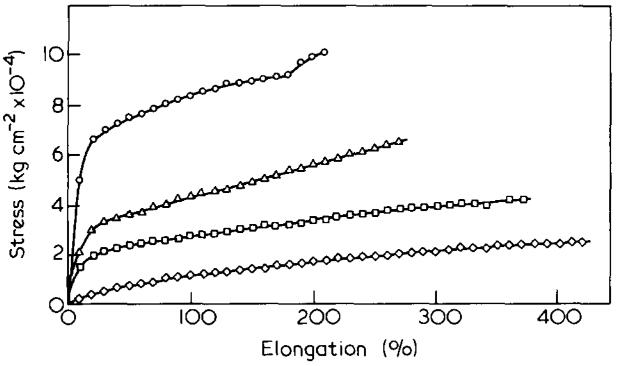

Figure 2 **Effects of compositions on the stress–strain behaviour of TMPS/DMS block copolymers IV-2 (○), IV-3 (△), IV-4 (□) and IV-5 (◇)**

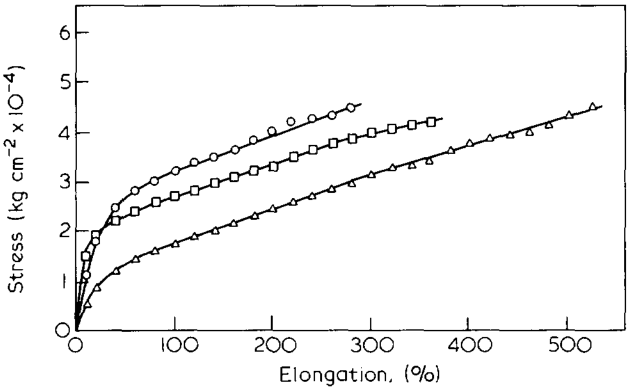

Figure 3 **Effects of DMS block lengths on the stress–strain behaviour of TMPS/DMS block copolymers II-4 (○), IV-4 (□) and V-4 (△)**

75 wt%, are higher than those of samples I-2, IV-2 and V-2, of which TMPS contents are 50 mol% in each case. In the comparisons between the samples of which TMPS contents are constant, the copolymers of $\bar{y}=380$ and 540 contains higher crystallinity than those of $\bar{y}=19$ within about 10% difference. It can be concluded that the proportion of crystalline part of TMPS component tends to be increased with increasing TMPS segment length.

Stress–strain behaviour

In *Figures 2* and *3* are shown the stress–strain behaviour obtained on elongation of the sample specimens directly to rupture. The sample numbers in the figures correspond to those used in *Table 1*. *Figure 2* indicates the effects of DMS contents of the copolymers of $\bar{y}=380$ on the stress–strain curves. As DMS content increases, the tensile strength is decreased but the elongation is increased. This tendency is in good agreement with the result of Merker *et al.*[1] for copolymers having DMS block size of 18. These effects would be attributed to the fact that the proportion of microcrystalline region is decreased and the copolymers are getting soft with increasing amount of flexible DMS component.

In comparison of the samples having the same DMS content, 64 wt%, tensile strengths are decreased and elongations are increased with increasing DMS segment length from 43 to 540 as shown in *Figure 3*. For this result, it may be suggested that the long sequence length causes large domains of hard and soft phases which consist of TMPS and DMS blocks respectively, because the large soft phase seems to increase the copolymers' elongation and decrease the tensile strength of rupture. Kawai *et al.*[13] carried out stress–strain measurements on styrene/isoprene rubbers having various compositions in connection with microdomain structures, which had been observed in electron micrographs. They suggested that the large domain of the isoprene phase, which was observed as cylindrical and lamellar domains in the electron micrographs, made the films' elongation longer and weakened the tensile strength in comparison with spherical domains of isoprene soft phase.

Dynamic mechanical properties

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

$$E^* = E' + iE'' \tag{2}$$

with 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 polymers. For the poly-TMPS and TMPS/DMS block copolymers synthesized, the dynamic mechanical measurements were carried out in order to clarify the effects of compositions and segment length of the copolymers upon the storage modulus, the loss modulus and the loss factor as a function of temperature.

E', E'' and $\tan\delta$ of poly-TMPS as a function of temperature were measured at various frequencies of 11, 35, 70 and 100 Hz, and were very similar to those obtained by Li and Magill[7]. Two transitions were observed in the region of 0°C and over 100°C for every curve at each of the frequencies. The former relaxation peaks are due to the glass transition of the amorphous phase of poly-TMPS, because T_g of poly-TMPS is found to be -20°C[6]. The high-temperature relaxations reflect the onset of melting via a rapid drop in the storage modulus, and a strong damping of $\tan\delta$. All measurements for each of the copolymers were made at a constant frequency of 11 Hz, since the relaxation peaks of E'' and $\tan\delta$ were the most clear at 11 Hz in comparison with others.

Figure 4 shows how E' and E'' vary with composition and temperature for the copolymers I-2, I-3 and I-4 of which DMS average segment lengths are constant, $\bar{y}=19$, and DMS contents are 26, 52 and 64 wt% respectively. The E'' transitions occurred at -50°C for I-2, -100°C for I-3 and -120°C for I-4 in accordance with a shift to lower temperature as DMS contents were increased. These relaxation peaks are considered to be due to shorter sequence length of TMPS in the main chain plus the presence of more flexible DMS component. The relaxations due to the melting of the copolymers also occurred at 100°C for I-2, 60°C for I-3 and 40°C for I-4. The depression of the relaxation temperature of melting with increasing DMS content is correlated with the drop of melting temperature. These behaviours are analogous to those of copolymers having DMS block size of 18 units obtained by Li and Magill[7]. They concluded that the relaxation temperature due to the amorphous TMPS component moved to lower temperature as the DMS content increased and the relaxation due to the DMS component first moved up the scale and then back down to lower temperature as DMS content became larger ($\geqslant$50 wt%) because of the superposition of the two relaxation peaks.

For copolymers IV-2, IV-3 and IV-4 of which DMS average segment lengths were 380 and DMS contents were the same as I-2, I-3 and I-4 respectively, the trends in behaviour were found to be different from those of copolymers I-2, I-3 and I-4. As can be seen in *Figure 5*, two major transitions were observed to be separated at around −50°C in every sample. In the lowest temperature region at −120°C, the observed relaxations are believed to correspond to the DMS long sequence of the copolymers because T_g of DMS homopolymer is known

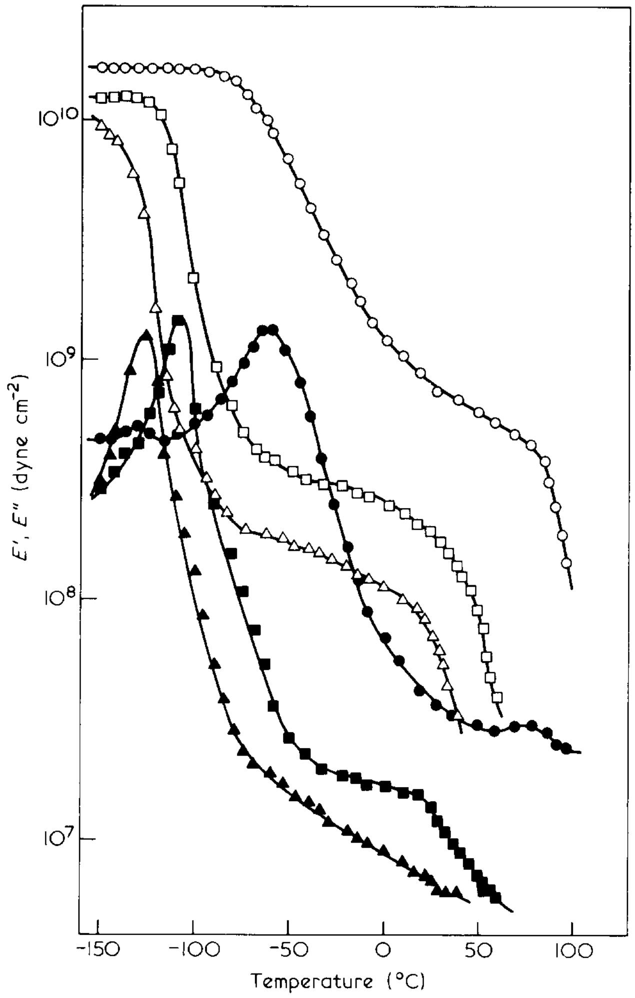

Figure 4 E′ and E″ of copolymers I-2 (E′, ○; E″, ●), I-3 (E′, □; E″, ■) and I-4 (E′, △; E″, ▲) plotted against temperature at 11 Hz

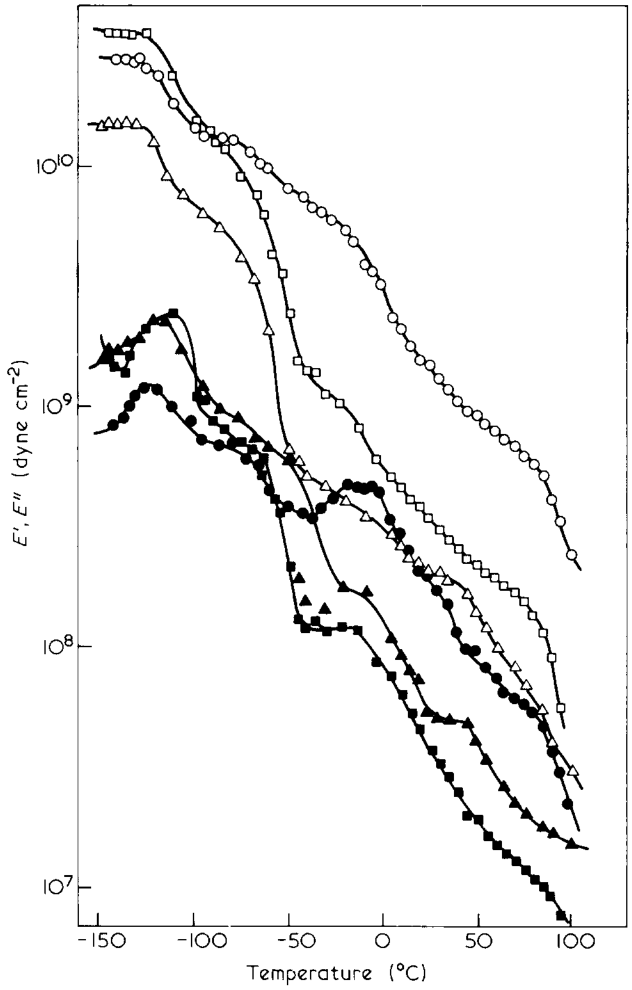

Figure 5 E′ and E″ of copolymers IV-2 (E′, ○; E″, ●), IV-3 (E′, □; E″, ■) and IV-4 (E′, △; E″, ▲) plotted against temperature at 11 Hz

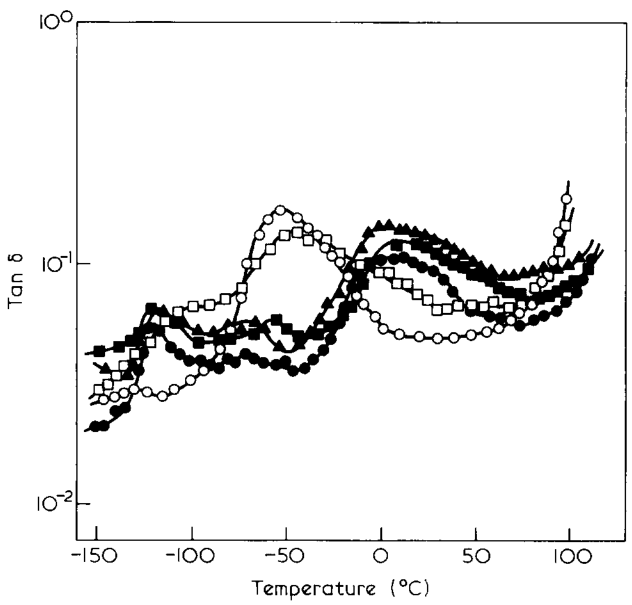

Figure 6 Tan δ of copolymers I-2 (○), II-2 (□), III-2 (▲), IV-2 (◐) and V-2 (■) plotted against temperature at 11 Hz

to be −120°C. The highest relaxation temperature may be due to the amorphous TMPS phase which can be separated from the DMS phase because of the long sequence length of TMPS and DMS blocks. The small transitions at −50°C are considered to be due to the mixture of the shorter TMPS block and DMS block as observed in copolymer I-2. The relaxation temperatures caused by melting were almost constant at 100°C for these copolymers.

The differences of the relaxation peaks between samples having short DMS segment ($\leqslant$43 units) and those having long DMS segment ($\geqslant$300 units) could be revealed by the comparison of $\tan\delta$ curves among the copolymers, of which DMS contents are constant at 25 wt% (*Figure 6*). In *Figure 6*, the two transition peaks at −120°C and −10°C appear clearly for copolymers III-2, IV-2 and V-2 of which DMS block sizes are 300, 380 and 540 respectively. But for copolymers I-2 and II-2, of which DMS block sizes are 19 and 43 respectively, the two transitions merge together at −50°C.

The separation of TMPS and DMS glass transitions for the copolymers having large DMS block size ($\geqslant$300 units) is thought to be caused by the presence of long segments of each component. Consequently, the long sequence of TMPS and DMS blocks causes the large domains of hard and soft phases in the copolymer films.

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REFERENCES

1 Merker, R. L., Scott, M. J. and Harberland, G. G. *J. Polym. Sci. A* 1964, **2**, 31
2 Okui, N. and Magill, J. H. *Polymer* 1977, **18**, 845
3 Okui, N., Magill, J. H. and Gardner, K. H. *J. Appl. Phys.* 1977, **48**, 4116
4 Li, H. M. and Magill, J. H. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1059
5 Okui, N. and Magill, J. H. *Polymer* 1977, **18**, 1152
6 Okui, N., Li, H. M. and Magill, J. H. *Polymer* 1978, **19**, 411
7 Li, H. M. and Magill, J. H. *Polymer* 1978, **19**, 829
8 Kojima, M. and Magill, J. H. *J. Macromol. Sci.–Phys. B* 1974, **10**, 419
9 Kojima, M., Magill, J. H. and Merker, R. L. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 317
10 Kojima, M. and Magill, J. H. *J. Macromol. Sci.–Phys. B* 1978, **15**, 63
11 Ikeda, M., Nakamura, T., Nagase, Y., Ikeda, K. and Sekine, Y. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 2595
12 Merker, R. L. and Scott, M. J. *J. Polym. Sci. A* 1964, **2**, 15
13 Kawai, H., Hashimoto, T., Miyoshi, K., Uno, H. and Fujimura, M. *J. Polym. Sci.–Phys. B* 1980. **17**, 427