Tetramethyl-*p*-silphenylenesiloxane/dimethylsiloxane block and graft copolymers as selective permeable membranes

Masato Ichikawa, Susumu Katagiri, Takao Yamanaka, Manshi Ohyanagi, Koji Ikeda and Yoshiro Sekine*
Department of Polymer Chemistry, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 160, Japan
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We synthesized tetramethyl-*p*-silphenylenesiloxane (TMPS)/dimethylsiloxane (DMS) copolymers as selective permeable membranes for oxygen and nitrogen, and investigated the relation between their permeability and selectivity and microstructure after preparing some membranes by a solvent casting method. First, we examined the permeability of TMPS/DMS block and graft copolymers (DMS segment length 100) using measurements of dynamic viscoelasticity, crystallinity, melting temperature (T_m) and glass transition temperature (T_g). These measurements showed the permeability to increase by mixing the TMPS and DMS phases, thus disturbing the fold crystallinity of the TMPS phase. Accordingly we investigated the permeability of block copolymers having shorter DMS segment lengths (DMS segment length 40,20). The membranes with mixed microstructures with shorter DMS segment lengths were successfully synthesized and showed excellent permeability. The selectivity also increased by shortening the DMS segment length, the selectivity being affected considerably by the TMPS phase. In particular, one of the copolymers containing 19% DMS (segment length 20) showed high permeability ($P_{O_2} = 2.3 \times 10^{-8}$ cm^3 cm/s cm^2 cmHg) and high selectivity ($\alpha = 3.0$).

(**Keywords: dimethylsiloxane; tetramethyl-*p*-silphenylenesiloxane; selective permeable membrane; block and graft copolymers; segment length; mixed microstructure**)

INTRODUCTION

Recently, gas separation, using polymer membranes, has been given attention in connection with energy conservation. Oxygen concentration from the air and hydrogen separation from coal gas are well known. A good material for selective permeable membranes must have high permeability, high selectivity and good film formation properties. Poly(dimethylsiloxane) (PDMS) has the highest permeability in synthetic polymers produced industrially, but has low selectivity and mechanical strength. To avoid this problem, copolymers of PDMS with other polymers having high selectivity and good film formation properties are required. For instance, a copolymer membrane with poly(vinyl phenol) has been synthesized by Asakawa *et al.*[1], and one based on polycarbonate by Ward *et al.*[2] The examined the permeability of these copolymers in detail. Many reports are available on permeability and selectivity, but few on the relation between those and microstructure, which depends on segment length effects. A study was thus carried out on various block and graft copolymers of DMS and tetramethyl-*p*-silphenylenesiloxane (TMPS), which has good film formation properties, and we investigated the effects of its microstructure on segment length. The microstructure was also examined with regard to dynamic viscoelasticity, crystallinity, melting temperature (T_m) and glass transition temperature (T_g), as well as the relationship between permeability and selectivity. It became clear that, for a membrane consisting of TMPS and DMS phases, both permeability and selectivity increase. The present report deals with this particular phenomenon.

EXPERIMENTAL

Materials

PTMPS. The method of Merker and Scott[3] involving *p*-bis(dimethylhydroxyl)benzene along with a catalyst of tetramethylguanidine di-2-ethylhexoate (0.025 g; 0.5 wt %) was used. Polymerization was carried out using an azeotrope trap filled with benzene to remove the water produced. The PTMPS obtained was reprecipitated in methanol to eliminate TMPS monomer not reacted during the catalysis, and dried *in vacuo* at 60°C for 24 h.

TMPS/DMS block copolymers. The method of Merker and Scott[4] was used to obtain three kinds of block copolymers whose DMS segment lengths were 100, 40 and 20. *Scheme I* was followed to obtain block copolymer (**4**), the DMS segment length of which was 100. Some vinyl groups were introduced so as to graft DMS, by the

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* To whom correspondence should be addressed.

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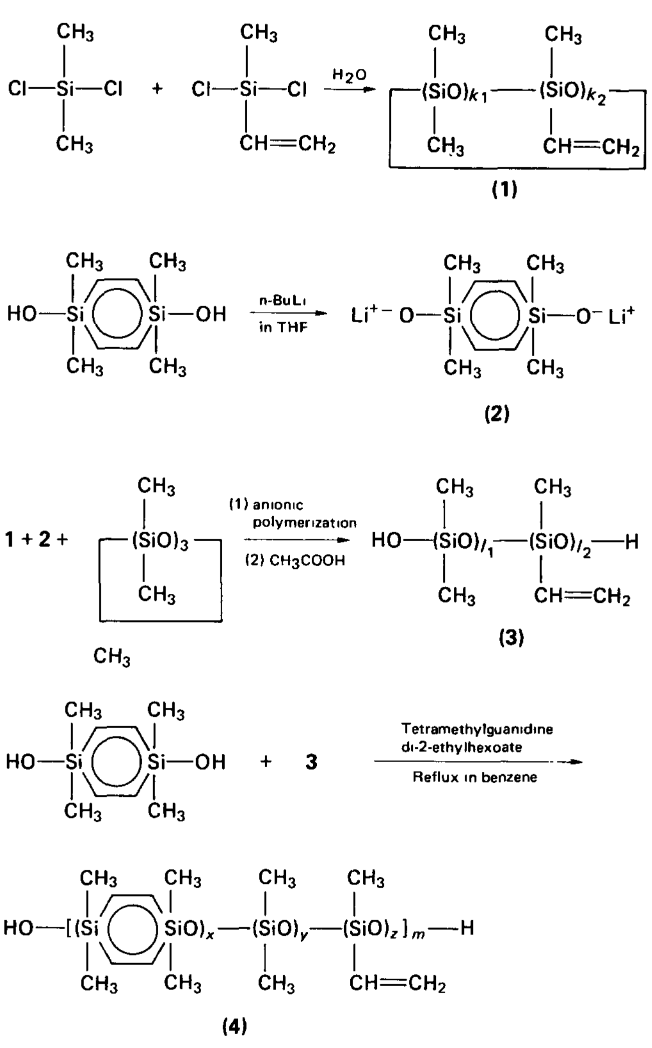
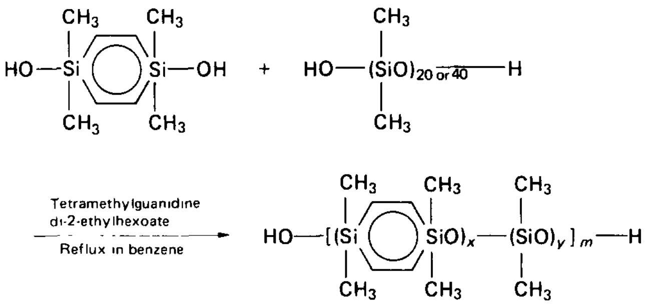
Scheme I



following procedure. First, the newly distilled dimethyldichlorosilane (121 ml; 1.0 mol) and methylvinyldichlorosilane (provided by Chisso Co.) (64 ml; 0.5 mol) were dissolved in diethyl ether (185 ml), followed by the addition of water (185 ml) at 0–5°C. For this more than 1 h was required. After extraction by diethyl ether, the solution was evaporated. The cyclic siloxane (**1**) was extracted at 100–120°C and 17 mmHg, and was then used. Secondly, under nitrogen atmosphere, *p*-bis(dimethylhydroxysilylbenzene) (provided by Chisso Co.) was dissolved in dried THF (100 ml), followed by addition of n-hexane solution of n-butyllithium, and was converted into an anion (**2**). To the solution **1** (20 ml) were added **2** and an adequate amount of hexamethylcyclotrisiloxane (D_3). The system was stirred at room temperature for 18 h. To stop the polymerization, excess acetic acid was added. The salt produced was filtered off and the solution evaporated. Thus the DMS oligomer (**3**), whose segment length was 100, contained a few vinyl groups and the ends were silanol. The degree of polymerization of **3** was controlled by the amount of D_3 added. Oligomer **3** was dehydrated and condensed as in the scheme for PTMPS. The obtained DMS block copolymer (segment length 100) was reprecipitated with benzene–methanol and dried *in vacuo* for 24 h. The block copolymers, whose DMS segment lengths were 40 and 20, are shown in *Scheme II*. They were obtained with commercially available DMS oligomers whose segment lengths were 40 and 20, dehydrated and condensed with *p*-bis(dimethylhydroxysilylbenzene).

TMPS/DMS graft copolymers. TMPS/DMS graft copolymers were obtained according to *Scheme III*. First DMS oligomers having monofunctional hydrosilyl terminal (**5**) were synthesized. Under nitrogen atmosphere, trimethylsilanol (1.0 g) was dissolved in dried THF (30 ml), and to this solution n-hexane solution of n-butyllithium and an adequate amount of D_3 were added. The reaction mixture was stirred for 18 h at room temperature. To this solution, excess dimethylchlorosilane was added to stop the polymerization reaction and to introduce the terminal hydrosilyl group. The solution was evaporated and dried *in vacuo* at 60°C. for 24 h. The degree of polymerization of the product (**5**) was controlled by the amount of D_3 added. Next, **5** (2.0 g) and equimolar **4** and ethanol solution of chloroplatinic acid (15 μl; 0.218 mol l^{-1}) in toluene (20 ml) was stirred at

Scheme II



Scheme III

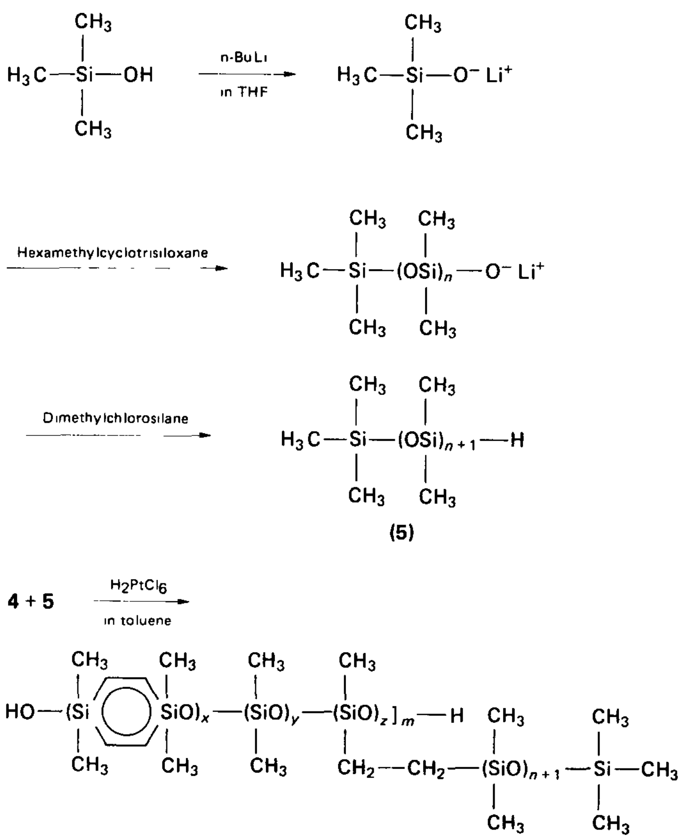


Table 1 Characterization of PTMPS and TMPS/DMS copolymers

Sample no.	$\bar{x}^a$	$\bar{y}+\bar{z}^b$	$\bar{n}^c$	DMS content (wt%)	$\bar{M}_n{}^d$ ($\times 10^{-4}$)	$\bar{M}_w{}^d$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$	Yield^e (%)
PTMPS	–	–	–	0	22.1	29.2	1.32	–
Ia	144	100	–	20	11.0	19.0	1.72	–
Ib	104	100	–	26	22.2	29.3	1.33	–
Ic	47	100	–	43	13.4	22.2	1.65	–
Id	37	100	–	49	11.3	20.7	1.83	–
Ib(1)	104	100	30	37	19.2	26.8	1.40	58
Ib(2)	104	100	74	56	25.0	32.0	1.28	48
Ic(1)	47	100	30	45	13.0	21.0	1 62	15
Ic(2)	47	100	74	79	14.5	24.5	1.69	76
Id(1)	37	100	30	64	13.5	20.5	1.51	67

[a] Average segment length of TMPS
[b] Average segment length of DMS
[c] Average degree of polymerization of the DMS oligomer (**5**)
[d] Determined by g.p.c. measurements
[e] Determined by ^{1}H n.m.r. spectra

70–80°C for three days. Graft copolymers obtained were reprecipitated with benzene–methanol and dried *in vacuo* for 24 h.

Characterizations

The composition ratio of TMPS/DMS and average TMPS segment length were determined by ^{1}H n.m.r. and recorded with Hitachi Perkin–Elmer 60 MHz n.m.r. using CCl_4 as the solvent. The methyl group proton signal (δ 0.1 ppm) could be distinguished from that of methyl group and phenylene group proton of TMPS (δ 0.3 and 7.4 ppm). The molecular weight and degree of dispersion were determined with a Waters Associates gel permeation chromatograph. THF was used as the solvent and standard polystyrenes for calibrating molecular weight.

Gas permeability measurements

The membranes for gas permeability measurements were prepared as follows. Chloroform solvent containing 10 wt% of the polymer was cast on a clear glass surface and the solvent was evaporated for 24 h. The polymer was then dried *in vacuo* and cut into a circular piece 39 mm in diameter. The thickness of the membrane was about 200 μm. The apparatus was Rikaseiki Kogyo gas permeability equipment K-315-N. The permeability coefficients of O_2 and N_2 (P_{O_2}, P_{N_2}) were measured under vacuum at 25°C. The permeability ratio (P_{O_2}/P_{N_2}) was used as the best value for determining the separation factor (α).

Dynamic viscoelasticity measurements

Dynamic viscoelasticity was measured by using an Iwamoto Instruments dynamic voscoelastometer. The temperature ranged from -150°C to the melting temperature of the polymer. The frequency was always 11 Hz. The samples were cast from the 10% chloroform solution of each polymer and measured $5.0 \times 0.5 \times 0.02$ cm.

D.s.c. measurements

T_m, T_g and heat of fusion were measured using a Shimazu SC-20 differential scanning calorimeter at a heating rate of 5°C min^{-1} in a stream of helium. Potassium nitrate and indium of high purity were used as calibration standards. The crystallinity was calculated by the following equation:

$$\text{crystallinity (\%)} = (\Delta H_f/\Delta H_f^*) \times (1/\text{mol fraction of TMPS}) \times 100$$

where ΔH_f = heat of fusion, ΔH_f^* = heat of fusion of complete crystallized PTMPS (13.0 cal g^{-1} (ref. 5)).

RESULTS AND DISCUSSION

Effect of microstructure differences of block and graft copolymers on permeability

TMPS/DMS copolymers consist of hard (TMPS) and soft (DMS) segments. It was presumed that gas permeation behaviour of copolymers would be affected not only by the composition ratio of both segments but also by the microdomain structure. Therefore some block and graft copolymers whose composition ratio differed were synthesized and the relation between microstructure and permeability were investigated in detail.

Segment length, DMS content, molecular weight and degree of dispersion of block copolymers (Ia–Id; DMS segment length 100) synthesized by *Scheme 1* are shown in *Table 1*. These block coplymers were random block copolymers obtained by dehydration of TMPS monomer and DMS oligomer (**3**) (segment length 100), the segment length of which was calculated from g.p.c. measurements. The vinyl group content of **3** was found to be 5.6 mol% by ^{1}H n.m.r. The average TMPS segment length $\bar{x}$ in *Table 1* was calculated from the composition ratio and $\bar{y}+\bar{z}$ (DMS segment length). According to the ^{1}H n.m.r., TMPS/DMS weight fraction ranged from 80/20 (Ia) to 51/49 (Id), and average TMPS segment length from 144 (Ia) to 37 (Id). According to g.p.c. measurements, the molecular weight ranged from 110 000 to 270 000, and the degree of dispersion from 1.32 to 1.83. The above differences in molecular weight were expected to affect the disposition of the copolymers to some extent. The polymers were fibrous. The membranes cast from chloroform solution became softer with increase in DMS content, but the strength of membranes was sufficient.

Graft copolymers were synthesized by hydrosilylation between the vinyl group of **4** and the terminal hydrosilyl group of **5**. These graft copolymers were synthesized by increasing DMS segment of block copolymers on the side chain. Degree of polymerization, molecular weight and degree of dispersion of **5** are shown in *Table 2*. The degree

Table 2 Characterization of the DMS oligomer (5)

Sample no.	$\bar{n}^a$	$\bar{M}_n{}^b$ ($\times 10^{-4}$)	$\bar{M}_w{}^b$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$
(1)	30	2.30	2.50	1.10
(2)	74	5.60	7.20	1.29

[a] Average degree of polymerization
[b] Determined by g.p.c. measurements

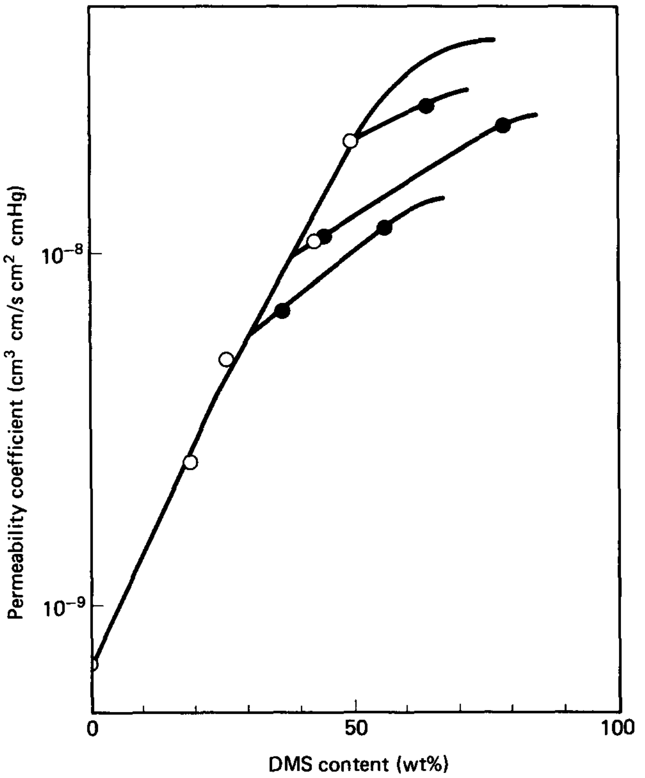


Figure 1 Plots of permeability coefficients P_{O_2} against DMS contents of TMPS/DMS copolymers: ○, block copolymers; ●, graft copolymers

of polymerization was calculated from the average molecular weight measured by g.p.c. and values of 30 and 74 were obtained. The characterizations of graft copolymers are shown in *Table 1*. The (1) and (2) (insertions in *Table 1*) of the samples indicate a difference of 5 grafted onto the block copolymers. Yield (the rate of grafting) was calculated on the basis of the disappearance of the vinyl group signals measured by ^{1}H n.m.r. and was found to vary. The strength of the membrane was sufficient, but Ic(2) was somewhat weak.

The oxygen permeability coefficient P_{O_2} (cm^3 cm/s cm^2 cmHg) was measured for each membrane cast from the chloroform solution. The thickness of the membranes was almost constant and was not taken into consideration. The relation of P_{O_2} to the DMS content (wt %) is shown in *Figure 1*. In *Figure 1*, PTMPS and block copolymers are shown by open symbols and graft copolymers, grafted to the block copolymers on the same line, by closed symbols. P_{O_2} of PTMPS was 6.7×10^{-10} and P_{O_2} increased with DMS content, approaching 6.0×10^{-8}, the value of a PDMS membrane. On comparing the block copolymers with graft copolymers, P_{O_2} was found to increase more in the block than in the graft copolymers, as DMS increased. Moreover, between polymers of the same DMS content, block copolymers had greater P_{O_2} than graft copolymers. It can thus be stated that P_{O_2} is greater when DMS exists in the main chain.

Significant information on the mixture of segments and mobility of the molecular chain by dynamic viscoelastic characteristics was obtained. The differences between block copolymers and graft copolymers were clearly shown by the measurements of dynamic viscoelasticity. Storage modulus (E'), loss modulus (E'') and loss factor (tan δ) of PTMPS and Ia–d at 11 Hz are shown in *Figures 2* and *3*. Generally, near T_g of the polymer, the main dispersion (decrease of E', maximum of E'' and maximum of tan δ) based on the molecular micro-Brownian motion from the amorphous part is shown. From *Figure 2*, around 0°C, the decrease of E' and maxima of E'' and tan δ were measured, and around 100°C, the decrease of E' and the increase of tan δ were measured. These are based on glass transition and melting of PTMPS respectively. From the curve of the block copolymers Ia–d in *Figure 3*, around -120, -75 to 0 and 100°C, three dispersion curves are shown. These are thought be based on the glass transition of DMS, glass transition of TMPS and melting of crystallized TMPS respectively. Around -150°C, when polymers are in the glassy state, E' is about 10^{10} dyn cm^{-2}, but around room temperature E' decreases to 10^8–10^9 dyn cm^{-2} and more so as the soft segment DMS content increases. E' of Id, whose DMS content is the largest, is 10^8 dyn cm^{-2}, and Id is a typical elastomer and has good film-forming properties. The dispersion peak of DMS did not easily change by an increase in DMS content. The dispersion peak of TMPS, however, shifted to lower temperature with an increase in DMS content. Particularly, in Id, the dispersion peaks of DMS and TMPS could be considered as one broad peak. Thus in block copolymers, when DMS content is small, they have micro separative structure, but when DMS content is large, the micro separative structure is

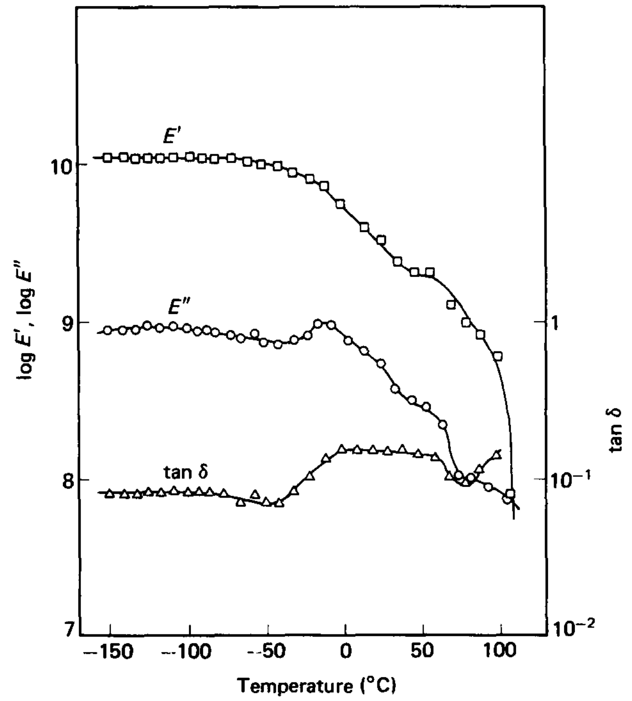


Figure 2 E', E'' and tan δ of PTMPS plotted against temperature at 11 Hz

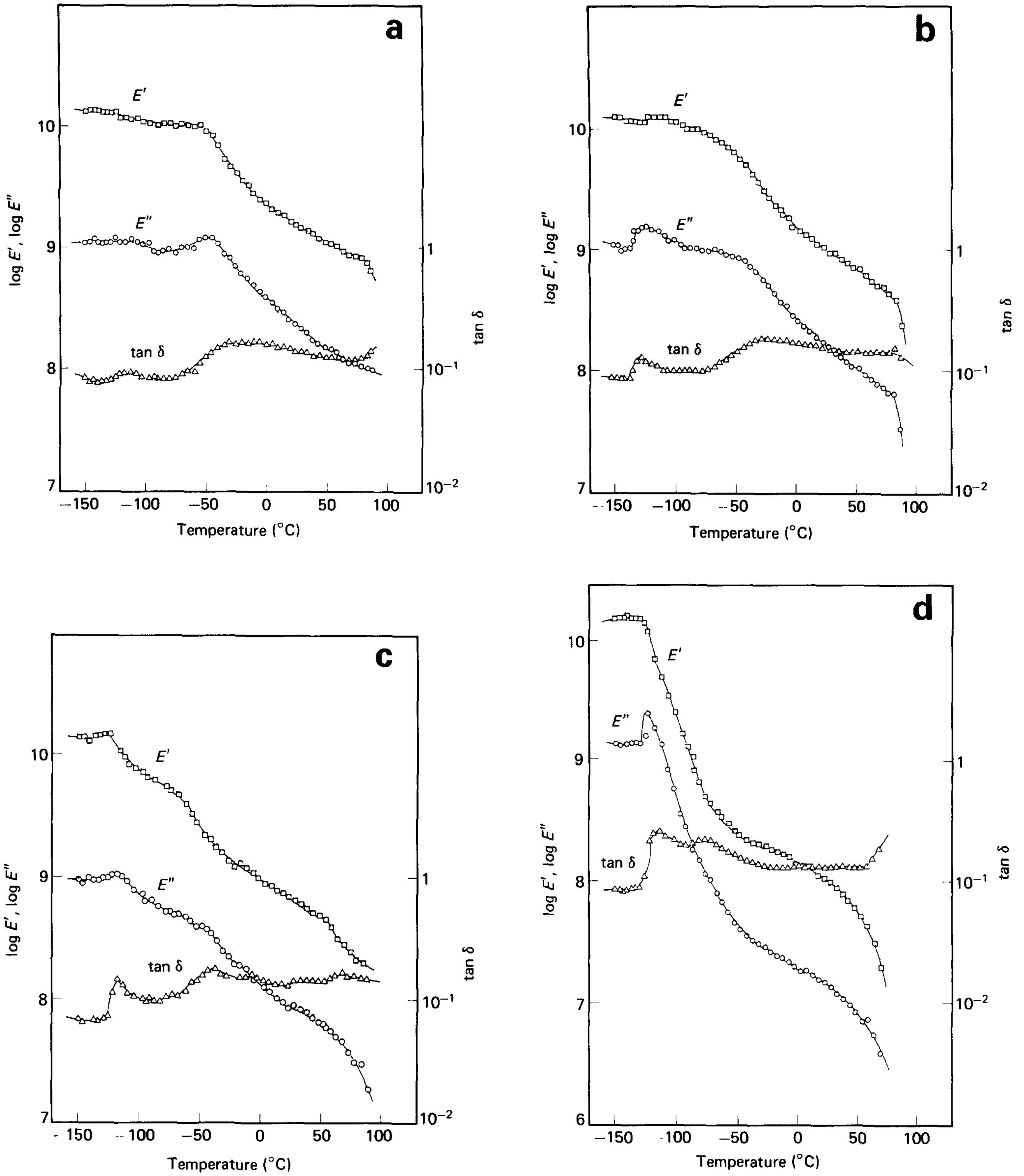


Figure 3 E', E'' and tan δ of block copolymers (a) Ia, (b) Ib, (c) Ic and (d) Id plotted against temperature at 11 Hz

prevented and they have mixed segment structures. The temperature dispersion curves of E', E'' and tan δ of Ib(1) and Ib(2) are shown in *Figure 4*. Those of Ic(1) and Ic(2) are shown in *Figure 5*. From *Figure 4* as in Ib, both Ib(1) and Ib(2) have three dispersions, around −120, −30 and 100°C. The E' of Ib(2) around room temperature is not so clear as the others. Ic(1) and Ic(2) have three peaks similar to those of Ic in *Figure 5*. Because the DMS content of Ic(2) is so large, E' decreases greatly as the temperature rises. Around room temperature, it is about 10^8. Thus because E' exceeds 10^8, the membranes should be easily obtained. With regard to TMPS and DMS dispersion peaks, even if the DMS content increases, both peaks cease to move greatly. Graft copolymers were thus found to differ from block copolymers, and the former was expected to maintain its micro separative structure. Block copolymers and graft copolymers clearly differ by comparing Id with Ib(2) which has almost the same composition ratio. In Id (DMS content 49%), the micro separative structure is destroyed, but Ib(2) (DMS content

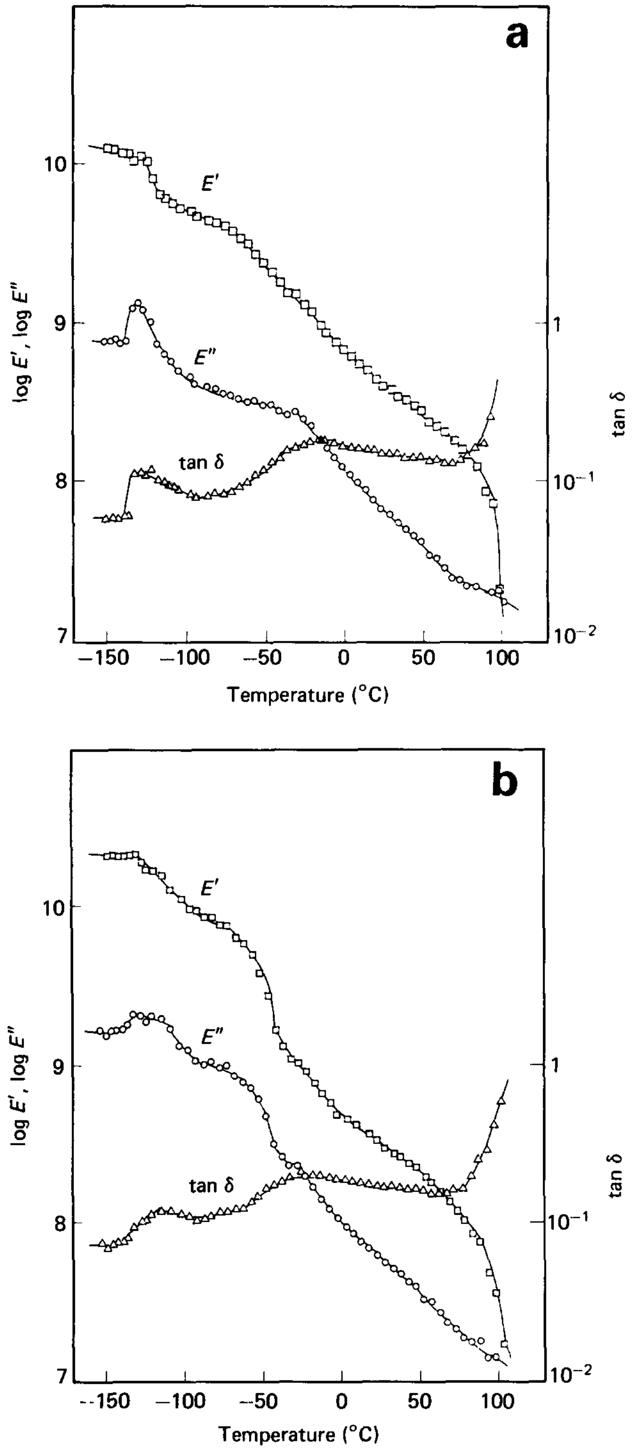


Figure 4 E', E'' and tan δ of graft copolymers (a) Ib(1) and (b) Ib(2) plotted against temperature at 11 Hz

56%) was shown to have the micro separative structure. These differences are thought to arise from the fact that TMPS chains are affected more when DMS is present more in the main chain than in the side chain.

The permeating gas molecules do not pass through crystallites. Therefore, by measuring the crystallinity of polymer, the effects of DMS segments on the crystallized TMPS area were investigated. The changes in crystallinity of TMPS with DMS content are shown in *Figure 6*. Block copolymers are shown by open symbols and graft ones by closed symbols. In *Figure 6*, crystallinity ranges from 46% of PTMPS to 7.7% of Id. The crystallinity of Id(1) could not be determined since the heat of fusion was so small. From this curve, the increase in the ratio of crystallinity with that of DMS content is greater in block copolymers than in graft copolymers. Thus, the fold crystallinity of TMPS is prevented to a greater extent when DMS exists more in the main chain than in the side chain. T_m and T_g change with DMS content, as shown in *Figure 7*. First, T_m is around 120°C while DMS content is less than 50 wt%. With greater

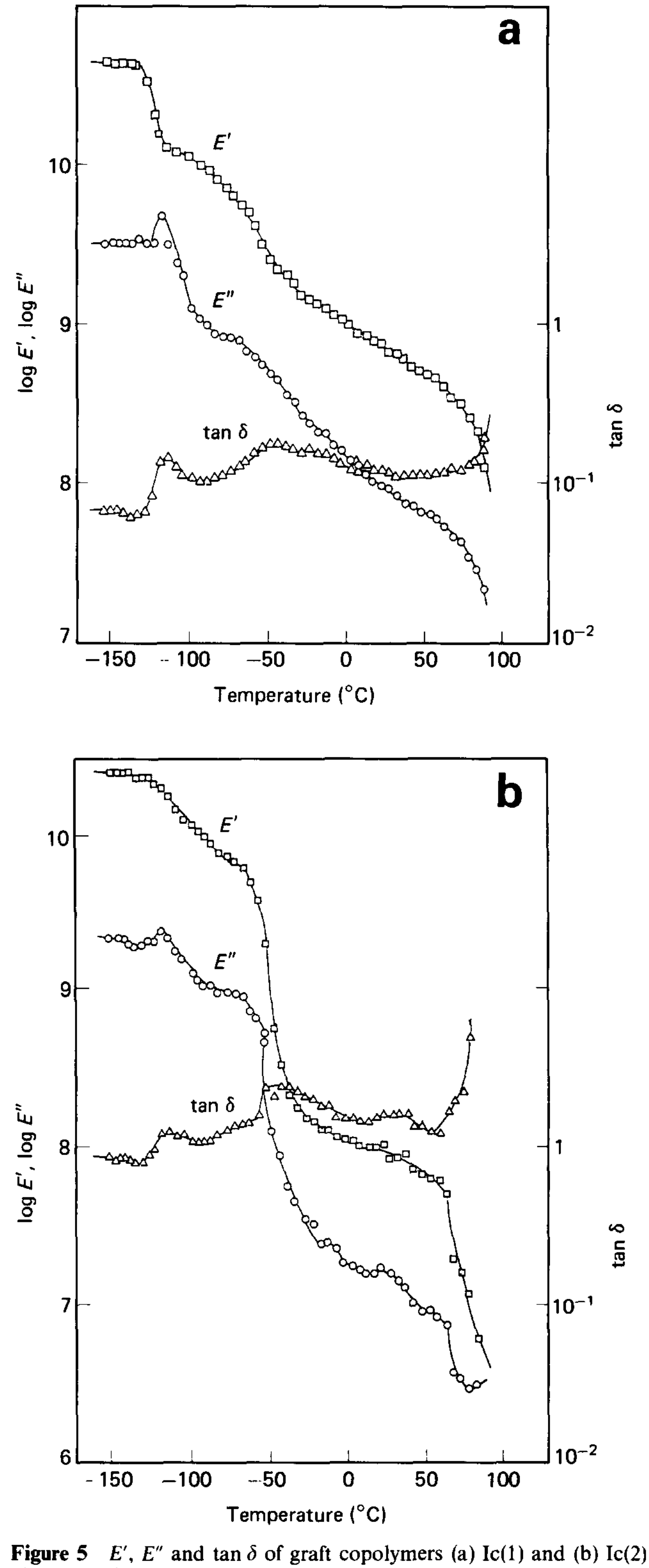


Figure 5 E', E'' and tan δ of graft copolymers (a) Ic(1) and (b) Ic(2) plotted against temperature at 11 Hz

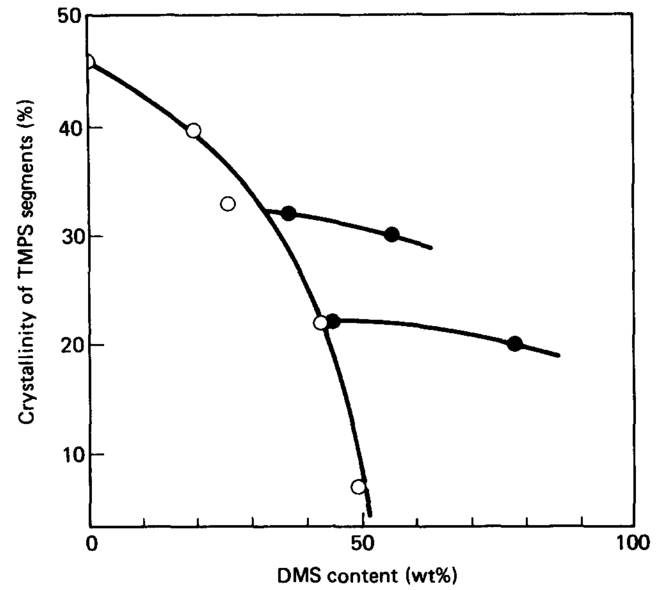


Figure 6 Plots of crystallinities against DMS contents of TMPS/DMS copolymers: ○, block copolymers; ●, graft copolymers

DMS content, T_m of block copolymers decrease rapidly, but that of graft copolymers does not decrease much. This shows that block copolymers affect fold crystallinity more than graft copolymers. The results for dynamic viscoelasticity show that micro separative structure is prevented by destroying TMPS fold crystallinity.

An investigation of T_g is very important to the study of polymer chain mobility. From *Figure 7*, T_g of PTMPS is -22°C, and as DMS content increases, T_g falls, and T_g of Id(1) is -67°C. Therefore T_g decreases more in block copolymers as DMS content increases. The molecular mobility is thus greater when DMS exists more in the main chain than in the side chain. This fact does not contradict the results of dynamic viscoelasticity studies. The following conclusions were drawn. Membranes with high permeability cannot easily form micro separative structures since the fold crystallinity of TMPS is prevented. Molecular mobility is also greater. Yamashita *et al.*[6] state that micro separative structure is not good for permeability, on the basis of a study of the permeability of a polystyrene membrane containing siloxane chains in the side chains.

Effect of microstructure differences in segment length on permeability and selectivity

Based on the above, TMPS/DMS copolymer membranes with greater permeability were designed. The relation between selectivity and microstructure of the membranes was investigated. In the above, the DMS segment length was always 100 and its effect was negligible. By shortening the DMS segment length, the micro separative structure cannot be formed easily and thus membranes with superior permeability can be expected. But as uniformity increases, membrane preparation is more difficult. This should be taken into consideration.

The characterizations of IIa–d and IIIa–d, whose DMS segment lengths are 40 and 20 and which were synthesized according to *Scheme II*, are shown in *Table 3*. From the ^{1}H n.m.r., the TMPS/DMS weight fraction ranged from 96/4 to 71/29 in samples II, and from 95/5 to 81/19 in III. Each membrane was strong enough, and membranes with greater DMS content could not form spontaneously. The molecular weight ranged from 53 000 to 160 000 and the degree of dispersion from 1.57 to 2.28.

To examine the effect of DMS segment length on microstructure, the dynamic viscoelasticity of block copolymers with similar composition ratios and different segment lengths was measured. Temperature dispersion curves of IIc (DMS segment length 40; DMS content 20 wt%), IIId (DMS segment length 20; DMS content 19 wt%) at 11 Hz are shown in *Figure 8*. The curves were compared with that of Ia (DMS segment length 100; DMS content 20 wt%) in *Figure 3*. *Figure 3* shows that in

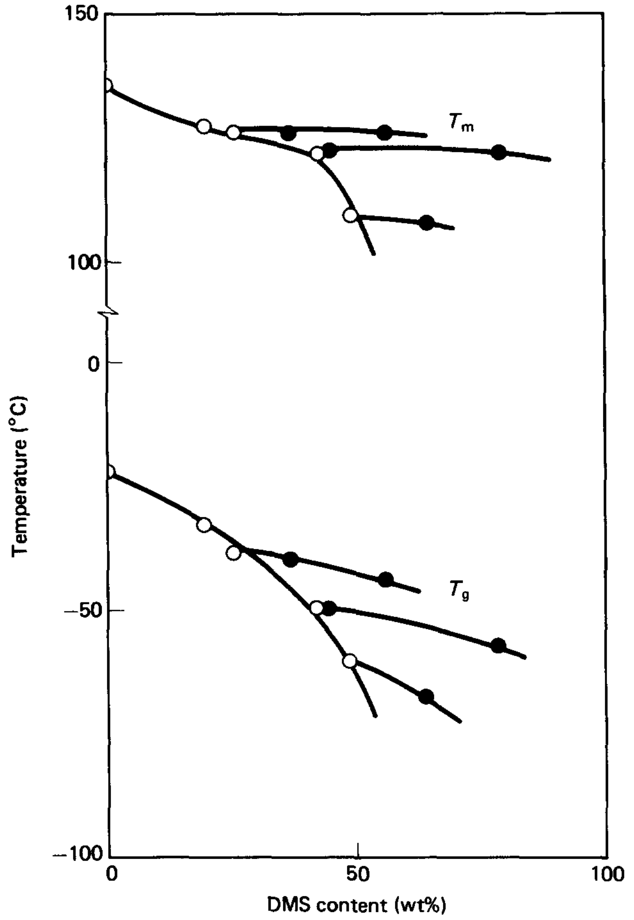


Figure 7 Plots of melting temperatures T_m and glass transition temperatures T_g against DMS contents of TMPS/DMS copolymers: ○, block copolymers; ●, graft copolymers

Table 3 Characterization of TMPS/DMS copolymers

Sample no.	$\bar{x}^a$	$\bar{y}^b$	DMS content (wt%)	$\overline{M}_n{}^c$ ($\times 10^{-4}$)	$\overline{M}_w{}^c$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$
IIa	324	40	4.0	6.89	13.6	1.97
IIb	89	40	14	9.20	16.7	1.81
IIc	55	40	20	6.43	10.1	1.57
IId	35	40	29	7.33	16.7	2.28
IIIa	123	20	5.0	16.0	28.7	1.79
IIIb	85	20	8.0	5.30	9.50	1.79
IIIc	43	20	14	9.30	14.8	1.59
IIId	30	20	19	6.70	11.6	1.73

[a] Average segment length of TMPS
[b] Average segment length of DMS
[c] Determined by g.p.c. measurements

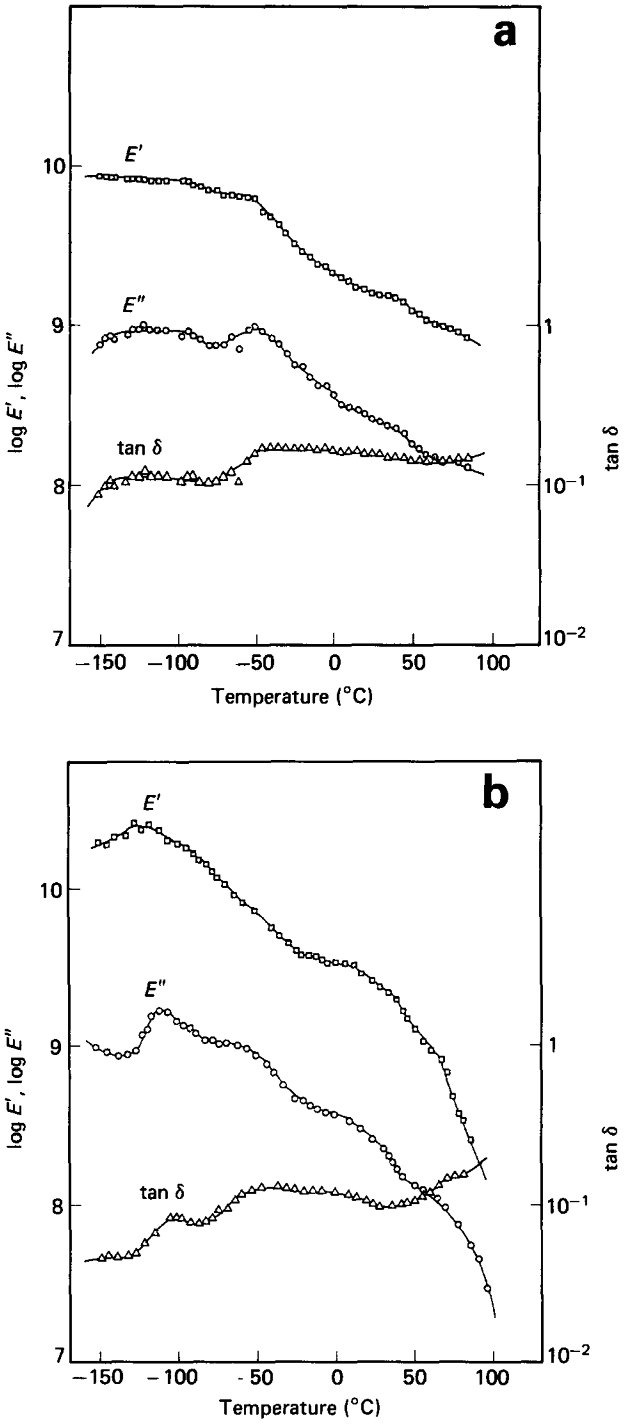


Figure 8 E', E'' and tan δ of block copolymers (a) IIc and (b) IIId plotted against temperature at 11 Hz

Ia, the DMS dispersion peak around −120°C and the TMPS dispersion peak around −40°C are clearly separated and have typical forms. From *Figure 8*, in IIc, the DMS dispersion peak around −120°C and the TMPS dispersion peaks around −50°C are separated to form micro separative structures, but the TMPS mobility of IIc exceeds that of Ia. In IIId, E'' and tan δ dispersion peaks are seen around −100 and −50°C and overlap. The decrease in E' is evident from around −120 to −20°C. Thus the micro separative structure of IIId is prevented more than that of Ia and IIc. This accounts for the molecular mobility being very large.

Crystallinity of TMPS plotted against the DMS content of each polymer is shown in *Figure 9*. The decrease in crystallinity with increase in DMS is clearer as the DMS segment length becomes shorter. The crystallinity of IIId is 11% and 89% of TMPS is in the amorphous part. Changes in T_m and T_g with the DMS content of each polymer are shown in *Figure 10*. T_m does not move from around 120°C at first, but rapidly decreases when DMS increases. The shorter the segment, the more rapidly T_m decreases. The d.s.c. measurements and dynamic viscoelasticity thus show that the shorter the segment the more the TMPS fold crystallization is obstructed, causing more TMPS to be in the amorphous area, and consequently the more the micro separated forms of both DMS and TMPS are obstructed. In *Figure 10* the shorter the DMS segment the more T_g decreases with DMS content. This is consistent with the dispersion peak of T_g of TMPS.

The relation between the P_{O_2} of each polymer and DMS content is shown in *Figure 11*, where the shorter the DMS segment length the greater is the increase in P_{O_2} with DMS content. Comparing polymers of the same composition, the shorter the DMS segment the larger is P_{O_2}. From these findings, it is evident that, in synthesizing almost random block copolymers, the fold crystallization of TMPS is obstructed, and membranes with mixed composition of TMPS and DMS and high P_{O_2} could be obtained.

The relation between the separation factor (α) and DMS content is shown in *Figure 12*. The value of α of the homopolymers is as follows: PTMPS has a value 3.17, and PDMS has a value 1.90. The reason that PTMPS is greater than PDMS may be due to a mutual interaction arising from electron movement of phenylene in the PTMPS and oxygen molecules. *Figure 12* shows that the values of α of block copolymers (DMS segment length 100) approach nearer and nearer to the α value of PDMS, and that the values of α of block copolymers (DMS segment length 40 or 20) do not move much from around 3.0. The reason for this may be that, in membranes with

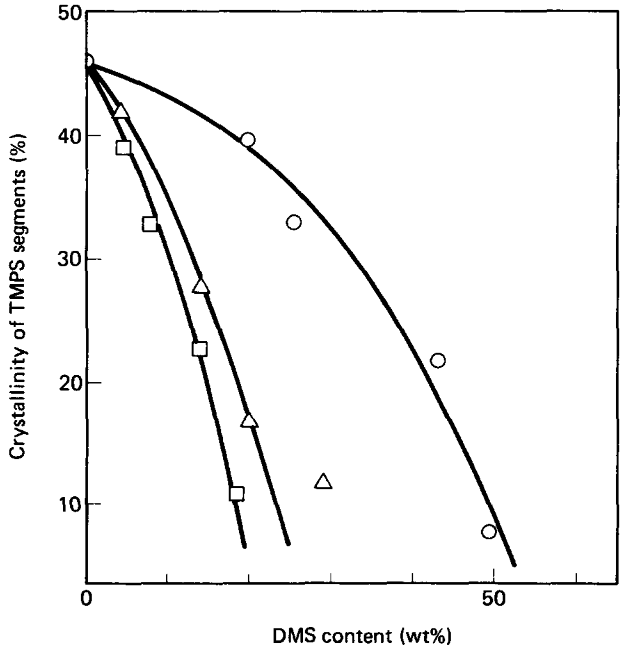


Figure 9 Plots of crystallinities against DMS contents of TMPS/DMS block copolymers: ○, $\bar{y}=100$; △, $\bar{y}=40$; □, $\bar{y}=20$

long DMS segments and in which DMS and TMPS are separated, gas molecules mainly permeate through DMS, but, in membranes with short DMS segments and in which DMS and TMPS are mixed, gas molecules permeate by the strong effects of TMPS. The values of α thus also increase. The increase in local mobility, which is due to the TMPS becoming amorphous, is considered to effect the increase in α. The PDMS membrane has an excellent value of $P_{O_2}=6.0\times10^{-8}$, but the value of α is small, $\alpha=1.9$. Generally speaking, the larger P_{O_2}, the smaller is α. The relation between P_{O_2} and α is shown in *Figure 13*. *Figure 13* shows the successful synthesis of membranes whose P_{O_2} values are not much smaller than those of PDMS (for example, about 2.0×10^{-8}). It also shows that the value of α was increased (the most favourable values, 2.3×10^{-8} and 3.0 for P_{O_2} and α respectively, were obtained from the copolymer whose DMS segment length was 20, and contained 19 wt% DMS). This indicates that this membrane should have high quality as a membrane for the concentration of oxygen, more so than other membranes.

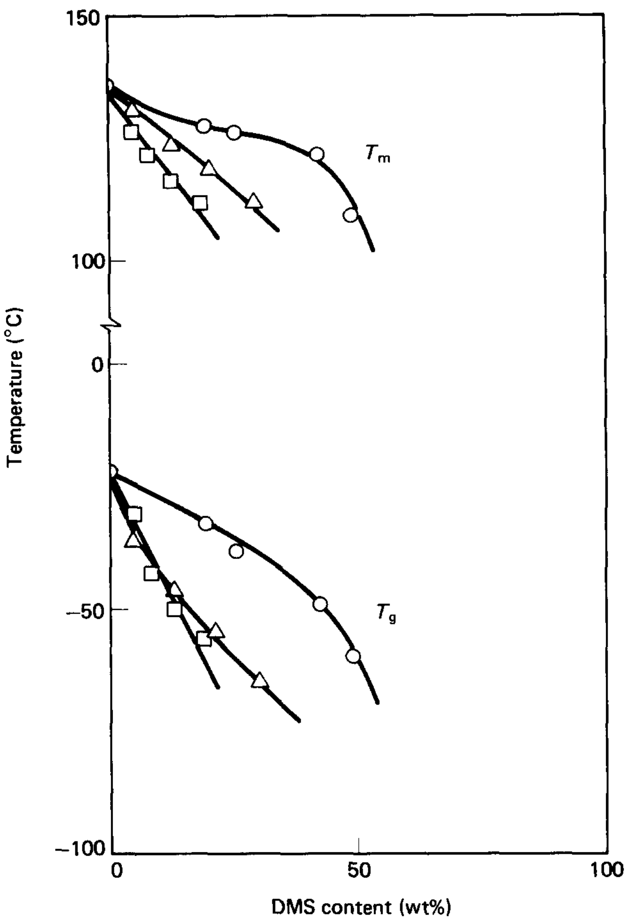


Figure 10 Plots of melting temperatures T_m and glass transition temperatures T_g against DMS contents of TMPS/DMS block copolymers: ○, $\bar{y}=100$; △, $\bar{y}=40$; □, $\bar{y}=20$

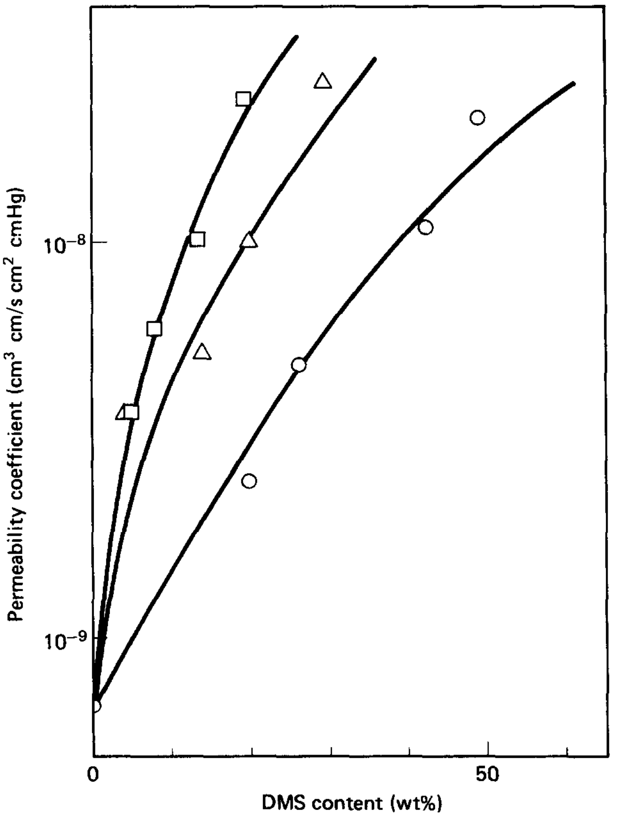


Figure 11 Plots of permeability coefficients P_{O_2} against DMS contents of TMPS/DMS block copolymers: ○, $\bar{y}=100$; △, $\bar{y}=40$; □, $\bar{y}=20$

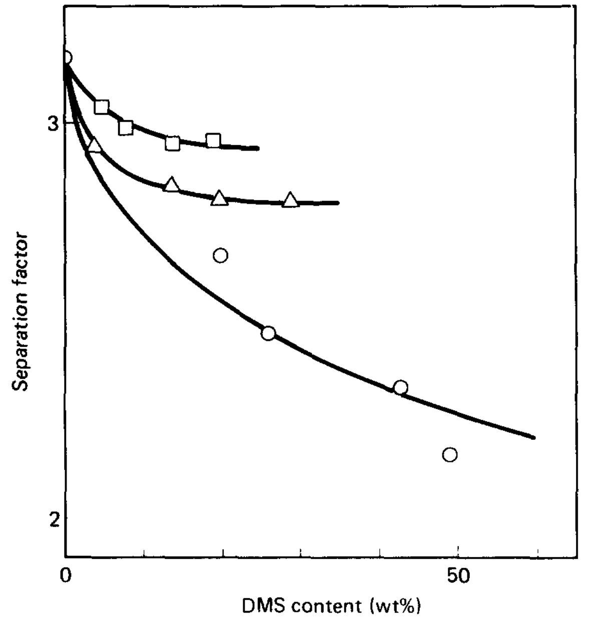


Figure 12 Plots of separation factors α against DMS contents of TMPS/DMS block copolymers: ○, $\bar{y}=100$; △, $\bar{y}=40$; □, $\bar{y}=20$

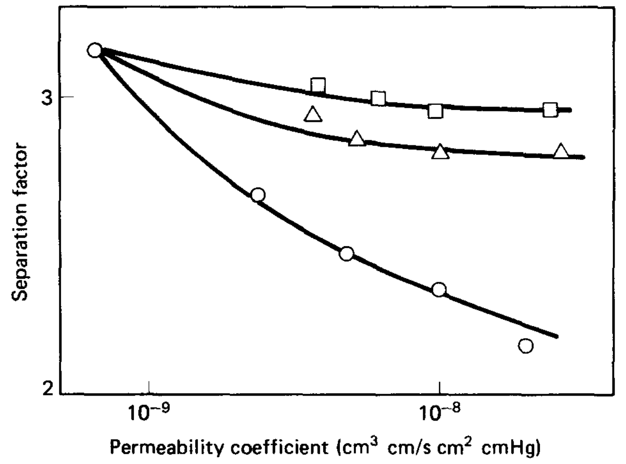


Figure 13 Plots of separation factors α against permeability coefficients P_{O_2} of TMPS/DMS block copolymers: ○, $\bar{y}=100$; △, $\bar{y}=40$; □, $\bar{y}=20$

In the present study, we polymerized DMS with TMPS, since TMPS could be used to form membranes very easily. However, high values of P_{O_2} and α should be possible using polymers that having mixed microstructure, in the case of polymerizing DMS with other monomers that have strong polarity and film-forming properties.

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