Synthesis of tetramethyl-*p*-silphenylenesiloxane/dimethylsiloxane triblock copolymer by employing living anionic polymerization

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Dimethylsiloxane–tetramethyl-*p*-silphenylenesiloxane–dimethylsiloxane (DMS–TMPS–DMS) triblock copolymer was synthesized by employing living anionic polymerization of hexamethylcyclotrisiloxane (D_3). Two synthetic methods were carried out for the polymerization. One of those methods was the anionic polymerization of D_3 initiated at the silanolate anion which was prepared from the terminal hydroxyl group of silanol-terminated TMPS prepolymer by reaction with n-butyllithium (method 1). The other was the coupling reaction of vinyl-terminated TMPS prepolymer with hydrosilyl-terminated DMS prepolymer obtained from the anionic polymerization of D_3 by using diphenylmethylsilanolate anion as initiator (method 2). In method 1, DMS contents of the copolymers ranged from 25.8 to 72.5 wt% and the values agreed with the ratio of D_3 to TMPS prepolymer. The weight-average molecular weights ranged from 1.36×10^4 to 19.4×10^4 and were close to the predicted values calculated from the $\bar{M}_v$ of the TMPS prepolymer and the amount of D_3 added. In the case of method 2, weight-average molecular weights ranged from 19.5×10^4 to 24.2×10^4. The high molecular weight copolymer could thus be obtained by method 2. Intrinsic viscosity values of the triblock copolymers agreed with calculated values obtained by considering the copolymer as a binary mixture of these homopolymers. Differential scanning calorimetry and thermogravimetry were carried out on the triblock copolymers. The equilibrium melting temperatures of each of the copolymers were very close to that of poly-TMPS (160°C). The glass transition temperature and heat of fusion were decreased as the DMS content was increased. The thermogravimetric curves for the copolymers indicated that the thermal stability of the triblock copolymer was intermediate between the DMS and TMPS homopolymers.

Keywords Polysilphenylene; polysiloxane; triblock copolymer; living polymerization; intrinsic viscosity; thermal analysis

INTRODUCTION

Several kinds of triblock copolymers containing dimethylsiloxane component as the soft segment have been prepared by application of the anionic polymerization of hexamethylcyclotrisiloxane (D_3). In particular, styrene or α-methylstyrene/dimethylsiloxane triblock copolymers have been extensively studied by several workers[1–6]. For these copolymers an enhancement in properties such as retention of flexibility at low temperature, excellent electrical properties, inertness towards chemicals and high degree of permeability towards gases could be conceived because of the presence of polydimethylsiloxane blocks. The most promising synthetic methods take advantage of the specificity of the 'living' polystyrene species. Bostick[7] also obtained diphenylsiloxane/dimethylsiloxane block copolymers by using the living anionic polymerization of hexaphenylcyclotrisiloxane and hexamethylcyclotrisiloxane initiated by silanolate anion produced from diphenylsilanediol and n-butyllithium (n-BuLi).

The present article describes the synthetic routes to a tetramethyl-*p*-silphenylenesiloxane/dimethylsiloxane (TMPS/DMS) triblock copolymer which involve its 'living' anionic polymerization of D_3. Magill *et al.* have investigated the physical properties of TMPS/DMS block copolymer precisely and found that the copolymer has interesting thermoplastic elastomeric character[8–12]. DMS–TMPS–DMS triblock copolymer is considered to be the simplest model for discussing the effects of TMPS or DMS segment length and TMPS/DMS composition on its physical and chemical properties, but until now it has not been synthesized. This might be attributed to the difficult preparation of pure cyclic compound containing TMPS monomer units[13], which is expected to be a starting material for the living anionic polymerization to the obtained TMPS segment. In our preparation method the TMPS segment is prepolymerized from its monomer instead of using cyclic TMPS oligomer.

Two methods for the preparation of the triblock copolymer are described. One of these uses silanol-terminated TMPS prepolymer and the other uses vinyl-terminated TMPS prepolymer as starting materials. The former method is the anionic polymerization of D_3 initiated by the silanolate anion prepared from the terminal hydroxyl group of TMPS prepolymer by reaction with n-BuLi. The latter is a coupling of vinyl-terminated TMPS with hydrosilyl-terminated DMS prepolymer obtained from the anionic polymerization of D_3 using diphenylsilanolate anion as initiator. Several

Table 1 Molecular weights, molecular weight distributions and melting temperatures of the silanol- and the vinyl-terminated TMPS prepolymers used in the copolymerizations

| No.	Terminal group	$\bar{M}_v$ $(\times 10^{-4})$	Degree of polymerization	$\bar{M}_n$ $(\times 10^{-4})$	$\bar{M}_w$ $(\times 10^{-4})$	$\bar{M}_w/\bar{M}_n$	T_m
I	silanol	0.85	41	0.63	1.02	1.61	136
II	silanol	7.73	370	5.58	8.48	1.52	138
III	silanol	8.34	400	6.82	8.84	1.30	139
IV	vinyl	14.8	710	9.80	15.3	1.57	140
V	vinyl	13.6	650	10.1	14.3	1.41	140
VI	vinyl	12.7	610	9.60	13.9	1.46	140

triblock copolymers having various segment lengths and compositions were prepared by these methods. In order to clarify the effects of sequence length and composition on some physical properties, differential scanning calorimetry (d.s.c.), thermogravimetric analysis (t.g.) and intrinsic viscosity measurements were carried out on the copolymers.

EXPERIMENTAL

Synthetic method 1

Preparation of silanol-terminated TMPS prepolymer. The method of Merker *et al.*[13] was used: 15 g of *p*-bis(dimethylhydroxylsilyl)benzene was polymerized in 70 ml of benzene solution with 0.2 g of tetramethyl-guanidine di-2-ethylhexoate as catalyst, using an azeotrope trap to remove water. Throughout its condensation reaction, water separated in the azeotrope trap was measured to control the molecular weights of the polymers. Poly-TMPS thus obtained was reprecipitated in ethanol to remove the catalyst. Fractionation of poly-TMPS was then accomplished by the addition of methanol to ~ 3 wt% solution in benzene. The fractionated poly-TMPS was dried *in vacuo* at 60°C for 24 h. Silanol-terminated TMPS prepolymers having three different molecular weights were prepared (see *Table 1*).

Copolymerization. The copolymerization was carried out in a dry box under nitrogen. The polymerization process is shown in equations (1), (2) and (3):
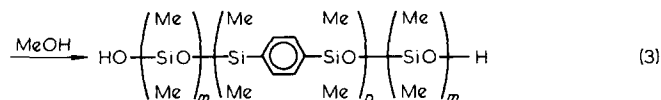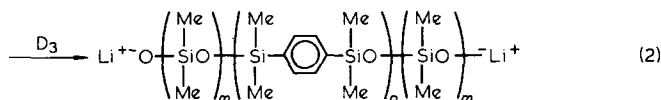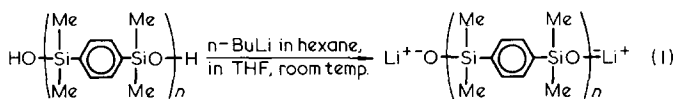
Hexamethylcyclotrisiloxane (D_3) was freshly distilled in a nitrogen atmosphere and dried *in vacuo* for 24 h. Tetrahydrofuran (THF) was dried over sodium wire, then distilled under nitrogen three times.

To 70 ml of THF solution containing 5 g of TMPS prepolymer was added a n-hexane solution of n-BuLi (1.631 mol l^{-1}). The solution was stirred for 20 min to complete the formation of silanolate anion and to this mixture D_3 was added dropwise, and the reaction mixture

stirred for 18 h at room temperature. The dimethyl-siloxane content of the copolymer was controlled by the amount of D_3 added. The mixture was poured into excess methanol to quench the reaction and the product was reprecipitated several times from benzene–ethanol to remove unreacted D_3 and dried *in vacuo* at 60°C for 24 h.

Synthetic method 2

Preparation of vinyl-terminated TMPS prepolymer. This prepolymer was prepared by the condensation reaction of dimethylvinylchlorosilane with the terminal hydroxyl group of silanol-terminated TMPS prepolymer.

To 5 ml of a benzene solution containing excess dimethylvinylchlorosilane, a mixture of pyridine and 5 g of silanol-terminated TMPS prepolymer in 80 ml of benzene was slowly added dropwise under nitrogen. After stirring for 24 h, the reaction mixture was poured into 800 ml of methanol and the white fibre-forming product was obtained. Three prepolymers were prepared as shown in *Table 1*.

Preparation of hydrosily-terminated DMS prepolymer. According to equations (4), (5) and (6), monofunctional hydrosilyl-terminated DMS prepolymer was synthesized[14].
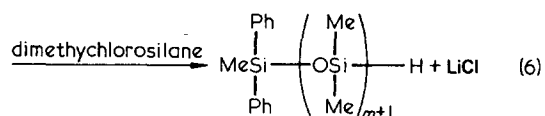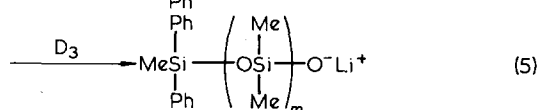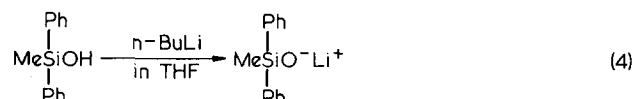
Methyldiphenylsilanol (3.5 g) was dissolved in 30 ml of THF, and to this solution 10 ml of n-hexane solution of n-BuLi and an adequate amount of D_3 were added dropwise. The amount of added D_3 controls the degree of polymerization of this monofunctional DMS prepolymer. The reaction mixture was stirred for 18 h at room temperature. To this solution, excess dimethylchloro-silane was added to quench the polymerization reaction and to introduce the terminal hydrosilyl group. The mixture was poured into excess methanol and the methanol was decanted off. The product was dried *in vacuo* for 90°C for 24 h and transparent viscous oil was obtained. The molecular weight and molecular weight distribution were determined from the intrinsic viscosity

Table 2 Characterizations of DMS—TMPS—DMS triblock copolymers prepared by synthetic method 1

Sample no.	TMPS prepolymer	Amount of D_3 (wt%)	DMS content (wt%)	$\overline{M}_c{}^a$ ($\times 10^{-4}$)	$\overline{M}_n$ ($\times 10^{-4}$)	$\overline{M}_w$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$	T_m (°C)
I-1	I	30	28.4	1.19	0.80	1.36	1.70	136
I-2	I	45	44.8	1.54	1.52	2.57	1.69	136
I-3	I	75	72.5	3.09	1.76	3.05	1.73	136
II-1	II	30	25.8	10.42	6.33	10.82	1.71	138
II-2	II	42	39.7	12.82	7.55	14.30	1.81	138
II-3	II	52	51.7	16.00	9.75	15.90	1.63	138
III-1	III	37	35.3	12.89	10.43	13.24	1.27	138
III-2	III	80	57.0	36.26	11.48	19.40	1.69	138

^{a} Calculated from $\overline{M}_v$ of TMPS prepolymer and amount of D_3 added

$(\overline{M}_v = 3.88 \times 10^4$, $[\eta] = 0.192)$ and g.p.c. measurement $(\overline{M}_w/\overline{M}_n = 1.65)$.

Copolymerization. The reaction scheme is shown in equation (7).
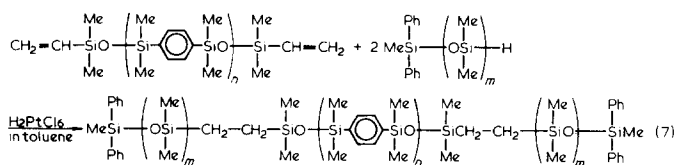
The reaction mixture of 1.0 g of vinyl-terminated TMPS prepolymer, two equivalents of hydrosilyl-terminated DMS prepolymer and 8 μl of ethanol solution of chloroplatinic acid $(0.218 \, mol \, l^{-1})$ in 10 ml of toluene was stirred at 70°–80°C under nitrogen atmosphere. After stirring for 12 h, the solution was poured into 400 ml of ethanol and the product was reprecipitated several times from benzene–ethanol to remove unreacted DMS prepolymer. The triblock copolymer thus obtained was dried *in vacuo* for 24 h.

Characterizations

^{1}H n.m.r. spectra of the polymers in carbon tetra-chloride were recorded on a JNM-PS-100 n.m.r. spectrometer. In the spectra of these triblock copolymers, signals of the methyl and phenylene protons of TMPS units were observed at 0.30 and 7.40 ppm respectively, and those of the methyl protons of the DMS units were observed at 0.11 ppm. The compositions were determined by the ratio of the integrated peaks of the methyl groups.

Intrinsic viscosity values of the prepolymers and copolymers were measured with an Ubbelohde viscometer in toluene at 25°C. $\overline{M}_v$ of TMPS and DMS prepolymers were calculated according to Staudinger equations for TMPS and DMS homopolymers to afford

$$[\eta] = 1.12 \times 10^{-4} \overline{M}_v{}^{0.75}$$

and

$$[\eta] = 2.0 \times 10^{-4} \overline{M}_v{}^{0.65}$$

respectively, from refs 13 and 6.

Molecular weight distributions were determined on a Water Associates gel permeation chromatograph using THF as the solvent. Aliquots of 0.1 ml of 0.2 wt% polymer solution in THF were injected into a series of four columns having porosity ratings of 10^6, 10^5, 10^4 and 10^3. Polystyrene standards $(M_w = 3600, 15\,000, 35\,000, 110\,000$ and 470 000) were used as the molecular weight standards.

The melting temperature and the heat of fusion were determined for each of the copolymers using a Shimadzu

SC-20 differential scanning calorimeter at 5°C min^{-1} in a helium stream. The glass transition temperature of the copolymer was also measured by this apparatus fitted with a low-temperature chamber filled with liquid nitrogen. Potassium nitrate and indium of high purity were used as calibration standards for melting point and heat of fusion determinations. The percentage crystallinities of the triblock copolymers were calculated according to:

$$\text{crystallinity} (\%) = (\Delta H_f/\Delta H_f{}^*) \times 100 \qquad (8)$$

where ΔH_f denotes the sample's heat of fusion and $\Delta H_f{}^*$ is the heat of fusion for perfectly crystalline poly-TMPS $(13 \, cal \, g^{-1})^{12}$. The thermogravimetric curves were recorded on a Shimadzu MTB-50 microthermobalance. A 10 mg sample was heated at 5°C min^{-1} under a helium flow of 40 ml min^{-1}.

RESULTS AND DISCUSSION

Results of syntheses

Table 2 shows the characterizations of DMS–TMPS–DMS triblock copolymers prepared by synthetic method 1. The amount of D_3 in the copolymerization process is expected to determine DMS contents of the copolymers. The DMS contents agreed with the amount of D_3 added except for copolymer III-2. The polymer yields were also very high (more than 95%). In the case of copolymer III-2, it is thought that the amount of D_3 was too large to be completely polymerized by the anionic polymerization process. For every copolymer, the molecular weights were greater than those of TMPS prepolymers (*Table 1*) and were close to the predicted values. The molecular weight distributions marginally increased on copolymerization.

In order to define the variation of molecular weight with reaction time, samples were removed at regular time intervals and quenched with methanol. These were then subjected to g.p.c. analysis. The growth of $\overline{M}_n$ and $\overline{M}_w$ was confirmed (*Figure 1*). The $\overline{M}_n$ and $\overline{M}_w$ of the prepolymer $(6.82 \times 10^4$ and $8.84 \times 10^4)$ were increased to 7.66×10^4 and 9.89×10^4 respectively and no further increase in molecular weight was observed after 10 h. The variation of n.m.r. spectra with reaction time (*Figure 2*) also confirms the increase with time of the proton signal of the DMS methyl group.

The melting temperatures of the triblock copolymers listed in *Table 2* are not greatly different from each other and are nearly the same as that of TMPS homopolymer (140°C). The melting temperature of TMPS/DMS block copolymer is thought to be dependent upon the TMPS sequence length. The melting points of these triblock
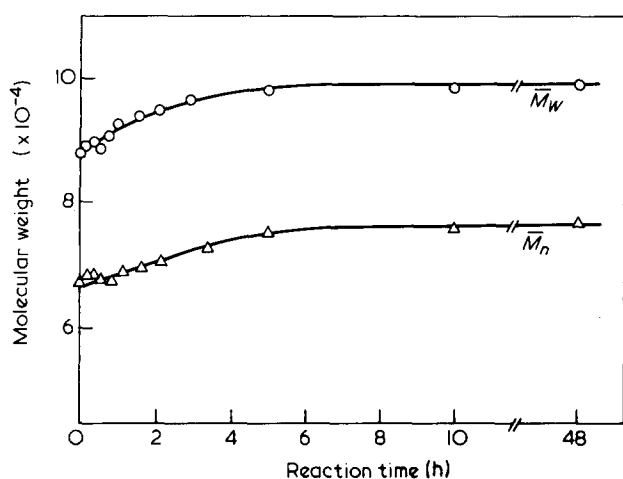
Figure 1 Dependence of reaction time on molecular weights of DMS–TMPS–DMS triblock copolymer prepared by synthetic method 1
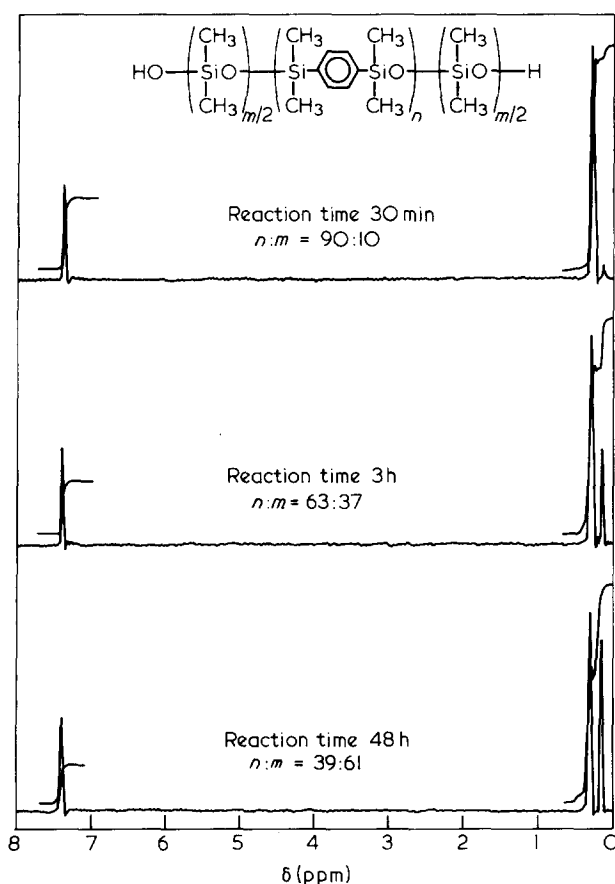

Figure 2 The variation of ^{1}H n.m.r. spectra with reaction time of copolymerization method 1

copolymers remain constant when the starting TMPS prepolymers are the same. This behaviour can be attributed to the constancy of the segment length of the prepolymer.

The effect of the initiator on the anionic copolymerization of D_3 with TMPS prepolymer was investigated by using sodium hydride instead of n-BuLi under the same conditions. *Figure 3* shows the variation of DMS mole content with reaction time and with each initiator. Most D_3 was consumed with n-BuLi; only half of the D_3 has been consumed in the sodium hydride

system even after 48 h. In general, a sodium ion is thought to be a stronger counter-cation than a lithium ion for living anionic polymerizations. But chain scission of the siloxane bond is possible in the polymerization of D_3 using sodium hydride as initiator. Bajaj *et al.*[5] have reported that the molecular weight distribution of styrene/dimethylsiloxane block copolymer prepared by the anionic polymerization of D_3 using sodium biphenyl as initiator was broader than that produced by lithium biphenyl. It is considered that their results suggest the chain scission of the siloxane bond by a terminal silanolate anion with sodium cation.

High molecular weight triblock copolymers could not be obtained by method 1. The reason might be that the silanolate anion produced from high molecular weight TMPS prepolymer ($\bar{M}_v \geq 10^5$) did not react with D_3 owing to the extremely low concentration of its terminal silanol group. Therefore, another method was examined involving hydrosilylation of α,ω-divinyl-terminated TMPS prepolymer with monofunctional hydrosilyl-terminated DMS prepolymer. Chaumont *et al.*[15] investigated this method of copolymerization in order to synthesize styrene/dimethylsiloxane block copolymer. Galin and Mathis[16] have also described a similar method for the preparation of ethylene oxide/dimethylsiloxane triblock copolymer.

Table 3 summarizes the characterizations of DMS–TMPS–DMS triblock copolymers prepared by the hydrosilylation reaction. Polymer yields were very high and weight-average molecular weights ranged from 19.5×10^4 to 24.2×10^4. These values were in good agreement with those calculated from the viscosity-average molecular weights of the TMPS and DMS prepolymers. The melting points of these copolymers were very close to TMPS homopolymer in each case.

Intrinsic viscosity measurement

Intrinsic viscosity measurements were developed for some of the triblock copolymers prepared by synthetic methods 1 and 2 in toluene at 25°C. The analytical values were compared with those calculated by considering the
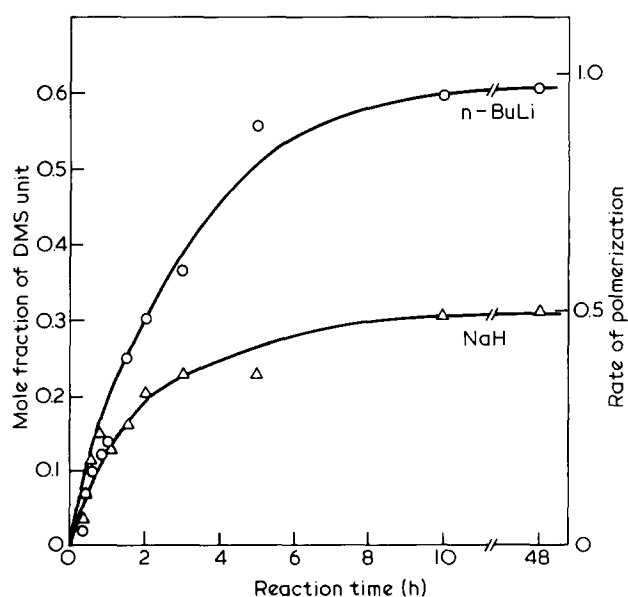

Figure 3 Dependence of reaction time on the rate of polymerization and DMS mole content of DMS–TMPS–DMS triblock copolymer prepared by synthetic method 1

Table 3 Characterizations of DMS—TMPS—DMS triblock copolymers prepared by synthetic method 2

Sample no.	$\bar{M}_V$ of TMPS pre-polymer	$\bar{M}_V$ of DMS pre-polymer	DMS content (wt%)		$\bar{M}_c{}^a$ (x10^{-4})	$\bar{M}_n$ (x10^{-4})	$\bar{M}_w$ (x10^{-4})	$\bar{M}_w/\bar{M}_n$	T_m ($^\circ$C)
			Theor.^{a}	Anal.					
IV-1	14.8 x 10^4	3.88 x 10^4	34.4	30.7	22.6	14.6	24.2	1.66	139
V-1	14.0 x 10^4	3.88 x 10^4	35.7	33.8	21.8	14.3	21.1	1.48	139
VI-1	12.4 x 10^4	3.88 x 10^4	38.5	37.5	20.2	13.7	19.5	1.42	139

^{a} Calculated from $\bar{M}_V$ of TMPS and DMS prepolymers

Table 4 Comparison between the analytical and theoretical intrinsic viscosities of DMS—TMPS—DMS triblock copolymers

Polymer no.	$\bar{M}_n$ (x10^{-4})	Mole fraction of DMS unit	[η] (dl g^{-1})	[η] *^{a} (dl g^{-1})
II-1	6.33	0.494	0.434	0.372
II-2	7.55	0.649	0.468	0.394
II-3	9.75	0.751	0.496	0.449
III-1	10.43	0.605	0.562	0.505
IV-1	14.60	0.518	0.695	0.669
V-1	14.30	0.556	0.671	0.647
VI-1	13.70	0.598	0.660	0.609

^{a} Calculated from the equation [η] * $= n_A K_A \bar{M}_n^{\alpha A} + n_B K_B \bar{M}_n^{\alpha B}$

Table 5 Equilibrium melting temperature T_m^o, glass transition temperature T_g and heat of fusion ΔH_f for DMS—TMPS—DMS triblock copolymers

Polymer no.	DMS content (wt%)	T_m^o ($^\circ$C)	T_g ($^\circ$C)	ΔH_f (cal g^{-1})	Crystal-linity (%)
III-1	35.3	157	−51	6.49	49.9
II-1	39.7	158	−62	5.90	45.4
II-2	51.7	157	−91	5.13	39.5
IV-1	27.7	157	−41	6.39	49.2
V-1	30.8	157	−46	5.93	45.6
VI-1	34.6	158	−50	5.64	43.4

Figure 4 Thermogravimetric curves of (A) TMPS homopolymer, (B) copolymer VI-2, (C) copolymer II-2, (D) a mixture of poly-TMPS and poly-DMS and (E) DMS homopolymer

copolymer as a binary mixture of homopolymers[3,6]. The empirical expression is

$$[\eta]^* = n_A[\eta]_A + n_B[\eta]_B \qquad (9)$$

This equation has been further expanded by using the Mark–Houwink relationship to give

$$[\eta]^* = n_A K_A \bar{M}_n^{\alpha A} + n_B K_B \bar{M}_n^{\alpha B} \qquad (10)$$

where [η]* is the calculated intrinsic viscosity, n_A and n_B are the mole fractions of TMPS and DMS segments and $\bar{M}_n$ is the overall number-average molecular weight for the copolymer. The values of K_A, K_B, α_A and α_B were given in the experimental section. The results are listed in *Table 4*. For all the copolymers, the values of [η] were in agreement with, but slightly higher than, [η]*. This may indicate expansion of the copolymer coils due to the interactions between the two segments as reported by Davies and Jones[3].

Thermal properties

Table 5 shows the equilibrium melting temperature, glass transition temperature and heat of fusion for some of the triblock copolymers. These were measured by using d.s.c. The equilibrium melting temperature for each of the
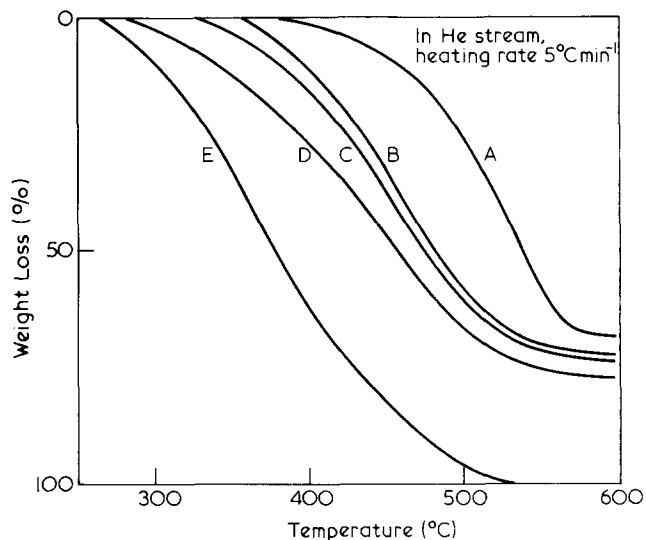
copolymers was determined by Hoffman's extrapolation method[17], which plot melting temperature T_m observed against the crystallization temperature T_c. The equilibrium melting temperatures of all the copolymers were very close to that of TMPS homopolymer (160°C)[10], whereas the glass transition temperatures decreased as the DMS content increased. The constancy of the equilibrium melting temperatures can be explained by the magnitude of the TMPS segment length in the copolymers (370 units). The variation of glass transition temperature with DMS content is compatible with the result of Okui et al.[10] Consequently, the equilibrium melting temperatures of the triblock copolymers are dependent on their TMPS sequence length but the glass transition temperatures are dependent on the composition of amorphous DMS unit. It is reasonable that the heat of fusion and the crystallinities of these triblock copolymer decreased with increasing amorphous DMS content.

Figure 4 represents thermogravimetric curves of copolymers II-2 and VI-1. The curves for TMPS, DMS homopolymers and the polymer mixture of 40 wt% DMS and 60 wt% TMPS were also measured under the same conditions. Ikeda et al.[18] obtained similar thermogravimetric curves of TMPS and DMS homopolymers. The thermal stability of DMS–TMPS–DMS triblock copolymer is situated between the DMS and TMPS homopolymers. The decomposition of the homopolymer mixture is initiated at lower temperature than that of the triblock copolymers, and so the depolymerization of the DMS unit in the triblock copolymers may be depressed relative to the DMS homopolymer and the mixture of poly-TMPS and poly-DMS.

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