Poly(diethylsiloxane-*co*-ethylphenylsiloxane) and poly(diethylsiloxane-*co*-methylphenylsiloxane): synthesis and characterization

J. R. Brewer*, K. Tsuchihara and R. Morita
National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305, Japan

and J. R. Jones and J. P. Bloxsidge
Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK

and S. Fujishige
Tokyo Kasei University, 1-1-18 Atabashi, Kaga, Tokyo 173, Japan
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Copolymers containing diethylsiloxane and functional siloxane groups of the form RR'SiO (where R = phenyl, and R' = ethyl or methyl) were synthesized by equilibrium polymerization of the appropriate cyclotrisiloxanes in the presence of KOH. Quantitative ^{29}Si n.m.r. spectroscopy indicated that the copolymers possessed random microstructures. Differential scanning calorimetry (d.s.c.) analysis showed that both substituents are effective in lowering the crystal melting and low-temperature crystal–crystal transitions with respect to the diethylsiloxane homopolymer, and ultimately lead to non-crystalline copolymers.

(Keywords: siloxane copolymers; poly(diethylsiloxane); ^{29}Si n.m.r. spectroscopy)

INTRODUCTION

Polysiloxanes are a remarkable class of polymers which maintain their properties over a wide temperature range[1]. In particular, they exhibit high thermal stability yet are flexible at very low temperatures. Poly(diethylsiloxane) (PDES) has the lowest glass transition temperature (−138°C) of any known polymer[2], but exists in a rigid crystal form at temperatures below −73°C, and as a conformationally disordered (condis) crystal at higher temperatures[3,4]. Molecular mechanics calculations have shown that two families of flat conformations satisfy the requirements of extended, straight-chain conformations for packing in the crystal and that the transition from one to the other, with a resultant 5% increase in volume, is responsible for the rigid crystal–condis transition[5]. Although the condis phase melts between −8 and 0°C, a high-temperature 'viscous crystalline phase' has been shown to exhibit considerable order up to 46°C[6–9].

In a recent paper, we demonstrated that the incorporation of bulky groups such as diphenylsiloxane into the mainchain successfully disrupted the crystal structures, and even at a relatively low aromatic content (8%), amorphous copolymers could be obtained[10]. These polymers were found to have glass transition temperatures as low as −128°C, which represents the lowest value reported to date for a non-crystalline polymer.

In this present paper, we report the effect, on the low temperature flexibility, of the incorporation of less bulky substituents, which contain only one phenyl group, into the polymer backbone. Thus, the synthesis and characterization of poly(diethylsiloxane-*co*-ethylphenylsiloxane) and poly(diethylsiloxane-*co*-methylphenylsiloxane), denoted by poly(DES-*co*-EPhS) and poly(DES-*co*-MPhS), respectively, are discussed in this work.

EXPERIMENTAL

Preparation of monomers

2,4,6-Triethyl-2,4,6-triphenylcyclotrisiloxane ($(EP)_3$) was prepared according to Young *et al.*[11]. 2,4,6-Trimethyl-2,4,6-triphenylcyclotrisiloxane ($(MP)_3$) was obtained from Shin-Etsu Co. and was used without further purification.

Synthesis of copolymers

All copolymers were prepared by the equilibrium polymerization of mixtures of the appropriate cyclotrisiloxanes, catalysed by KOH. Since there is a large difference in reactivity between the diethyl (E_3), and the ethylphenyl ($(EP)_3$) and methylphenyl ($(MP)_3$) cyclic trimers, reactions were conducted at elevated temperature (160°C) for 24 h to allow full equilibration to be achieved. In order to control the molecular weight, and also sharpen the molecular weight distribution, the copolym-

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*To whom correspondence should be addressed

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erization reactions were conducted in the presence of the difunctional chain stopper, 1,3-divinyl-1,3-diphenyl-1,3-dimethyldisiloxane. Molecular weights were kept low (<20000) in order to facilitate quantitative analysis by ^{29}Si n.m.r. spectroscopy, including the chain ends.

^{29}Si n.m.r. spectroscopy

^{29}Si n.m.r. spectra were obtained on a Bruker AC300 spectrometer operating at 59.6 MHz. Typically, a solution of chromium acetylacetonate ($Cr(acac)_3$) (0.1 M) was added in order to suppress nuclear Overhauser enhancements (n.O.es) and to shorten the T_1 spin-lattice relaxation times. The latter were checked by the inversion-recovery method and were generally less than 1 s. Therefore, to satisfy the condition for quantitative spectra, i.e. pulse interval $> 5T_1$, a standard pulse interval of 5 s was used. In order to ensure equal suppression of the n.O.es, spectra were acquired with gated decoupling (decoupler off throughout the pulse interval) in order to allow the residual n.O.es to decay. All spectra were recorded in benzene-d_6 solution and chemical shifts are quoted relative to tetramethylsilane (TMS). Depending on the natural line widths, line broadening functions between 0.5 and 2 Hz, with single zero-fills, were applied to facilitate peak integration.

Molecular weight measurements

Apparent molecular weights were obtained via size exclusion chromatography (s.e.c.) at 40°C in tetrahydrofuran (THF) with the use of a Tosoh 8020 liquid chromatograph equipped with Styragel columns.

Calorimetry

D.s.c. measurements were recorded using a Seiko SII instrument which had previously been calibrated using samples of high-purity indium. In all cases, the sample (10 mg) was isotropized at 50°C for 10 min before the cooling run was started, in order to remove any thermal memory effects. (PDES samples are renown for showing d.s.c. behaviour which is dependent on their previous thermal history.) Samples were cooled to -180°C at a rate of 8°C min^{-1}, and in all cases an equilibration period of 10 min was followed by heating at a rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The composition and molecular weights of all of the copolymers studied in this work are given in *Table 1*. Perusal of these data indicates that the observed comonomer contents are similar to the feed ratios, thus indicating that equilibrium has been reached. Unlike the case with the diphenyl cyclic trimer (P_3)[10], the reaction mixtures for both of the alkylphenyl cyclic trimers remained homogenous throughout the equilibration reaction, and copolymers containing higher levels of the functional comonomer were readily prepared.

The microstructure of the copolymers was examined by ^{29}Si n.m.r. spectroscopy. The main chain region of the quantitative ^{29}Si n.m.r. spectrum of polymer sample EEP5 (*Figures 1a* and *1c*) comprises two multiplet signals, in the ranges -19 to -21 and -33 to -35 ppm, respectively. Assignment of the downfield signal to the diethylsiloxane unit was made by reference to the chemical shift of poly(diethylsiloxane) homopolymer.

If the diethylsiloxane signal is considered first, for a random copolymer, the silicon nucleus is affected in three different ways according to the triad structures I–III (*Table 2*). Statistically, there are two ways of forming the central triad II, so therefore its intensity is doubled and the n.m.r. signal assumes the shape of a triplet (for a 1:1 copolymer). At higher magnetic fields the triad sequences are further influenced by the second neighbouring nucleus to give rise to pentad sequences (*Table 3*). The n.m.r. spectrum shown in *Figure 1a* exhibits three regions at -19, -20 and -21 ppm corresponding to the triads I, II and III, respectively. Assignment of the triad sequences was based on the assumption that the replacement of an ethyl group by ethylphenyl causes a downfield shift, in analogy to poly(dimethylsiloxane-*co*-diphenylsiloxane)[12]. These regions can be further resolved into pentad sequences and the diethyl-rich pentads (Ic, IId and IIIc) are clearly observed as the upfield signal of each group. The signals corresponding to the central pentad sequences, Ib, IIb, IIc and IIIb, are observed at slightly higher frequencies, while the diethyl-deficient pentads, Ia, IIa and IIIa, are barely discernible due to their low abundance. Similarly, the upfield region shows the three ethylphenylsiloxane-centred triads, IV–VI (*Table 2*), and analogous pentad structures can be observed. The ^{29}Si

Table 1 Composition and properties of poly(DES-*co*-EPhS) and poly(DES-*co*-MPhS) copolymers[a]

Polymer	X[b]	Feed[b] (%)	Found[c] (%)	$\bar{M}_n$[d] ($\times 10^{-4}$)	$\bar{M}_w$[d] ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$[d]	T_g (°C)	Type
EEP1	$(EP)_3$	2.50	2.21	2.21	3.59	1.62	-135.0	Crystalline
EEP2	$(EP)_3$	5.00	4.66	1.89	2.92	1.54	-132.8	Crystalline
EEP3	$(EP)_3$	7.50	6.70	1.56	2.24	1.44	-131.8	Crystalline
EEP4	$(EP)_3$	10.00	8.35	1.66	2.59	1.56	-131.0	Crystalline
EEP5	$(EP)_3$	20.00	16.42	1.59	2.71	1.71	-124.4	Amorphous
EMP1	$(MP)_3$	5.00	4.80	2.20	3.67	1.67	-134.5	Crystalline
EMP2	$(MP)_3$	10.00	9.13	2.14	3.79	1.77	-131.8	Crystalline
EMP3	$(MP)_3$	20.00	19.65	1.56	2.87	1.84	-122.5	Amorphous

[a] Mole ratio of monomers (total)/catalyst = 1580/1; mole ratio of monomers (total)/chain stopper = 110/1
[b] X = comonomer
[c] Determined by ^{1}H n.m.r. spectroscopy
[d] Determined by s.e.c.

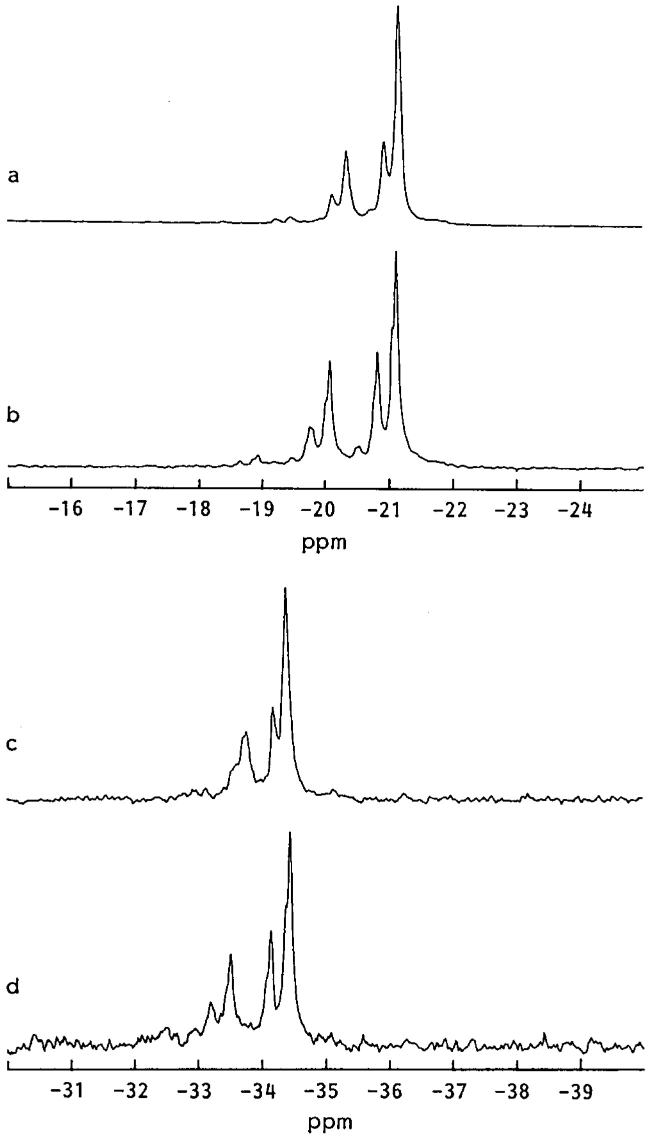

Figure 1 ^{29}Si n.m.r. spectra of the copolymers: (a) diethylsiloxane region of sample EEP5; (b) diethylsiloxane region of sample EMP3; (c) ethylphenylsiloxane region of sample EEP5; (d) methylphenylsiloxane region of sample EMP3

Table 2 Triad sequences for EEP copolymers

Triad	Sequence
I[a]	$-SiEtPhO-SiEt_2O-SiEtPhO-$
II[a]	$-SiEtPhO-SiEt_2O-SiEt_2O-$
III[a]	$-SiEt_2O-SiEt_2O-SiEt_2O-$
IV[b]	$-SiEtPhO-SiEtPhO-SiEtPhO-$
V[b]	$-SiEtPhO-SiEtPhO-SiEt_2O-$
VI[b]	$-SiEt_2O-SiEtPhO-SiEt_2O-$

[a] E-centred triads
[b] EP-centred triads

Table 3 Diethylsiloxy-centred pentad sequences in EEP copolymers

Pentad	Sequence
Ia	$-SiEtPhO-SiEtPhO-SiEt_2O-SiEtPhO-SiEtPhO-$
Ib	$-SiEtPhO-SiEtPhO-SiEt_2O-SiEtPhO-SiEt_2O-$
Ic	$-SiEt_2O-SiEtPhO-SiEt_2O-SiEtPhO-SiEt_2O-$
IIa	$-SiEtPhO-SiEtPhO-SiEt_2O-SiEt_2O-SiEtPhO-$
IIb	$-SiEt_2O-SiEtPhO-SiEt_2O-SiEt_2O-SiEtPhO-$
IIc	$-SiEtPhO-SiEtPhO-SiEt_2O-SiEt_2O-SiEt_2O-$
IId	$-SiEt_2O-SiEtPhO-SiEt_2O-SiEt_2O-SiEt_2O-$
IIIa	$-SiEtPhO-SiEt_2O-SiEt_2O-SiEt_2O-SiEtPhO-$
IIIb	$-SiEtPhO-SiEt_2O-SiEt_2O-SiEt_2O-SiEt_2O-$
IIIc	$-SiEt_2O-SiEt_2O-SiEt_2O-SiEt_2O-SiEt_2O-$

Table 4 Experimental and calculated run numbers of poly(DES-*co*-EPhS) and poly(DES-*co*-MPHS)

Polymer	X[a]	E content (%)	X content (%)	R_E[b]	R_R[c]
EEP5	EP	83.58	16.42	26.99	27.46
EMP3	MP	80.35	19.65	30.74	31.58

[a] X = comonomer
[b] Calculated from ^{29}Si n.m.r. signal intensities of E-centred triads
[c] Run number calculated for a random distribution

Table 5 Copolymer probability factors and average sequence lengths of poly(DES-*co*-EPhS) and poly(DES-*co*-MPhS)

Polymer	X[a]	P_{E-E}	P_{E-X}	P_{X-E}	P_{X-X}	l_E	l_X
EP5	EP	0.84	0.16	0.83	0.18	6.19	1.22
EF5	MP	0.81	0.19	0.78	0.22	5.22	1.28

[a] X = comonomer

n.m.r. spectrum of the copolymer sample EMP3, shown in *Figures 1b* and *1d* is similar to that of sample EEP5.

The copolymer microstructure of an AB copolymer can be expressed in terms of the run number concept[13], where the run number (R) describes the average number of monomer sequences (runs) in 100 repeat units of a copolymer chain. R is related to the ^{29}Si n.m.r. signal intensities by the following relationship:

$$R = f_A M_A = f_B M_B$$

where M_A and M_B refer to the mole fractions of the monomeric units A and B in the copolymer, and f_A and f_B are derived from the signal intensity ratios of the A and B triad units in the ^{29}Si n.m.r. spectrum:

$$f_A = 2[I/(I + II + III)]^{0.5}$$

$$f_B = 2[VI/(IV + V + VI)]^{0.5}$$

The calculated microstructure parameters for the copolymers EEP5 and EMP3 are shown in *Table 4*. These values were obtained by using the signal intensities of the diethyl-rich pentads of the triads I–III. Due to the absence of triad IV in the spectra, run numbers could only be obtained from the diethylsiloxane-centred triad region. The experimental R values were close to those calculated for a complete random distribution (R_{rand}), so therefore the microstructures were assumed to be random. Further microstructure parameters[13], such as the probability factors, P_{E-E}, P_{E-X}, P_{X-E}, and P_{X-X}, and the average sequence lengths, l_E and l_X, are given in *Table 5*.

D.s.c. studies

PDES has been shown to exhibit d.s.c. behaviour which depends strongly on the initial cooling rate of the sample[3,14], the conditions of annealing (if any)[3], and the molecular weight and previous thermal history[14]. In our studies, we have sought to remove these complications by isotropizing all samples at 50°C for 10 min prior to cooling (at a rate of 8°C min^{-1}). Since all the polymers used in this study are of equivalent molecular weights this particular aspect can be discounted.

For purposes of comparison, we have prepared a PDES homopolymer ($\bar{M}_n = 14\,500$), which is denoted by PDES-1. This polymer exhibited a glass transition (T_g) at -137°C, a rigid crystal–condis transition (T_d) at -73°C and a condis melting transition (T_m) at -8°C, all in accordance with the literature[2,3]. No evidence for the existence of the viscous crystalline phase was found, and this is attributed to the rather low molecular weights used in this study. Papkov *et al.* have demonstrated a strong molecular weight dependence for the formation of this phase[14,15].

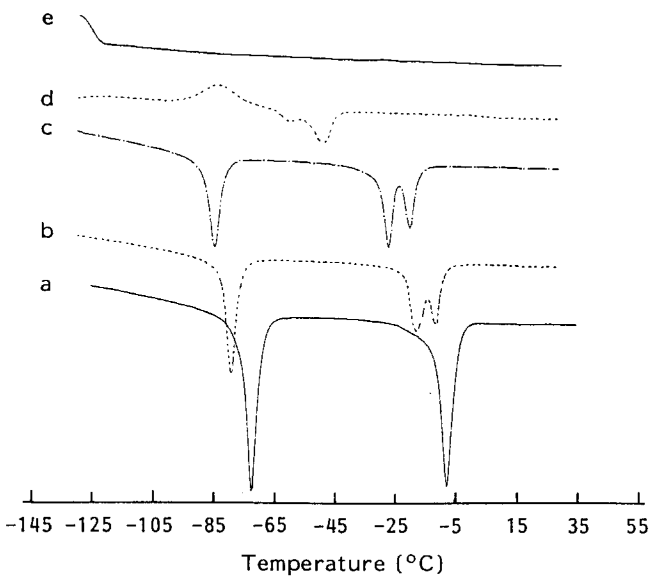

Figure 2 D.s.c. heating traces of poly(DES-*co*-EPhS) copolymers: (a) homopolymer PDES-1; (b) EEP1; (c) EEP2; (d) EEP4; (e) EEP5

D.s.c. heating traces of the homopolymer PDES-1 and the copolymers EEP1, 2, 4 and 5 are shown in *Figure 2*. Peak and onset temperatures, and transition heats and entropies are given in *Table 6*. The results clearly show that increasing the ethylphenylsiloxane (EP) content results in a decrease in the temperatures of both the T_d and T_m transitions. This is accompanied by a reduction in both the entropy and heats of transition, indicating that the crystallinity is being disrupted. The copolymer EEP5, which contained the highest level of EP (16.4%), was found to be non-crystalline, with a T_g of -124°C. Interestingly, this EP content is approximately double the amount of diphenylsiloxane required to produce an amorphous poly(diethylsiloxane-*co*-diphenylsiloxane) copolymer.

Two further phenomena are associated with increasing EP content. The first is the appearance of the condis melting transition as a doublet, the higher temperature peak of which becomes important with increasing EP content. This observation has also been made in the case of poly(diethylsiloxane-*co*-diphenylsiloxane) and poly(diethylsiloxane-*co*-3,3,3-trifluoropropylmethylsiloxane)[10]. As in the previous case, we infer that two condis phases exist in this range of compositions, with the higher melting (T_{m_2}) and lower melting (T_{m_1}) forms being favoured by the EP-rich copolymers and PDES, respectively. It is of note that the T_{m_2} transition in the copolymer EEP4 appears at about the same temperature as the glass transition (-47°C) in the poly(ethylphenylsiloxane) homopolymer.

The second unusual phenomenon is the replacement of the T_d transition by cold crystallization (T_{cc}) in the case of the copolymer EEP4. At this point we have no explanation for this; however, it probably arises from an intermediate structure lying somewhere between the amorphous and crystalline phases. No cold crystallization was observed in the case of poly(diethylsiloxane-*co*-diphenylsiloxane)[10].

Table 6 D.s.c. crystal transition parameters for poly(DES-*co*-EPhS) and poly(DES-*co*-MPhS)

Polymer	EP/(MP) (%)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J g^{-1})	ΔS (10^2 J g^{-1} K^{-1})	Assignment
EEP1	2.22	-17.1	-11.4	11.9	-	T_{m_2}
		-22.4	-17.8			T_{m_1}
		-82.7	-79.0	10.4	5.4	T_d
EEP2	4.66	-24.2	-19.8	9.6	-	T_{m_2}
		-30.9	-26.8			T_{m_1}
		-89.8	-84.2	8.2	4.3	T_d
EEP3	6.70	-35.6	-30.4	7.5	-	T_{m_2}
		-44.6	-38.9			T_{m_1}
		-97.5	-90.4	6.3	3.5	T_d
EEP4	8.35	-57.8	-49.0	5.6	-	T_{m_2}
		-65.4	-59.7			T_{m_1}
		-94.8	-83.4	-3.9	-2.0	T_{cc}
EMP1	(4.80)	-38.2	-31.8	7.5	-	T_{m_2}
		-46.5	-41.5			T_{m_1}
		-91.0	-85.5	6.2	3.3	T_d
EMP2	(9.13)	-57.4	-47.7	4.8	-	T_{m_2}
		-64.9	-58.5			T_{m_1}
		-93.6	-82.1	-3.9	-2.0	T_{cc}

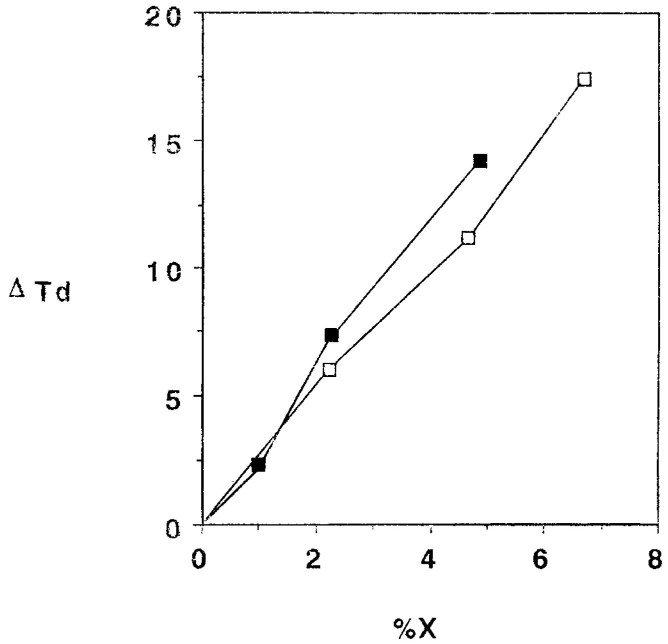

Figure 3 Plot of T_d depression *versus* aromatic siloxane content of comonomer: (■) X = diphenylsiloxane; (□) X = ethylphenylsiloxane

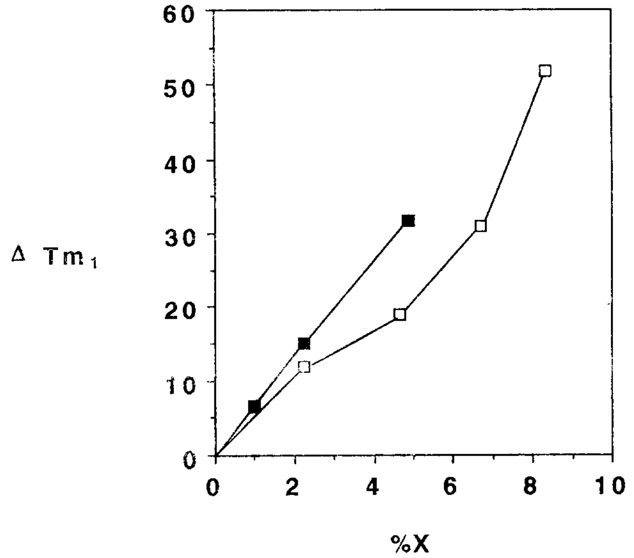

Figure 4 Plot of T_{m_1} depression *versus* aromatic siloxane content of comonomer: (■) X = diphenylsiloxane; (□) X = ethylphenylsiloxane

It is not surprising that the incorporation of the less bulky ethylphenyl and methylphenylsiloxane groups results in a smaller disruption of the crystal structure, relative to poly(diethylsiloxane-*co*-diphenylsiloxane). Thus, T_d and the two melting transition temperatures suffer a smaller shift with respect to the homopolymer (*Figures 3–5*). It is also of note that the melting transitions of poly(DES-*co*-EPhS) decrease by as much as 50°C, whereas the T_d transition is only shifted by up to one third of this. This is evidence indicating that the perturbation of the conformationally disordered crystal lattice, caused by the presence of the phenyl groups, is greater than that suffered by the rigid crystal.

Entirely analogous results were obtained for poly(DES-*co*-MPhS), as manifested by *Figure 6* and *Table 6*. The glass transition–composition plots for both copolymers (shown in *Figures 7* and *8*) are linear, and extrapolate to reasonable glass transition temperatures for the corresponding alkylphenylsiloxane homopolymers, thereby further confirming the random nature of their polymer microstructures.

Finally, the two amorphous polymers EEP5 and EMP3 gave changes in heat capacity (ΔC_p) of 0.22 and 0.29 J K^{-1} g^{-1}, respectively. If the copolymers are considered to have $E_1EP_{0.16}$ and $E_1MP_{0.20}$ repeat units, respectively, the former correspond to molar increases in heat capacity of 27.38 and 37.45 J K^{-1} mol^{-1}, respectively. These compare with a predicted value of 30.65 J K^{-1} mol^{-1} for the PDES homopolymer[3]. Recently, a value of 34.48 J K^{-1} mol^{-1} has been recommended, following a critical review of the literature[2].

CONCLUSIONS

The calorimetric data clearly show the effect of a single aromatic group in eliminating crystallinity, presumably

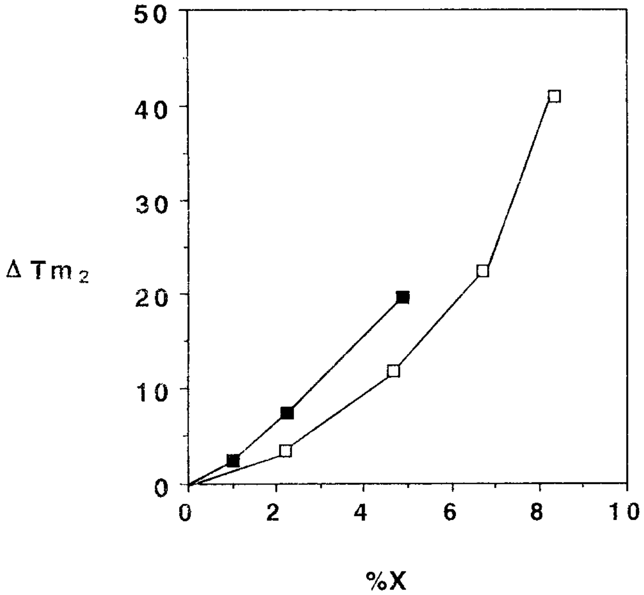

Figure 5 Plot of T_{m_2} depression *versus* aromatic siloxane content of comonomer: (■) X = diphenylsiloxane; (□) X = ethylphenylsiloxane

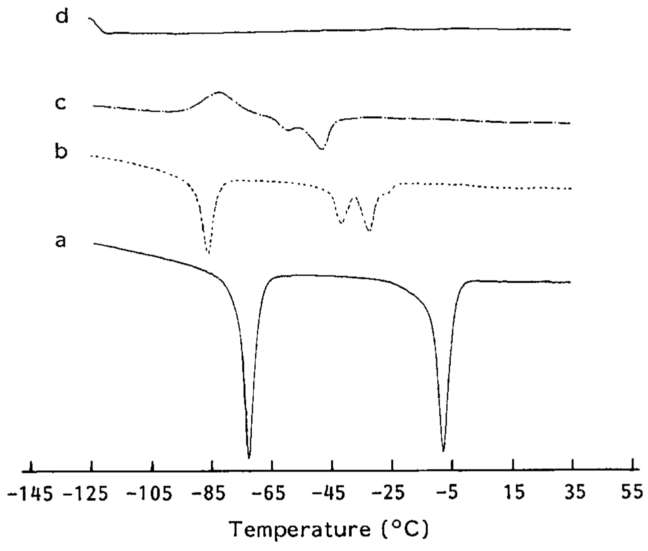

Figure 6 D.s.c. heating traces of poly(DES-*co*-MPhS) copolymers: (a) homopolymer PDES-1; (b) EMP1; (c) EMP2; (d) EMP3

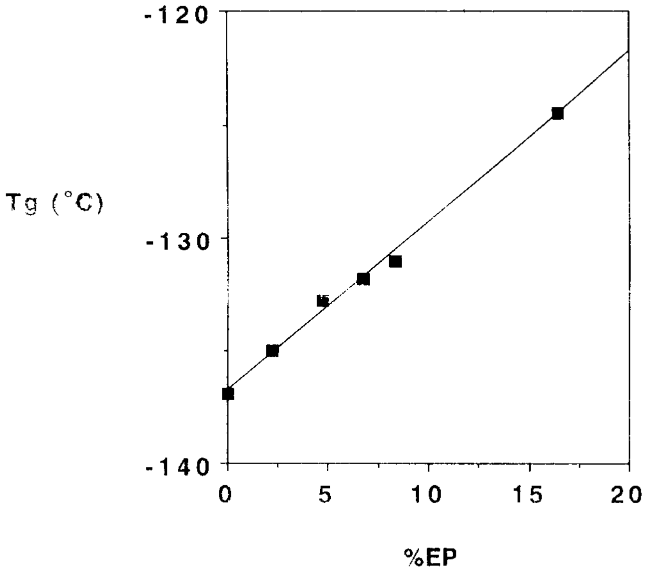

Figure 7 Glass transition temperature–composition plot for poly(DES-*co*-EPhS)

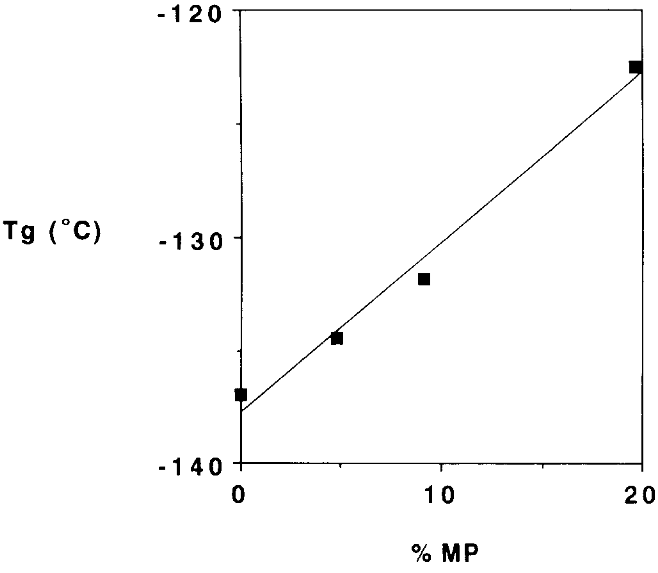

Figure 8 Glass transition temperature–composition plot for poly(DES-*co*-MPhS)

by increasing the distance between the ethyl side groups in parallel chains. Moreover, the ^{29}Si n.m.r. results indicate that a maximum average sequence length of five and six E units are required for poly(DES-*co*-EPhS) and poly(DES-*co*-MPhS) to be amorphous, respectively. Increasing the diethylsiloxane sequence length above this favours crystallization.

The extremely low glass transition temperatures observed for the copolymers EEP5 and EMP3 are at worst equivalent to that of poly(dimethylsiloxane) and represent an improvement of some 10°C over commercial Silastic elastomers. In view of the relative oxidative instability of the ethyl group at higher temperatures, potential speciality applications of these copolymers may exist in the low-temperature elastomer area. Finally, the origin of the two melting transitions T_{m_1} and T_{m_2} is not clearly understood, and we are initiating X-ray and solid-state n.m.r. investigations in order to clarify this aspect.

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REFERENCES

1 Noll, W. 'Chemistry and Technology of Silicones', Academic Press, New York, 1968
2 Varmar-Nair, M., Wesson, J. P. and Wunderlich, B. *J. Therm. Anal.* 1989, **35**, 1913
3 Wiedermann, H. E., Wunderlich, B. and Wesson, J. P. *Mol. Cryst. Liq. Cryst.* 1988, **155**, 469
4 Kogler, G., Hasendhindl, A. and Moller, M. *Macromolecules* 1989, **22**, 4190
5 Miller, K. J., Grebowicz, J., Wesson, J. P. and Wunderlich, B. *Macromolecules* 1990, **23**, 849
6 Pochan, J. M., Beatty, C. L., Hinman, D. D. and Karasz, F. E. *J. Polym. Sci. Polym. Phys. Edn* 1975, **13**, 977
7 Beatty, C. L., Pochan, J. M., Froix, M. F. and Hinman, D. D. *Macromolecules* 1975, **8**, 547
8 Froix, M. F., Beatty, C. L., Pochan, J. M. and Hinman, D. D. *J. Polym. Sci., Polym. Phys. Edn* 1975, **13**, 1269
9 Pochan, J. M., Hinman, D. D. and Froix, M. F. *Macromolecules* 1976, **9**, 611
10 Brewer, J. R., Tsuchihara, K., Morita, R., Jones, J. R., Bloxsidge, J. P., Kagas, S., Otsuki, T. and Fujishige, S. *Polymer* 1994, **35**, 5109
11 Young, C. W., Servais, P.C., Currie, C. and Hunter, M. J. *J. Am. Chem. Soc.* 1948, **70**, 3760
12 Babu, G. N., Christopher, S. S. and Newmark, R. A. *Macromolecules* 1987, **20**, 2654
13 Harwood, H. J. and Ritchey, W. M. *J. Polym. Sci.* (B) 1964, **2**, 601
14 Papkov, V. S., Godovsky, Y. K., Svistunov, V. S., Litvinov, V. M. and Zhdanov, A. A. *J. Polym. Sci., Polym. Chem. Edn* 1984 **22**, 3617
15 Papkov, V. S., Svistunov, V. S., Godovsky, Y. K. and Zhdanov, A. A. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1859