

Polymerization of poly(dimethylsiloxane) macromers: 2. Glass transition temperatures of macromer/styrene copolymers

G. Gordon Cameron* and Michael S. Chisholm†

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland, UK

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Methacrylate-ended poly(dimethylsiloxane) (PDMS) macromers of \bar{M}_n 500, 1160 and 9750 were prepared and copolymerized with styrene to yield three series of graft copolymers comprising PDMS chains on a polystyrene (PS) backbone. The low \bar{M}_n values of these copolymers (29 000–40 000) can be accounted for by the relatively low molar concentrations of polymerizable groups. D.s.c. examination of the copolymers showed that they all had a two-phase morphology consisting of PS and PDMS domains. In the case of the copolymers from the macromer of highest \bar{M}_n there was little penetration of the PS phase by PDMS, but in the other two series of copolymers the PDMS grafts had a plasticizing effect on the PS domains as indicated by a significant lowering of T_g (PS). Over the concentration range covered by these experiments (0–50% by weight PDMS), the T_g (PDMS) was higher than T_g of the free macromers and remained relatively invariant (165–170 K) with composition. This suggests that in this composition range the PDMS domains are saturated with PS segments.

(Keywords: poly(dimethylsiloxane) macromers; polystyrene-g-poly(dimethylsiloxane); glass transition temperature)

INTRODUCTION

In a previous paper¹ we described the preparation and characterization of 3-methacryloyloxypropyl poly(dimethylsiloxane) macromers which are essentially poly(dimethylsiloxane) (PDMS) oligomers with a polymerizable methacrylate terminal group. The copolymerization of these PDMS–MA macromers with styrene yields graft copolymers comprising a polystyrene (PS) backbone with PDMS side chains (*Figure 1*). The synthesis of graft copolymers in this manner has several advantages. In particular it is relatively easy to prepare graft copolymers with a predictable number of grafts per macromolecule and to control the molecular weight of the grafts; this versatility has sometimes been difficult to achieve using traditional grafting methods. By copolymerizing PDMS–MA macromers with styrene we have prepared a series of graft copolymers varying in composition and in the length of the graft chains. The effects of these two variables on the glass transition temperatures (T_g) of the copolymers are discussed in this paper.

EXPERIMENTAL

Three PDMS–MA macromers having \bar{M}_n 500, 1160 and 9750, designated PDMS–MA1 to –MA3, respectively, and their copolymers with styrene were those described previously¹. Two additional macromers PDMS–MA4 and –MA5 with \bar{M}_n 1110 and 420 respectively were prepared by the same method for use in polymer blends.

* To whom correspondence should be addressed.

† Present address: New Science Group, Imperial Chemical Industries PLC, PO Box 11, The Heath, Runcorn, Cheshire WA7 7QE, UK.

Blends of PDMS–MA4 and –MA5 with a homopolystyrene (\bar{M}_n 29 400) were prepared by dissolving the appropriate proportions in dichloromethane and allowing the solvent to evaporate at room temperature. Solvent removal was completed by drying the blends to constant weight under vacuum at room temperature.

The glass transition temperatures of all samples were determined with a Perkin–Elmer DSC-2C differential scanning calorimeter operating in the sub-ambient mode and calibrated over the 130–400 K temperature range with cyclopentane, distilled water and hexatriacontane standards. Polymer samples varied in weight from 10–25 mg and were heated at 10 K min⁻¹ under a constant stream of helium. From the thermograms the parameters T_g , T_{g1} , T_{g2} and ΔT_g (as defined in *Figure 2*) were determined as averages of several scans.

RESULTS AND DISCUSSION

PDMS–MA macromers and polyacromer

The thermal data for each of the PDMS–MA macromers are detailed in *Table 1* and a typical glass transition is shown in *Figure 2*. Cowie and McEwen² showed that the T_g 's of a series of PDMS fractions increase with increasing molecular weight according to the well-established empirical formula³

$$T_g = T_g^\infty - M_n^K \quad (1)$$

in which T_g^∞ is the glass transition temperature of a sample containing molecules of infinite molecular weight and K is a positive constant. Using d.s.c. extrapolated to infinitely slow heating rates, they found that the T_g of pure linear PDMS samples of $\bar{M}_n = 540$ and 1200 (comparable

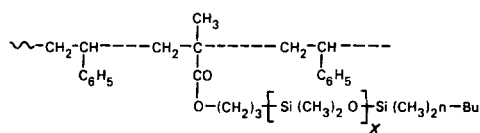
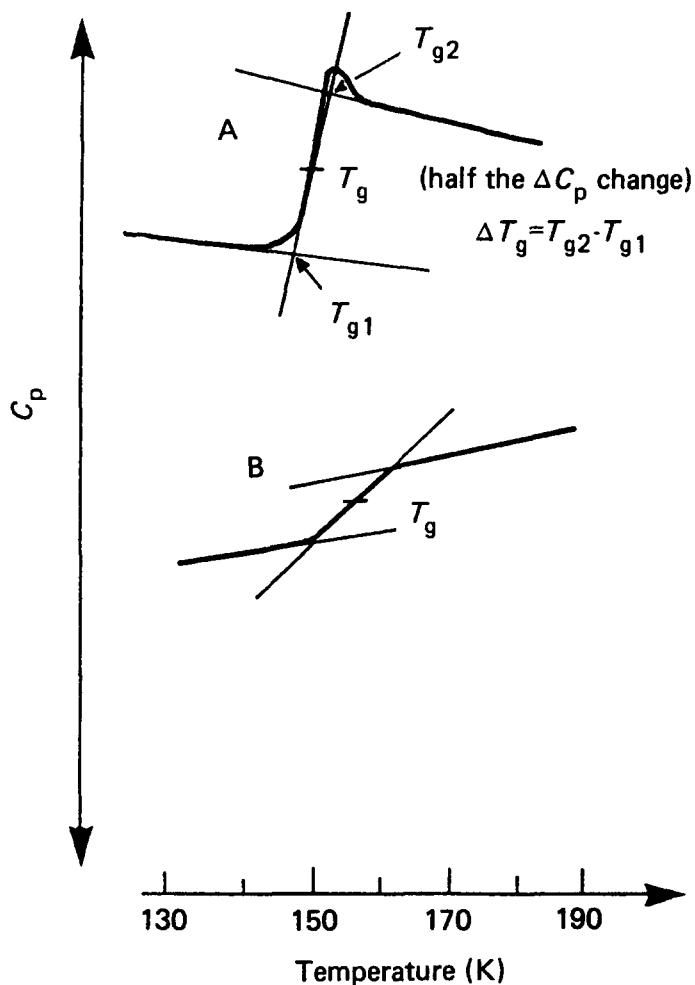


Figure 1 Styrene-co-PDMS macromer


 Figure 2 Glass transitions of: (A) PDMS-MA3 and (B) Poly(PDMS-MA3). Position of T_g and value of ΔT_g defined on curve (A)

with PDMS-MA1 and -MA2 respectively) are 136 and 141 K respectively. At $\bar{M}_n > 4200$ T_g reaches a limiting value of 148 K. Krause *et al.*⁴ and Adachi *et al.*⁵ obtained similar results. Table 1 reveals that the T_g 's of our macromers deviate from the normal T_g - \bar{M}_n relationship. The polar, terminal methacrylate group on each macromer molecule apparently increases the T_g of the low molecular weight macromer above that of pure PDMS (by about 16 K for PDMS-MA1 and 3.5 K for PDMS-MA2). With high molecular weight macromers the methacrylate end group constitutes only a very small part of the total polymer chain and its influence on the T_g is minimal. Hence, the T_g of PDMS-MA3 (\bar{M}_n 9750) is close to that of a pure, linear PDMS sample.

It is interesting to compare the thermal data of a PDMS-MA macromer with that of its polymacromer (Figure 2) (poly(PDMS-MA3)), prepared from the radical homopolymerization of PDMS-MA3. The T_g of the polymacromer (\bar{M}_n 92 200, DP 9.5) is 6.5 K higher than that of PDMS-MA3. This increase in T_g on homopolymerization is presumably a result of the restrictions on segmental motion imposed by the close

proximity of the macromer chains in the highly branched polymacromer. This restriction of segmental motion is likely to be greater on segments close to the polymacromer backbone than on those segments nearer the free chain ends. This could explain the higher value of ΔT_g of the polymacromer.

Poly(styrene-co-PDMS-MA) copolymers

Poly(styrene-co-PDMS-MA) copolymers were prepared from each macromer, thus providing three copolymer series varying in graft length. Composition, molecular weight, and the number of graft chains per macromolecule for each copolymer are listed in Table 2. Values of \bar{M}_n for each copolymer were determined by g.p.c. calibrated with polystyrene standards. Because this calibration is strictly valid only for linear polymers the molecular weights, and hence also the number of graft chains per macromolecule, should be regarded as approximate.

Table 2 reveals that the values of \bar{M}_n within each series of copolymers and among the three series do not vary much, although there is a trend to higher molecular weights with increasing macromer content, and copolymers in the PDMS-MA3 series have somewhat lower molecular weights than the others. All the copolymers, however, have low molecular weights. This effect has been noted by other workers^{6,7} who have suggested that it is a general feature of macromer-small monomer copolymerizations resulting from the reluctance of macromers to polymerize (steric effects), the low concentration of vinyl groups in the macromer, or transfer reactions between growing radicals and initiator molecules. In our macromer-styrene system we believe that low molecular weights are simply a consequence of the low concentration of polymerizable vinyl groups. To check this point a homo-polystyrene was prepared with temperature, monomer and initiator concentrations identical to those employed in the macromer copolymerizations. The \bar{M}_n of the resulting polystyrene was 29 400, which is comparable to the molecular weights of macromer copolymers. A theoretical calculation⁸ based on kinetic data quoted in the literature yielded a \bar{M}_n value of 37 600; again of comparable magnitude. It is quite probable that most of the assumed peculiarities of macromer polymerizations can be attributed to low molar concentrations of monomer and that there is otherwise no essential difference between the polymerization of a macromer and that of a conventional small monomer.

The thermograms of each styrene-siloxane copolymer showed two glass transitions, indicating a two-phase morphology. Between 300 and 380 K there was a clear, discrete transition attributable to PS domains, while the polysiloxane domains were manifest by a much weaker transition in the range 165-170 K.

Table 1 Glass transition data on macromers

Macromer	\bar{M}_n	T_g (K)	ΔT_g (K)
PDMS-MA1	500 ^a	152	4
PDMS-MA2	1160 ^a	144	3
PDMS-MA3	9750 ^a	149	3.5
Poly(PDMS-MA3)	92 200 ^b	155.5	11

^a By v.p.o.

^b By g.p.c. with PS standards

Table 2 Physical data on polymers and blends

Sample	Wt. fraction of macromer	No. graft chains per macromolecule ^a	\bar{M}_n^b	PS domains		PDMS domains	
				T_g (K)	ΔT_g (K)	T_g (K)	ΔT_g (K)
Poly(styrene-co-PDMS-MA1)	0.11	7.4	33 700	360	9.5	169	8
	0.23	15.0	32 800	340	4.5	168	4
	0.28	21.2	37 800	333	15.0	168	8.5
	0.38	29.6	39 000	320	16.5	167	7
	0.45	37.8	42 000	301	18.5	170	4.5
Poly(styrene-co-PDMS-MA2)	0.13	3.8	34 200	363	8.5	167.5	5
	0.22	5.9	31 400	349	15	167	8.5
	0.33	9.0	31 500	339	21.5	166	8
	0.40	12.5	36 200	324	17	166	9
	0.50	21.8	50 600	311	18	165	8.5
Poly(styrene-co-PDMS-MA3)	0.03	0.1	27 300	380	7	165	8.5
	0.04	0.1	26 900	380	9	167.5	5
	0.06	0.2	30 000	381	6	166	9
	0.07	0.2	27 900	377	10	167	8.5
	0.13	0.4	28 600	377	7	166	8
PS	0	0	29 400	381	8	-	-
PS/PDMS-MA4 blend	0.26	-	-	359.5	11	147	4
	0.51	-	-	362	16	146.5	3
PS/PDMS-MA5 blend	0.26	-	-	346	16	147	5.5
	0.50	-	-	347	23	148	4

^aNo. graft chains per macromolecule = \bar{M}_n (copolymer) \times wt. fraction macromer \div \bar{M}_n (macromer)

^bBy g.p.c. with PS standards

Figure 3 shows typical PS glass transitions from the copolymers and includes a glass transition from the homo-polystyrene ($\bar{M}_n = 29\,400$) for comparison. The T_g data for the PS domains of the copolymers are presented graphically in Figure 4, the vertical bars representing ΔT_g . A number of trends are discernible in Figure 4. Firstly, as the weight fraction of polysiloxane is increased the T_g (PS) decreases, the depressing effect being greatest in copolymers containing the macromers of shortest chain length. Secondly, for the PS/PDMS-MA1 and -MA2 series of copolymers values of ΔT_g (PS) are greater than that of the PS standard and show an increasing trend up to ca. 18.5 K as the proportion of macromer in the copolymer increases. For the copolymer containing the long-chain macromer PDMS-MA3, however, ΔT_g (PS) is ca. 8 K, comparable with that of the homo-polystyrene standard.

These results suggest that in copolymers with long graft chains but low graft densities (i.e. from PDMS-MA3) the microphases are well developed and the phase boundaries reasonably sharp. With short graft chains at higher densities, however, there is considerable penetration of the PS domains by siloxane chains resulting in more diffuse phase boundaries (wider ΔT_g) and a plasticizing effect of siloxane on PS (lowering of T_g (PS)). The degree of interpenetration of the two components of the PS/PDMS-MA copolymers can be judged also by comparing the T_g 's with those which would arise from complete miscibility. For this purpose the Gordon-Taylor equation⁹

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (2)$$

gives the glass transition temperature T_g of a miscible blend in terms of the glass transition temperatures T_{g1} and T_{g2} of the two components, and w_1 and w_2 , their respective weight fractions. Taking T_g 's as 381 K and 155.5 K for PS

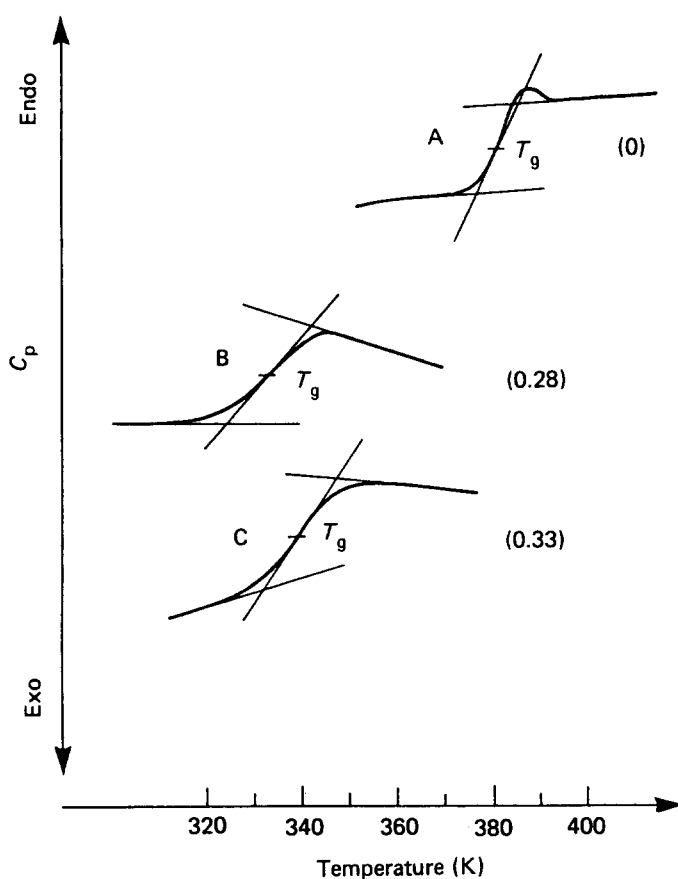


Figure 3 Typical polystyrene glass transitions of: (A) polystyrene ($M_n = 29\,400$); (B) styrene-co-PDMS-MA1; (C) styrene-co-PDMS-MA2. Weight fraction of macromer in brackets

and polysiloxane (PDMS-MA3) respectively, the Gordon-Taylor curve in Figure 4 was generated. The proximity of this curve to the experimental one for PDMS-MA1 copolymers supports the view that an

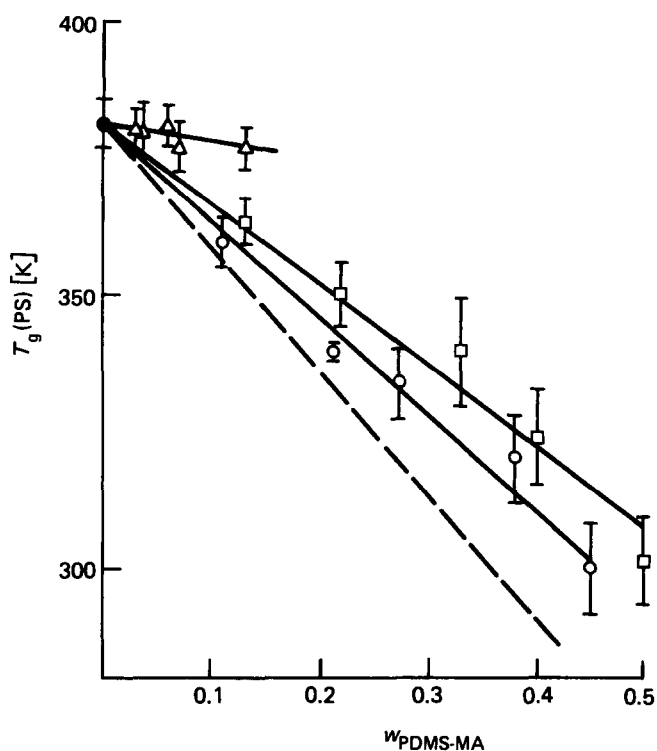


Figure 4 Glass transition temperatures of polystyrene domains $T_g(\text{PS})$ versus weight fraction $w_{\text{PDMS-MA}}$ of macromer in copolymers of: (○), PDMS-MA1; (□), PDMS-MA2; (△), PDMS-MA3. Vertical bars represent ΔT_g . Broken line from equation (2)

appreciable degree of phase miscibility exists in these copolymers. In a blend of PS and low MW PDMS the extent of miscibility is much less than in the copolymers. Thus, Table 2 shows that the blends of PDMS-MA5 and -MA4 with PS (\bar{M}_n 29 400) show appreciably higher T_g 's (PS) than the copolymers of PDMS-MA1 and -MA2 with comparable PDMS content. Also, the blends were opaque, in contrast to the optically clear films produced by the macromer copolymers—again an indication of the more limited miscibility in blends compared with the graft copolymers produced by the macromers. Incorporation of PDMS as graft chains on PS therefore achieves a degree of enforced miscibility.

The values of $T_g(\text{PDMS})$ in Table 1 show, in contrast to the T_g 's (PS), little variation with copolymer composition or graft length. All values lie within the range 165–170 K which is 15–25 K higher than the T_g 's of the unbound macromers, and the values of $\Delta T_g(\text{PDMS})$ are two to three times those of the pure macromers. This behaviour is consistent with a degree of admixing of PS segments in the PDMS microphases, but it is also conceivable that

there is a loss of mobility in the PDMS chains when they are connected to a polymer backbone; this effect was noted when PDMS-MA3 was polymerized. The relative invariance in $T_g(\text{PDMS})$ with composition indicates that, if there is penetration of the PDMS domains by PS segments, over the composition range 0–50% PDMS by weight the PDMS phase is saturated with PS. It is conceivable, however, that at the other end of the composition range, 50–100% PDMS, there would be a dependence of $T_g(\text{PDMS})$ on composition. This end of the range is not readily accessible by the macromer copolymerization approach.

Diblock PS/PDMS copolymers show thermal behaviour broadly in line with that of our graft copolymers and Krause *et al.*⁴ have interpreted this in a similar manner. In general the morphology of block copolymers has received more attention than that of graft copolymers. Price *et al.*¹⁰ have studied phase separation in PS-polyisoprene graft copolymers and have shown by electron microscopy that these have a two phase morphology of regular PS domains in a polyisoprene matrix. They observed, however, that domain boundaries were diffuse and that structural features were present within domains, both observations indicating that the less ordered molecular structure of graft copolymers can lead to less efficient ordering on a macroscopic scale. In the absence of more experimental data, e.g. electron micrographs, we are unable to comment in such detail on the morphology of our PS-PDMS graft copolymers.

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