# Polymerization of poly(dimethylsiloxane) macromers: 3. Copolymers with acrylonitrile

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Copolymers of acrylonitrile ($M_2$) and two methacrylate-ended polysiloxane (PDMS) macromers have been prepared and characterized. As in previous investigations, the errors in $r_1$ render their values meaningless. Values of $r_2$ could be determined with more precision and increased from 0.41 to 0.89 as the molecular weight ($M_n$) of the macromer increased from 500 to 1100. This effect, which has been noted previously, is probably due to a steric or excluded-volume effect, possibly involving repulsion between the growing chain and that of the macromer chain. Differential scanning calorimetry examination showed that the copolymers had a two-phase morphology comprising polyacrylonitrile and PDMS domains. There was slight interpenetration of one domain by the other and the PDMS exerted a significant plasticizing effect on the glassy domain only when the macromonomer content exceeded 60–70% by weight. The general lack of miscibility can be ascribed to the relatively high degree of incompatibility between PDMS and polyacrylonitrile.

**(Keywords: poly(dimethylsiloxane) macromers; copolymers with acrylonitrile; reactivity ratios; thermal properties)**

## INTRODUCTION

In a previous paper[1] we described the preparation and characterization of 3-methacryloyloxypropyl poly(dimethylsiloxane) macromers (poly(dimethylsiloxane) (PDMS) oligomers with a polymerizable methacrylate terminal group). The copolymerization of these PDMS–MA macromers with styrene yielded graft copolymers comprising a polystyrene (PS) backbone with PDMS side chains. The effect of graft copolymer composition and graft chain length on the glass transition temperatures ($T_g$) of these copolymers has also been described[2]. This paper discusses the copolymerization of PDMS–MA macromers with acrylonitrile (AN) and the thermal properties of the resultant graft copolymers shown in *Figure 1*.

## EXPERIMENTAL

The preparation of PDMS–MA macromers (designated PDMS-MA1 ($M_n = 500$) and -MA4 ($M_n = 1110$)) has been described previously[1]. These macromers were copolymerized in benzene/DMF (1:1) solutions with 1.0 mol% azobisisobutyronitrile (AIBN) initiator at 60°C. Polymerizations were made under vacuum in glass dilatometers to low conversion. For each macromer/AN pair, five copolymers of varying compositions were prepared, the mole fraction of AN ($M_2$) in the monomer feed being varied as widely as possible to optimize accuracy in the calculation of reactivity ratios. For PDMS–MA1, the mole fraction of AN varied from 0.92 to 0.99, and for PDMS–MA4, the corresponding range was 0.95–0.97.

After precipitating the copolymers in petroleum ether (b.p. 40°C–60°C), unreacted macromer and AN was removed by multiple precipitation from *N,N'*-dimethylformamide solution into petroleum ether. The precipitation process was monitored by periodically recording i.r. spectra of the copolymers. Precipitation was continued until all the free macromer had been removed as indicated by the constancy of the intensity of the PDMS–MA C=O absorption peak at 1720 $cm^{-1}$ (usually after three precipitations).

The composition of the copolymers was calculated by elemental analyses of both nitrogen and silicon. The nitrogen, as determined by the Kjeldahl method[3], gave the AN content. Silicon was estimated gravimetrically[4], after a prior acid/perchlorate digestion, to give the PDMS–MA content. The reactivity ratios were calculated from the copolymer compositions by the Kelen–Tüdös method[5].

The glass transition temperatures of the copolymers were determined with a Perkin–Elmer DSC-2C differential scanning calorimeter operating in the sub-ambient mode and calibrated over the 130 K–400 K temperature range with cyclopentane, distilled water, and hexatriacontane standards. Polymer samples (10–25 mg) were heated at 10 K $min^{-1}$ under a constant stream of helium. From the thermograms the parameters $T_g$ and $\Delta T_g$ (as defined previously[2]) were calculated.

## RESULTS AND DISCUSSION

### *Reactivity ratios*

The reactivity ratios for each macromer/AN copolymer series, calculated from nitrogen and silicon analyses, are given in *Table 1*. For copolymers of the macromer of lower molecular weight PDMS–MA1, the macromer contents calculated from silicon analyses were consistently lower than the values obtained from the nitrogen analyses. Examination of the analytical data for PDMS–MA1 and –MA4 copolymers suggested that the nitrogen analyses were more reliable and that the silicon analyses of

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PDMS–MA1 copolymers did not account for all the silicon present. The most plausible explanation for this is that in the acid/perchlorate digestion stage of analyses some of the silicon was lost in volatile fragments by scission of the short PDMS side chains. The side chains in the PDMS–MA4 series, being longer, were not so susceptible to loss in this manner. Because of the unreliability of the silicon analyses for PDMS–MA1 copolymers, only the reactivity ratios calculated from the nitrogen contents of these copolymers are quoted in *Table 1*.

The values of $r_1$ in *Table 1* are meaningless because of the associated large error that is commonly observed in macromer/small-monomer copolymerizations. The values of $r_2$ are more significant, however, varying from 0.41 for the PDMS–MA1/AN system to $r_2 = 0.89$, 1.14 for the PDMS–MA4/AN pair. For the copolymerization of methyl methacrylate ($M_1$) with AN the literature gives $r_1 = 1.20$ and $r_2 = 0.15$ (ref. 6); the corresponding data for n-butyl methacrylate ($M_1$) and AN ($M_2$) are $r_1 = 1.08$ and $r_2 = 0.31$ (ref. 7). These values for $r_2$ are plotted with the corresponding data for the two macromers *versus* the length of the extended ester side chain in *Figure 2*. Although the data are limited in number in this instance, the graph shows the same type of sigmoidal increase in $r_2$ with side-chain length as we reported for the styrene/macromer copolymerizations[1]. With the proviso that the shape of this curve may be influenced by the change from methylene to siloxane groups, this behaviour was explained in terms of a 'steric' effect, more precisely an excluded-volume effect, by which the long side chain hinders access of the active radical to the terminal double bond of the macromer, thus depressing the rate constant $k_{21}$ and hence leading to a rise in $r_2$. A similar effect has recently been recorded for poly(ethylene oxide) macromers by Ito *et al.*[9], who elaborated on this explanation and pointed out the importance of repulsive effects between the macromer chain and the chain of the growing polymer. It is noteworthy that in *Figure 2*, the region of rapid rise in $r_2$ occurs when the macromer side-chain length reaches 25–40 Å, while the corresponding figure for the PDMS–MA/styrene system is 5–15 Å (ref. 1). This may be due to the difference in the sizes of the phenyl and nitrile groups. At the dimensions of a conventional small monomer copolymerization, this effect probably has a negligible influence on $r_2$. However, macromer copolymerizations may be more sensitive to such effects and when $M_2$ contains the bulky phenyl group, steric interactions between the macromer side chain and the active $M_2$ radical may occur with relatively short macromers. When $M_2$ carries the smaller nitrile group steric interactions may become apparent only with longer macromers.

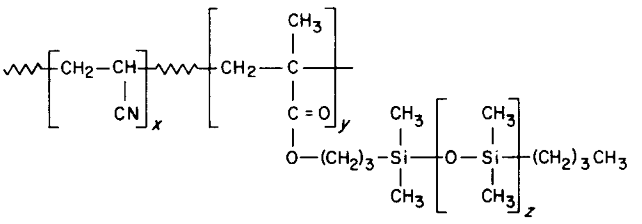

**Figure 1** Structure of PDMS–MA macromer/acrylonitrile copolymer

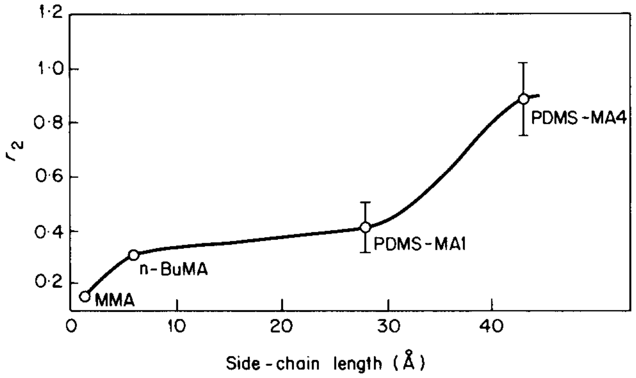

**Figure 2** Reactivity ratio $r_2$ for acrylonitrile ($M_2$)/n-alkyl methacrylate copolymerizations *versus* length of extended side chain

By setting $Q$ and $e$ values for styrene as 1.00 and $-0.80$ respectively[10,11] the $Q$ and $e$ values for PDMS–MA1 and –MA4 shown in *Table 1* were calculated from the macromer/styrene reactivity ratios published previously[1]. Bearing in mind the considerable errors involved in such calculations, the average $Q$ and $e$ values of the two macromers, 0.37 and 0.40 respectively, compare reasonably well with $Q = 0.74$ and $e = 0.40$ for the structurally related methyl metacrylate[12]. The $e$ values, as might be expected, are particularly close. These data were then combined with the $Q$–$e$ values of AN ($Q = 0.60$, $e = 1.20$ (ref. 12)) to yield calculated values of $r_1$ and $r_2$ for the macromer/AN ($M_2$) copolymerizations (*Table 1*). For the PDMS–MA4/AN pair the observed and calculated values of $r_2$ agree reasonably well within the combined error limits. (Values of $r_1$ are not compared because of the large error in the experimental values.) The theoretical and experimental values of $r_2$ for the PDMS–MA1/AN do not agree so well. This may be due in part to the fact that the side chain length of PDMS–MA1 lies within the range that is most sensitive to differences in steric interactions when the comonomer is changed from styrene to AN (see above). The $Q$–$e$ scheme, however, is not exact; in particular it does not make adequate allowance for steric effects. The extent of agreement between theory and experiment discussed above is quite acceptable and serves

**Table 1** Experimental and calculated reactivity ratios for PDMS–MA macromer($M_1$)/acrylonitrile($M_2$) copolymerizations

| | Experimental values | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Si analysis | | N analysis | | Calculated values | | | |
| Macromer | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $Q^a$ | $e^a$ | $r_1{}^c$ | $r_2{}^c$ |
| PDMS–MA1 | - | – | 1.93 ± 2.36 | 0.41 ± 0.09 | 0.34 ± 0.07 | 0.48 ± 0.14 | 0.80 ± 0.21 | 0.74 ± 0.22 |
| PDMS–MA4 | 10.6 ± 9.6 | 1.14 ± 0.21 | 5.4 ± 11.1 | 0.89 ± 0.15 | 0.39 ± 0.13[b] | 0.32 ± 0.21[b] | 0.86 ± 0.34 | 0.54 ± 0.27 |

[a] Calculated from PDMS–MA/styrene copolymerizations (ref. 1); for styrene $Q = 1.00$, $e = -0.80$

[b] From data for PDMS–MA2 (ref. 1) ($\bar{M}_n = 1160$ cf. $\bar{M}_n = 1110$ for PDMS–MA4)

[c] From $Q$ and $e$ values of macromers with $Q = 0.60$ and $e = 1.20$ for acrylonitrile

to underline the point made elsewhere[1] that in their copolymerization behaviour there are no fundamental differences that distinguish macromers from conventional small monomers.

### *Glass transition temperatures*

The d.s.c. thermograms of each PDMS–MA/AN copolymer showed two glass transitions, one in the range 327 K–365 K attributable to PAN microphases, and the other, which was much weaker and sometimes difficult to discern, at 156 K–158 K attributable to PDMS domains. A sample of homo-PAN, prepared under conditions identical to those for the copolymers, gave $T_g = 372$ K, which agrees with literature data[13,14], and $\Delta T_g = 14$ K. The glass transition data are summarized in *Table 2* and the values of $T_g$ (PAN) are plotted *versus* the weight fraction of copolymerized macromer in *Figure 3*.

The data in *Table 2* and *Figure 3* show that the PDMS graft chains have a plasticizing effect on the PAN domains; when compared with the standard homo-PAN, $T_g$ (PAN) is lowered and $\Delta T_g$ is widened slightly. As for polystyrene/PDMS–MA copolymers, the shorter siloxane chains are more effective in this respect. However, the plasticizing effect is very much less marked when PAN replaces PS as the hard component. Thus $T_g$ (PS) is lowered by more than 80 K in a copolymer containing 50 wt% of PDMS–MA1, while the corresponding decrement in $T_g$ (PAN) is under 20 K. The marked difference in thermal behaviour of the PS and PAN series of copolymers can be attributed to the lower miscibility of PAN with the siloxane graft chains. Only when the PDMS–MA1 content exceeds 60–70 wt% is there an appreciable decrease in $T_g$ (PAN) (curve 2, *Figure 3*) from which the value of $T_g$ presumably declines towards that of poly(PDMS–MA): *ca.* 155 K (ref. 2). It is possible that somewhere in this region the copolymer acquires a single-phase morphology as the length and number of PAN segments declines and the polymer acquires the characteristics of a random, rather than a graft, copolymer.

In contrast to the $T_g$s of the PAN phases, the values of $T_g$ (PDMS) in *Table 2* show little variation with copolymer composition or graft length. All values lie within the range 156 K–158 K, which is 10 K–12 K higher than the $T_g$s of the unbound macromers, while the $\Delta T_g$ (PDMS) values are equal to or only slightly greater than those of the pure macromer[2]. The elevation in $T_g$ (PDMS) is presumably the result of some penetration of PAN segments into the PDMS microphases, but the invariance of $T_g$ (PDMS) with graft length and composition indicates that, over the composition range covered in this work, saturation of the PDMS phases by PAN has occurred. The elevation of $T_g$ (PDMS) in these copolymers is appreciably less than was observed in the corresponding styrene copolymers. Again this can be attributed to the relatively high degreee of immiscibility of PAN, compared with PS, and the siloxane graft chains. In the PAN series of copolymers the two phases are more sharply defined and the values of $T_g$ are closer to those of the constituent polymers.

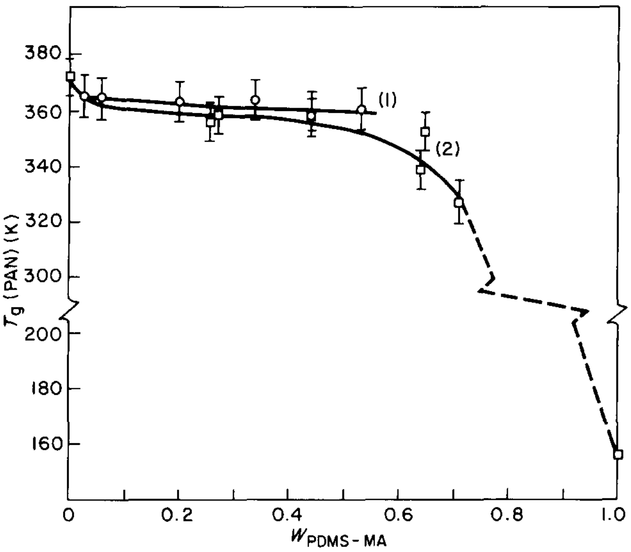

**Figure 3** Glass transition temperatures of polyacrylonitrile domains $T_g$ (PAN) *versus* weight fraction $W_{PDMS-MA}$ of macromer in copolymers: curve (1), PDMS-MA4; curve (2) PDMS-MA1. Vertical bars represent $\Delta T_g$

**Table 2** Thermal properties of poly(acrylonitrile-co-PDMS–MA) copolymers

| End group (sample) | Wt. fraction of macromer | PAN domains | | PDMS domains | |
|---|---|---|---|---|---|
| | | $T_g$ (K) | $\Delta T_g$ (K) | $T_g$ (K) | $\Delta T_g$ (K) |
| -MA1 | 0.26 | 356 | 14 | 158 | 4 |
| | 0.27 | 358 | 13 | 158 | 3 |
| | 0.44 | 358 | 12 | 156 | 3 |
| | 0.65 | 353 | 15 | 158 | 5 |
| | 0.64 | 338 | 16.5 | 158 | 3 |
| | 0.71 | 327 | 17 | 158 | 3 |
| -MA4 | 0.03 | 365 | 17.5 | 157 | 4 |
| | 0.06 | 364 | 17 | 158 | 5 |
| | 0.20 | 363 | 16 | 156 | 3 |
| | 0.34 | 363 | 16 | 156 | 3 |
| | 0.44 | 358 | 16.5 | 156 | 3 |
| | 0.53 | 360 | 17 | 156 | 3 |
| PAN | 0 | 372 | 14 | – | – |

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