Bulk copolymerization of methacryloyloxypropyl functionalized siloxane macromonomers with styrene:
2. Graft copolymer formation

Michael S. O'Shea[*] **and Graeme A. George**[†]
School of Chemistry, Queensland University of Technology, Brisbane 4000, Australia
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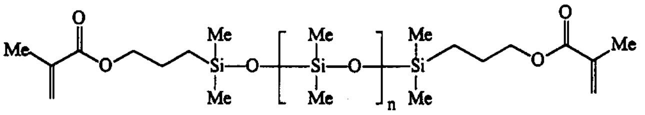
An α,ω-(3-methacryloyloxypropyl dimethyl siloxane) macromonomer (I) with a molecular weight of 21 300 g mol^{-1} was copolymerized with styrene in bulk at 60°C using azobisisobutyronitrile as the initiator. Loadings from 10 to 50 wt% of the macromonomer were used. Cloud point and optical microscopy studies showed mixtures containing > 10 wt% macromonomer were phase separated before polymerization, whereas mixtures containing 10 wt% macromonomer became phase separated after 18 min reaction time. The siloxane–polystyrene copolymers formed have a graft structure containing up to three macromonomers in a polystyrene backbone with no crosslinking. ^{1}H n.m.r. analysis showed one unreacted methacryloyloxypropyl group remained per macromonomer. Compositional and molecular weight studies showed that the macromonomer did not homopolymerize under these conditions. The differences between this behaviour and that of a lower molecular weight macromonomer (3700 g mol^{-1}) which formed both siloxane homopolymer and a crosslinked network is believed to be related to shielding of the methacryloyloxypropyl reactive groups.



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(Keywords: macromonomer; siloxanes; styrene copolymers)

INTRODUCTION

Many useful materials such as impact modified polymers, gas permeable membranes and microlithographic coatings have been produced using graft copolymers made from siloxane macromonomers, siloxanes and organic monomers or blends of these graft copolymers with organic polymers[1–3].

Macromonomers can be used in a variety of polymerization reactions (i.e. free radical, ionic, condensation or co-ordination systems) to prepare controlled polymer structures. The reactivity of a macromonomer towards the comonomer is controlled by the type of terminal functional group present and the length of the macromonomer chain. In turn, the macromonomer reactivity determines the number of grafts expected in a copolymer for various feed compositions[4].

Free radical polymerization of monofunctional macromonomers with unsaturated monomers is by far the most common method for preparing siloxane-containing graft copolymers. Various comonomers have been used including acrylonitrile[5], styrene or its analogues[4,6–10] and acrylates[1,4,9–12].

Tsukahara *et al.*[11], Cameron and Chisholm[6,7] and Kawakami and Yamashita[4] noticed a decrease in the reactivity of methacrylate and styrene monofunctional siloxane macromonomers with increasing molecular weight. Cameron and Chisholm[6,7] postulated that the decreased reactivity with increased macromonomer molecular weight was due to steric or excluded volume effects, possibly involving repulsion between the growing polymer chain and that of the macromonomer chain.

Tsukahara *et al.*[11] proposed that for homogeneous copolymerizations a large macromonomer could not sufficiently interpenetrate the propagating comonomer chain to bring its end group near the radical site due to the incompatibility between the siloxane macromonomer and the polymerized comonomer [i.e. poly(methyl methacrylate) (PMMA)]. Overlap concentrations calculated from the radius of gyration data for polydimethylsiloxane (PDMS) and PMMA showed a decrease with increasing molecular weight of the siloxane macromonomer or comonomer. They[11] also proposed that high molecular weight macromonomers were more likely to form a random coil, whereas low molecular weight macromonomers did not. This meant that end groups on

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[*] Present address: CRC for Polymer Blends, Faculty of Engineering, Monash University, Wellington Road, Clayton, Vic 3168, Australia
[†] To whom correspondence should be addressed

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smaller macromonomers could always approach and contact a propagating radical without significant interpenetration.

Tenhu and Heino[13] copolymerized dimethacryloyloxypropyl functionalized siloxane macromonomers of molecular weight 35 000 g mol^{-1} in aqueous solution with styrene for 8 h at 80°C producing a phase separated graft copolymer showing no indication of crosslinking.

In a study of the crosslinking of diacrylate functionalized siloxane macromonomers of various chain lengths, Katz and Zewi[14] found that incomplete reaction of the acrylate functional groups occurred, especially for the diacrylate siloxanes with the higher molecular weights (chain lengths). This resulted in some of the siloxane macromonomers acting as grafts, with one acrylate on the macromonomer remaining unreacted, thus resulting in a free siloxane chain end. In a related study[14] of the free radical copolymerization of hydroxy terminated difumarate functionalized siloxane macromonomers of various chain lengths with styrene monomer in bulk, it was found that as the degree of polymerization of the dimethylsiloxy unit was increased above eleven the polymerization mixture became opaque. This was attributed to the limited solubility of siloxane in styrene and the incompatibility between PDMS and polystyrene (PS), both of which depend on chain length.

Suzuki and Okawa[12] copolymerized macromonomers containing both alkenyl and methacryl functional groups attached to opposite ends of siloxane macromonomers with methyl methacrylate and styrene under free radical conditions. It was found that generally only the methacryl functional group on the siloxane reacted. This produced PMMA-*g*-PDMS and PS-*g*-PDMS graft copolymers with the siloxane grafts containing unreacted alkenyl groups at the ends of the grafts.

In this study, a siloxane macromonomer with 3-methacryloyloxypropyl (MOP) end groups and peak molar mass (M_p) of 21 300 g mol^{-1} was copolymerized with styrene using a free radical initiator (azobisisobutyronitrile, AIBN) to investigate the effect of macromonomer concentration and conversion time on the reactivities of the macromonomer and styrene and the structure of the resultant polymer. The effect of molecular weight between functional groups is also investigated by comparison with earlier work by these authors using a shorter, difunctional macromonomer ($M_p = 3700$ g mol^{-1}) copolymerized under identical conditions.

EXPERIMENTAL

Synthesis of siloxane macromonomers

Duplock *et al.*[15] synthesized the difunctional PDMS macromonomer with MOP end groups used in this study by reaction of allyl methacrylate with a silyl hydride functional siloxane prepolymer.

As in the previous study[16] the inhibitor was removed from styrene monomer (Merck Schuchardt, >99% pure) just prior to each polymerization. AIBN (Aldrich) was reprecipitated from methanol and stored in a freezer until required.

Macromonomer purity and characterization

^{1}H n.m.r. was used to determine the relative amounts of organic groups attached to the siloxane macromonomer (both neo and iso) and the amount of polymerizable impurities[16].

It was determined that $87.2 \pm 7.4\%$ of unsaturated functional groups were MOP endcapped siloxane macromonomer (assuming no isobutyrate endcapped chains) of which 80% were attached by propyl and 20% by isopropyl chains. The amount of residual allyl isobutyrate and propyl methacrylate was estimated to be $6.9 \pm 2.9\%$ and $5.9 \pm 3.0\%$, respectively. As for the lower molar mass macromonomer previously studied[16], it was assumed that the reactive impurities present would have only a minor effect on the crosslinking, physical properties or the reactivity of this macromonomer.

The molecular weight of the MOP encapped siloxane macromonomer was estimated from ^{1}H n.m.r. to be $28\,285 \pm 3625$ g mol^{-1} by assuming a functionality of two.

G.p.c. analysis in toluene showed a M_p of 21 310 ± 3075 g mol^{-1} and number- and weight-average molecular weights (M_n and M_w, respectively) of 12 420 and 26 540 g mol^{-1}, respectively. This corresponded to a polydispersity (M_w/M_n) of 2.14. The M_p was deemed to be more reliable due to the presence of octamethylcyclotetrasiloxane in the macromonomer which biases the M_n to lower values.

Since the molecular weights determined by ^{1}H n.m.r. and g.p.c. agreed fairly well, it was assumed that most of the siloxane chains are endblocked by a MOP group, yielding a net functionality of two.

Copolymerization reactions and analysis

The macromonomer was copolymerized with styrene in the absence of solvent using 0.67 mol% AIBN as the initiator at 60°C (i.e. 0.67% of the total number of moles of unsaturated groups present from macromonomer and styrene for each loading) following the same procedure as before[16]. Loadings of 10, 20, 30, 40 and 50 wt% of the macromonomer in styrene were polymerized. The upper limit of conversion times was 10 h.

The post-copolymerization analysis was carried out in distinct stages as previously described[16]. This enabled the separation of fractions soluble and insoluble in hexane and the determination of the conversion of the functional groups of the co-reactants and the molecular weights and composition of the copolymers formed. This higher molar mass macromonomer was highly insoluble in methanol, so unlike studies of the low molar mass macromonomer[16] no correction of bulk MOP conversion was required. The hexane soluble fraction may contain one or more of a copolymer having relatively short PS chains ($\leqslant 20$ monomer units in length), siloxane homopolymer with a low degree of crosslinking, unreacted macromonomer or low molecular weight homopolystyrene.

The hexane insoluble fraction is rich in PS but may also contain siloxane which has been highly crosslinked. As with earlier studies[16] the weight losses were $\leqslant 1\%$ of the initial weight of bulk polymer before extraction. Composition and MOP consumption data for the hexane soluble and insoluble fractions were determined by ^{1}H n.m.r. in deuterated chloroform.

Molecular weight analysis

G.p.c. analysis of the hexane insoluble and soluble fractions was performed in different solvents[16]. The hexane insoluble fractions were analysed in tetrahydrofuran (THF) using both refractive index (RI) and u.v. (= 260 nm) detectors. The hexane soluble fraction, being high in siloxane, was analysed in toluene using only a RI detector.

Measurement of the phase separation during reaction

Using the same equipment and procedures as earlier studies[16], the clouding (macroscopic consequences of phase separation) and microscopic phase separation of the mixtures were measured by transmittance and optical microscopy, respectively.

RESULTS

Phase separation during polymerization: transmission measurements

The cloud point curves (*Figure 1*) for copolymerization of this larger macromonomer with styrene show a more rapid decrease in percentage transmittance (%T) and at shorter times than the copolymerization of the lower molar mass macromonomer previously studied[16]. The samples containing 10 and 20 wt% macromonomer showed the highest transparency. The 10 wt% sample showed a rapid decrease in the %T after 18 min as phase separation occurred. The 20 and 40 wt% samples showed a rapid decrease in %T as the ampoules were heated. This effect was not reversed as the sample was cooled, and the samples remained white in colour.

The %T of the 50 wt% sample decreased more slowly than the 40 wt% sample. A 60 wt% sample was made to confirm this trend and it showed a still slower rate of decrease in %T. The behaviour of the samples at high macromonomer loadings suggests that phase inversion has occurred with the siloxane forming the continuous phase.

Optical microscopy

Optical micrographs showed no phase separation of the 10 wt% sample at zero reaction time, whereas the 20, 30, 40 and 50 wt% mixtures phase separated after mixing.

The 10 wt% sample showed the first indication of phase separation at 12 min reaction time. At 13 min the sample was dominated by spherical domains of uniform size. The size and extent of the domains increased with conversion time up to 60 min, where smaller domains appeared along with the larger ones present. The phase separation behaviour of the 10 wt% sample matched the phase behaviour indicated by the cloud point (*Figure 1*).

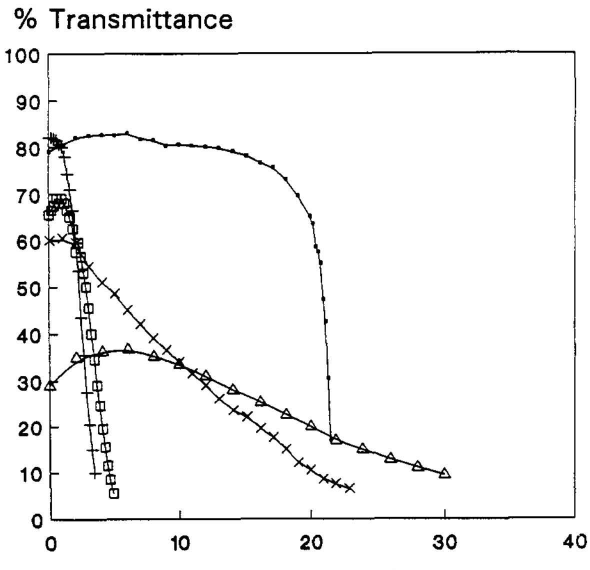

Figure 1 Clouding curves from the macromonomer–styrene–AIBN mixtures for feeds from 10 to 50 wt% macromonomer: (■) 10; (+) 20; (□) 40; (×) 50; (△) 60 wt%

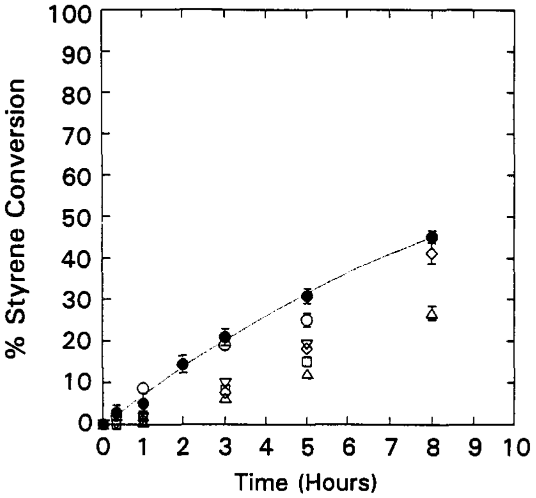

Figure 2 Percentage styrene conversion as determined by u.v. analysis for feeds from 10 to 50 wt% macromonomer (AIBN = 0.67 mol% of total unsaturation): (●) HomoPS; ○ (10); (▽) 20; (□) 30; (△) 40; (◇) 50 wt%

The 20 and 40 wt% samples showed a range of domain sizes after mixing at room temperature. Heating to 60°C resulted in a significant increase in the extent of phase separation. The size and degree of phase separation in both the 20 and 40 wt% samples increased with conversion time up to 180 min.

While phase separation was found before polymerization in the 50 wt% sample the changes in domain size with increasing reaction time were small and it appeared that phase inversion similar to that observed for the low molar mass siloxane at the same concentration had occurred[16].

Styrene and MOP conversions

The styrene consumption during the copolymerization is shown in *Figure 2*. The styrene homopolymerization curve under the same conditions is shown on the same figure to indicate the effect of the macromonomer on styrene conversion. Results show styrene is converted at a slower rate when siloxane is present and this rate decreases as the amount of macromonomer is increased.

The MOP conversion (*Figure 3*) shows a high value at low times (~20% after 1 h) and then a slow increase in conversion with reaction time. No significant differences in MOP conversion were found with increasing amount of macromonomer in the feed.

Compositional analysis of hexane insoluble and hexane soluble copolymers

The yield and weight per cent PS composition of the hexane insoluble fraction are shown in *Table 1*. The weight per cent hexane insoluble material generally increases with conversion time and decreases with increasing weight per cent macromonomer in the feed. The composition of the hexane insoluble fraction shows an increased weight per cent PS with increasing conversion time, but a decreased weight per cent PS with increasing weight per cent macromonomer in the feed. At low conversion times (i.e. 1 h) more than one MOP per macromonomer has reacted, but at high conversions, essentially 1 MOP group remains unreacted per macromonomer.

Table 1 Copolymerization of styrene and macromonomer: yield of hexane insoluble polymer (and wt% PS) as a function of feed, composition and polymerization time[a]

Time (h)	Hexane insoluble fraction				
	10 wt%[b]	20 wt%[b]	30 wt%[b]	40 wt%[b]	50 wt%[b]
0.3	1.1 ± 0.1 (50.6 ± 2.0)	0.0 ± 0.1 –	0.0 ± 0.1 –	– —	 —
1	7.5 ± 0.2 (69.1 ± 0.9)	3.5 ± 0.2 (38.4 ± 5.5)	0.3 ± 0.1 –	0.0 ± 0.1 –	0.0 ± 0.1 –
3	18.2 ± 0.9 (65.7 ± 1.6)	14.3 ± 0.3 (32.1 ± 4.1)	4.1 ± 0.2 (26.4 ± 3.1)	0.0 ± 0.1 –	0.0 ± 0.1 –
5	26.8 ± 1.6 (75.0 ± 1.0)	25.0 ± 0.9 (39.7 ± 6.7)	9.3 ± 0.3 (24.3 ± 4.0)	21.4 ± 0.5 (18.9 ± 1.9)	5.1 ± 0.1 (29.2 ± 2.1)
8	– –	– –	– –	33.1 ± 0.5 (29.0 ± 2.5)	27.3 ± 0.5 (44.4 ± 2.2)

[a] $\text{Yield} = \dfrac{100 \times (\text{weight remaining after Soxhlet extraction})}{(\text{wt styrene} + \text{wt macromonomer})\text{ in feed}}$

[b] Macromonomer in feed

Table 2 Copolymerization of styrene and macromonomer: hexane insoluble polymer g.p.c. M_p

Feed (wt% macromonomer)	Polymerization time (h)				
	0.3	1	3	5	8
10	73 700 ± 6000[a]	74 300 ± 6000	75 700 ± 6200	80 400 ± 6700	–
20	–	34 200 ± 1700[a]	31 400 ± 1400	35 400 ± 1800	–
30	–	–	27 400 ± 700	28 200 ± 1100	–
40	–	–	–	27 400 ± 800	28 900 ± 1200
50	–	–	–	84 200 ± 7200	>66 300

[a] More than 1 MOP consumed per macromonomer, indicating some crosslinking has occurred

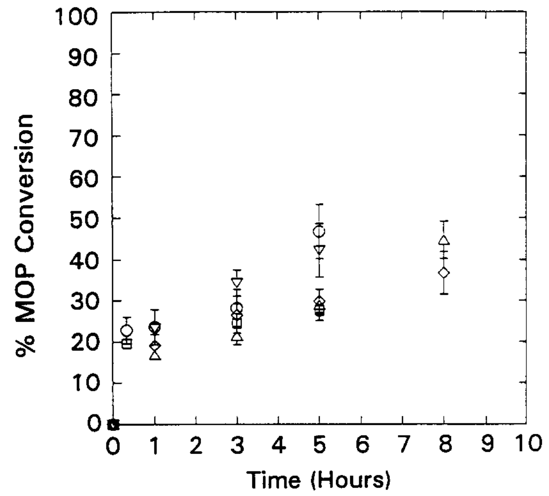

Figure 3 Percentage MOP conversion as determined by ^{1}H n.m.r. analysis for feeds from 10 to 50 wt% macromonomer (AIBN = 0.67 mol% of total unsaturation): (○) 10; (▽) 20; (□) 30; (△) 40; (◇) 50 wt%

The g.p.c. molecular weights of the hexane insoluble fraction are shown in *Table 2*. For the 10–40 wt% samples there is a slight increase in the M_p with conversion time and a decrease with increasing weight per cent macromonomer in the feed. The M_p is largest in the 50 wt% samples.

The yield and weight per cent PS composition of the hexane soluble fraction is shown in *Table 3*. The total weight per cent hexane soluble fraction varies little with time for the 10, 20 and 30 wt% samples. The composition of the hexane soluble fraction generally shows an increase in the weight per cent PS with increasing weight per cent macromonomer in the feed and conversion time.

DISCUSSION

Conversion–time curves for copolymerization of macromonomers

The decrease in the rate of styrene conversion with macromonomer present compared to homopolymerization may be due to one or a combination of:

1. a decrease in the propagation rate constant[18];
2. a decrease in the initiator efficiency[17,19];
3. an enhancement of the diffusion controlled termination rate of the growing radical chains caused by a reduction of their coil dimensions[17,20]. The presence of siloxane in the polymerizing medium could be making the solvent (styrene) thermodynamically poorer, so causing the polymer chain to shrink[20].

It is expected that the extent of styrene polymerization being initiated by MOP radicals was low due to the small number of MOP groups present and the proportion of MOP initiated styrene conversions would decrease with conversion time because once the MOP groups at the siloxane–styrene interface react, diffusion of MOP groups to the macromonomer–styrene interface would be slow due to the relatively high viscosity of the siloxane-rich phase. This would effectively decrease the rate of propagation in the styrene-rich zone[19].

Table 3 Copolymerization of styrene and macromonomer: yield of hexane soluble material (and wt% PS) as a function of feed, composition and polymerization time[a]

Time (h)	Hexane soluble fraction				
	10 wt%[b]	20 wt%[b]	30 wt%[b]	40 wt%[b]	50 wt%[b]
0.3	6.4 ± 0.5 (3.1 ± 1.0)	14.9 ± 0.6 (3.8 ± 1.0)	13.2 ± 0.2 (2.4 ± 1.0)[c]	– –	– –
1	4.7 ± 0.2 (5.3 ± 1.0)[c]	11.1 ± 1.0 (5.5 ± 1.4)[c]	13.7 ± 0.2 –	15.1 ± 0.4 (12.4 ± 1.6)[c]	18.7 ± 0.4 (5.3 ± 1.0)[c]
3	5.0 ± 0.2 (13.7 ± 2.0)	13.3 ± 0.3 (3.9 ± 1.0)[c]	13.9 ± 0.6 (18.6 ± 2.6)	14.0 ± 0.4 (20.6 ± 3.0)[c]	24.3 ± 0.5 (13.9 ± 2.2)[c]
5	5.3 ± 0.3 (3.8 ± 1.0)	10.2 ± 0.4 (15.0 ± 1.6)	14.5 ± 0.4 (20.0 ± 3.2)	8.1 ± 0.4 (27.1 ± 2.7)[c]	24.8 ± 0.5 (15.7 ± 2.5)[c]
8	– –	– –	– –	8.8 ± 0.3 (32.4 ± 3.5)	37.6 ± 0.7

[a] $\text{Yield} = \dfrac{200 \times (\text{weight lost during Soxhlet extraction})}{(\text{wt styrene} + \text{wt macromonomer})\ \text{in feed}}$

[b] Macromonomer in feed

[c] Corrected to remove unreacted macromonomer

Structure elucidation of hexane insoluble copolymers

Calculation of the expected molecular weights of the hexane insoluble copolymers from the compositional data assuming one macromonomer per chain (*Table 1*) shows that the calculated molar mass is equal or less than the g.p.c. M_p (*Table 2*) within the error values. This indicates the hexane insoluble fraction is mostly copolymer. If homopolystyrene was present in significant amounts the calculated molar mass for the copolymers having 10–40 wt% macromonomer in the feed would be lower than the g.p.c. M_p and the g.p.c. peak shape would be distorted. The proposed structure of the hexane insoluble copolymer for macromonomer feeds from 10 to 50 wt% is shown in *Figure 4*.

Structure elucidation of hexane soluble copolymers

The copolymers with 10 wt% macromonomer in the feed have a molar mass higher than the macromonomer, indicating only one macromonomer is joined to each PS chain. The calculated molar mass matches the g.p.c. molecular weight within error bounds, indicating low molecular weight homopolystyrene is not present in significant amounts. The structures of the hexane soluble (*Figure 5*) and hexane insoluble copolymers (*Figure 4*) deduced from compositional and molecular weight analysis are very similar. However, data for the hexane soluble samples with 20 and 30 wt% macromonomer in the feed indicate that two macromonomers are joined by styrene units or have short PS chains attached. It is unlikely that two MOP groups on separate macromonomers have co-reacted due to the low concentration of MOP groups compared to styrene (for a styrene-rich phase) or compared to dimethylsiloxy units (for a siloxane-rich phase). It is expected that the macromonomers may have joined by either: (1) co-termination of growing PS chains after separate initiation of MOP groups; or (2) after initiation (or propagation) of one MOP group, the resulting growing PS chain may initiate a MOP group on another macromonomer.

Phase chemistry during polymerization

The composition of the copolymer will be affected by the phase chemistry of the siloxane–styrene system during the course of polymerization. From copolymer compositions, optical microscopy and cloud point results the

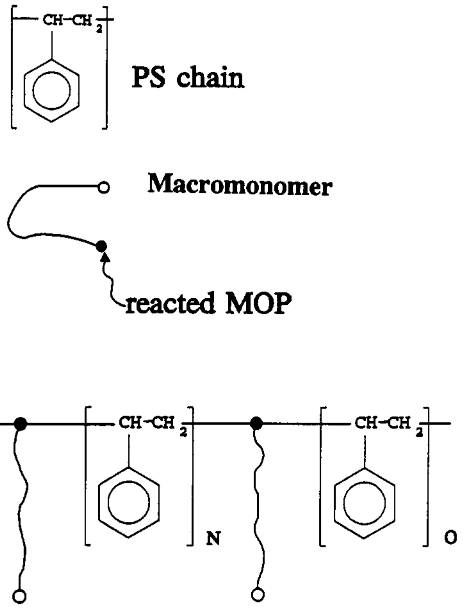

Figure 4 Proposed structure for the hexane insoluble copolymer

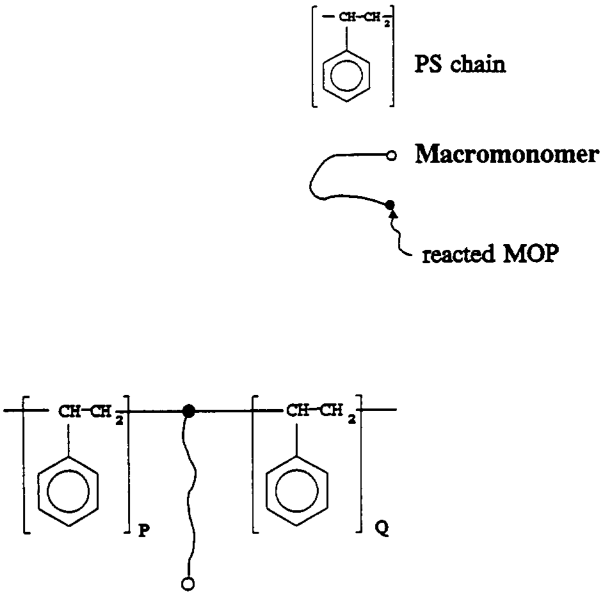

Figure 5 Proposed structure for the hexane soluble copolymer

general phase chemistry of the ternary system (styrene, macromonomer and copolymer) was considered assuming that one phase is rich in styrene and the other is rich in siloxane. The composition of the hexane soluble and insoluble copolymers are similar. This suggested that either: (1) the hexane soluble and insoluble copolymers were formed under similar conditions in one phase; or (2) the copolymers were formed in two separate phases of similar composition.

It is more likely that the hexane soluble and insoluble copolymers were formed in the one phase as optical micrographs of the macromonomer–styrene system showed relatively sharp phase boundaries, indicating phases dissimilar in composition.

This indicates that separation into hexane soluble and insoluble fractions is only related to compositional variation and not copolymer origin. It is suggested that the copolymer is formed by MOP groups on the macromonomer being soluble in the styrene phase or concentrated at the macromonomer–styrene phase boundary. The MOP groups near the phase boundary could participate in polymerization reactions with styrene, growing PS chains or radicals from initiator decomposition to produce the copolymer.

Reasons for low number of macromonomers in the copolymers and lack of macromonomer homopolymerization

The structures of the hexane insoluble and soluble copolymers predicted from composition and molecular weight data indicate that there are fewer than three macromonomers per copolymer chain. This can be explained in accordance with the overlap concentrations calculated. From the computed radius of gyration for the macromonomer in the presence of PS chains of various lengths shown in *Table 4*, the degree of overlap is low. Therefore, the chances of a MOP group coming into contact with a growing PS chain are also low. This suggests that the majority of MOP groups react by initiation or propagation when the PS chain length is short. It is expected that the main route by which two macromonomers are included in the copolymer is through co-termination of two growing PS chains attached to macromonomers.

The lack of macromonomer homopolymerization is most likely related to the low concentration of MOP groups in the siloxane-rich phase. This means that even if AIBN dissociation occurs near a MOP group in the siloxane-rich phase and initiation results, it is expected that the probability is low that another MOP group would be close enough to react due to the large diluent effect of the dimethylsiloxy units. The initiated MOP group would most likely recombine with the other AIBN radical fragment[19]. In addition, the attached siloxane chain may form a random coil[1] around the MOP groups to minimize the surface and free energy of the system.

Table 4 Overlap concentrations for PS of various chain lengths with the siloxanemacromonomer

No. of styryl units	PS molecular weight ($g\,mol^{-1}$)	Overlap concentration[a] ($g\,ml^{-1}$)
25	2604	0.37
50	5208	0.26
100	10415	0.20
200	20830	0.17
500	52073	0.09

[a] Calculated for PDMS in toluene and PS in benzene

Reasons for the phase separation behaviour shown during polymerization

The increase in domain size for the samples containing 10, 20, 30 and 40 wt% macromonomer in the feed with increasing conversion time indicates coalescence of the macromonomers to minimize the surface free energy of the system. The styrene (which acts as a solvent) is being consumed and the PS formed is highly incompatible with the macromonomer[21,22]. Presumably the siloxane segments of the copolymers remain in the siloxane-rich phase (as shown by micrographs of blends, block and graft copolymers of PS and PDMS[23]). The ability of the system to adjust its structure quickly during polymerization is most likely related to the high mobility of the system due to the negligible amount of crosslinking at the conversions studied.

Effect of difunctional siloxane macromonomer molecular weight on copolymer structure

We have shown by this and a previous study[16] that radical copolymerization of the difunctional PDMS macromonomers with molecular weights of $M_n = 3700\,g\,mol^{-1}$ and $M_n = 21\,300\,g\,mol^{-1}$ with styrene results in copolymers with distinctly different structures.

We[16] and others[13] have previously shown that crosslinked insoluble copolymers are formed by the bulk radical polymerization of difunctional siloxane macromonomers with molecular weights ranging from 200 to $3700\,g\,mol^{-1}$. We have also shown that a low molecular weight macromonomer was able to homopolymerize during bulk copolymerization with styrene. In contrast, the higher molecular weight macromonomer forms a graft copolymer with no crosslinking and there is no siloxane homopolymer formed.

The differences in the structure of these copolymers is most likely the result of: (1) differences in thermodynamic repulsive interactions between the macromonomers and the propagating PS chains (i.e. mixtures containing the longer macromonomer would show a much lower degree of interpenetration of PDMS and PS phases than for mixtures containing the shorter macromonomer); (2) the longer macromonomer chains being able to form a random coil[11], which would result in an increase in the shielding of the MOP groups. This would decrease the ability to homopolymerize due to the lower probability of MOP groups coming into contact with each other (for homopolymerization) or propagating PS chains at both MOP groups for crosslinking. In contrast, the shorter macromonomer is not expected to form a random coil. Consequently the MOP groups are less shielded and will also be present in much higher concentration in the siloxane phase.

CONCLUSIONS

The copolymers of high molar mass macromonomer and styrene have a graft structure containing up to three macromonomers in a PS backbone with virtually no crosslinking. This is similar to the structure proposed by Tenhu and Heino[13] for PS–PDMS copolymers containing difunctional PDMS macromonomers with $M_n = 35\,000\,\mathrm{g\,mol^{-1}}$. ^{1}H n.m.r. analysis showed that on average one unreacted MOP remained per macromonomer. Molecular weight and compositional analysis indicated that the macromonomer did not homopolymerize under these conditions. This has been shown by others[7,14] for mono- and difunctional macromonomers of comparable molecular weight. By increasing the weight per cent macromonomer in the feed (from 10 to 50 wt%) there was a corresponding increase in the weight per cent PDMS in the copolymer.

The dependence of the structure of the copolymer on the macromonomer molecular weight is believed to arise from shielding of reactive groups by random coil formation.

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