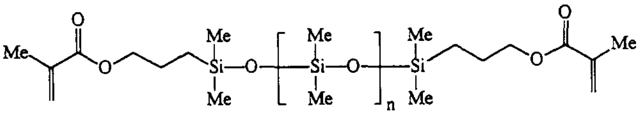
Bulk copolymerization of methacryloyloxypropyl functionalized siloxane macromonomers with styrene:
1. Network formation

Michael S. O'Shea* **and Graeme A. George†**
School of Chemistry, Queensland University of Technology, Brisbane 4000, Australia
(Received 29 June 1993; revised 1 March 1994)

An α,ω-(3-methacryloyloxypropyl dimethyl siloxane) macromonomer (I) with a molecular weight of 3700 g mol^{-1} was copolymerized with styrene in bulk at 60°C using azobisisobutyronitrile as the initiator. Phase separation during polymerization was monitored macroscopically by clouding and microscopically by domain formation. The copolymer was separated into hexane soluble and insoluble fractions. From u.v., ^{1}H n.m.r. and g.p.c. analysis of these fractions, the composition of the copolymers was determined as a function of feed composition (up to 50 wt% macromonomer) and reaction time (up to 6 h). Analysis of the hexane insoluble fraction showed that the macromonomer rapidly formed a crosslinked network copolymer with styrene, showing little residual functionality. The hexane soluble fraction contained a copolymer with blocks of dimers and trimers of I.



I

(Keywords: macromonomer; siloxanes; styrene copolymers)

INTRODUCTION

Polysiloxanes, especially polydimethylsiloxanes (PDMSs) possess a unique combination of properties which are not shown by any other polymeric material, e.g. hydrophobicity, biocompatibility, high chain flexibility, low glass transition temperature, high electrical resistance, low surface tension, low surface energy, thermal and u.v. stability, high solubility in many organic solvents, high gas permeability and incompatibility with almost all other polymeric systems. The major route to make useful products from siloxane polymers is to fill them with high surface area silica and crosslink them by various methods[1-4]. The resulting silicone elastomers display only fair mechanical properties, with low tear strengths being a major drawback. To overcome these difficulties siloxanes can be chemically linked with organic polymers by the formation of ladder and network copolymers.

Multifunctional siloxane macromonomers have been used to form crosslinked copolymer networks[5-10] and ladder copolymers[11,12] with linear and network-forming organic polymers. Crosslinked siloxane homopolymer networks[11,12] have also been made from multifunctional siloxane macromonomers. Yang and Peppas[12] copolymerized difunctional dimethylsiloxanes having methacryloyloxymethyl functional groups with methyl methacrylate by γ radiation. Swelling measurements suggested that the system was highly crosslinked. Thus a high proportion of both reactive groups on the disiloxane had polymerized into adjacent chains, producing a three-dimensional network. Williams[13] in a similar study used difunctional PDMS macromonomers with urethane methacrylate end groups with molecular weights ranging from 1000 to 3000 g mol^{-1} in a typical formulation for a contact lens. A photoinitiator and u.v. light was used to crosslink the reaction mixture. Oxygen permeability measurements indicated a change in morphology from discontinuous to continuous siloxane phase structure at ~40 wt% PDMS.

Tenhu and Heino[14] copolymerized dimethacryloyloxypropyl functionalized siloxane macromonomers with molecular weights from 200 to 2000 g mol^{-1} with styrene in bulk and in solution using benzoyl peroxide as the free radical initiator at 70°C to form crosslinked networks. The degree of crosslinking was varied by altering the amount of siloxane macromonomer in the feed.

Katz and Zewi[10] studied the crosslinking of diacrylate functionalized siloxane macromonomers of various chain lengths by u.v. initiated free radical polymerization. The products were three-dimensional ladder polymers, where

---

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

0032-3861/94/19/4181-09

the siloxane chains acted as elastic bridges between the acrylate chains. Katz and Zewi[10] also studied the free radical copolymerization of hydroxy terminated difumarate functionalized siloxane macromonomers of various chain lengths with styrene monomer in bulk. They found that as the degree of polymerization of the dimethylsiloxy unit was increased above eleven the polymerization mixture became opaque, as did the resultant copolymers. This was attributed to limited solubility of siloxane in styrene and the incompatibility between PDMS and polystyrene (PS), both of which depend on chain length.

Tsukahara *et al.*[15] proposed that even for copolymerization under transparent (homogeneous) conditions a small macromonomer could interpenetrate the propagating comonomer chain to bring its end group near the radical site as the incompatibility between the siloxane macromonomer and the polymerized comonomer, i.e. poly(methyl methacrylate) (PMMA), is less significant for smaller molecules. The overlap concentration was calculated from the radius of gyration data for PDMS and PMMA, and showed that the overlap concentration decreased as the molecular weight of the siloxane macromonomer or comonomer chain increased. They also proposed that low molecular weight macromonomers did not form a random coil. Thus end groups on smaller macromonomers could contact a propagating radical without significant interpenetration. This reduces the importance of the incompatibility effect for small macromonomers.

In this study a small siloxane macromonomer with methacroyloxypropyl (MOP) end groups and a peak molar mass in the molecular weight distribution curves by g.p.c. of 3700 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 resulting copolymer.

Subsequent papers will investigate the effects of molecular weight between functional groups and the degree of functionality of MOP functional siloxane macromonomers on the polymerization rate and structure of the resulting copolymers.

EXPERIMENTAL

Synthesis of siloxane macromonomer

The difunctional PDMS macromonomer with 3-methacryloyloxypropyl end groups was synthesized by reaction of allyl methacrylate with silyl hydrides on a low molecular weight siloxane polymer using a platinum-on-carbon catalyst[16].

Styrene monomer (Merck Schuchardt, >99% pure) was passed through an alumina column (Merck, art 1077) to remove the inhibitor (4-t-butyl catechol). Purification was performed just prior to each polymerization. AIBN (Aldrich) was reprecipitated from methanol and stored in a freezer until required.

The siloxane macromonomer was characterized by ^{1}H n.m.r. and g.p.c. ^{1}H n.m.r. was performed in deuterated chloroform using a JEOL GX400 *FT*-n.m.r. spectrometer fitted with a 5 mm probe. A Waters Associates 6000A g.p.c. instrument equipped with ultrastyragel columns of pore sizes 10^5, 10^4, 10^3, 10^2 and 10 Å was used for molecular weight characterization. Toluene was the eluting solvent at ambient temperature. Calibration was performed using PS and siloxane standards. A refractive index (RI) detector was used to obtain the chromatograms.

Macromonomer purity and characterization

The two products from the reaction of allyl methacrylate with silyl hydride groups on the siloxane are 3-methacryloyloxypropyl and 2-methacryloyloxypropyl substituents on the siloxane. The possible impurities in the siloxane macromonomer due to impurities in the allyl methacrylate are allyl isobutyrate, propyl methacrylate and propyl isobutyrate. Only allyl isobutyrate can react under hydrosilation conditions to produce propyl isobutyrate groups attached to the siloxane macromonomer.

The relative amounts of organic groups attached to the siloxane macromonomers and the amount of polymerizable impurities were determined by ^{1}H n.m.r.

Assuming no isobutyrate endcapped chains, 92.1 ± 5.8% of the species in the macromonomer mixture containing unsaturated functional groups were MOP endcapped siloxane macromonomer of which 93% were attached by propyl chains and 7% by isopropyl chains. Rao and Babu[17] showed that methacryl groups attached by propyl linkages to the siloxane are slightly more reactive towards styrene than those attached by isopropyl chains.

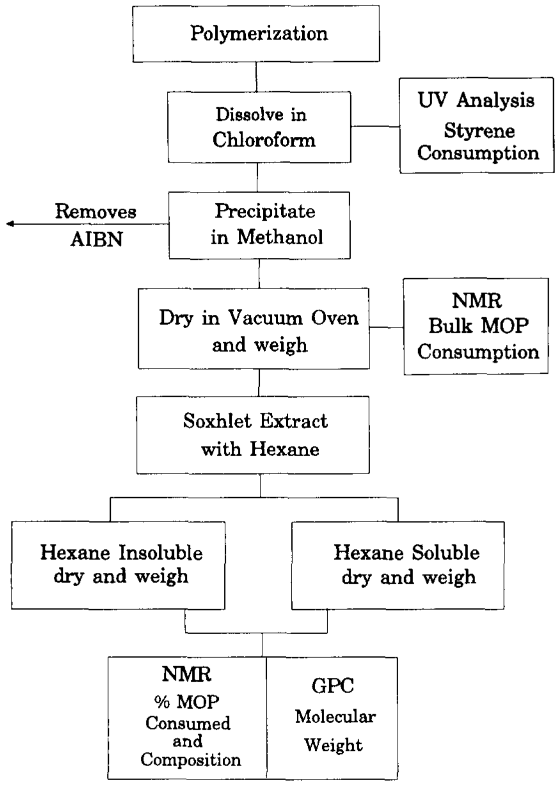
Residual allyl methacrylate and propyl methacrylate was estimated to be 3.9 ± 1.3 and 4.1 ± 2.6%, respectively. The allyl methacrylate should not cause crosslinking due to the low reactivity of the allyl group under the mild conditions used in this study[9]. The allyl methacrylate and propyl methacrylate impurities are not expected to adversely affect the reactivity of the MOP groups on the siloxane toward the styrene (or vice versa) or the physical and chemical properties of the resultant copolymers.

From ^{1}H n.m.r. analysis the macromonomer molecular weight was estimated to be 3124 ± 296 g mol^{-1} using the ratio of attached MOP groups to methyl groups on the siloxane backbone, assuming a functionality of two.

From g.p.c. analysis the macromonomer was shown to have a peak molecular weight (M_p) of 3730 ± 710 g mol^{-1} and number- and weight-average molecular weights (M_n and M_w, respectively) of 2970 and 4190 g mol^{-1}, respectively, corresponding to a polydispersity (M_w/M_n) of 1.41. The g.p.c. M_p was more reliable than M_n or M_w as the macromonomer contained small amounts of octamethylcyclotetrasiloxane (molecular weight = 296 g mol^{-1}) which would lower the M_n value. As the molecular weights determined by ^{1}H n.m.r. and g.p.c. correlate, it can be assumed that the siloxane chains are endblocked by a MOP group, so the net functionality is two.

Copolymerization reactions and analysis

The α,ω-(3-methacryloyloxypropyl dimethyl siloxane) macromonomer (I) was copolymerized with styrene in the absence of solvent using 0.67 mol% AIBN as the initiator (i.e. 0.67% of the total number of moles of unsaturated groups present from macromonomer and styrene for each loading). Polymerizations were conducted in glass ampoules under vacuum after removal of dissolved oxygen. The ampoules were covered in aluminium foil to prevent light decomposition of AIBN. After sealing, the ampoules were placed in a water bath set at 60 ± 0.1°C. At predetermined copolymerization times, the ampoules were removed from the water bath, frozen in liquid nitrogen and placed in a freezer until they were analysed.



Scheme 1 Scheme used for copolymerization, material work-up and subsequent analysis

Loadings of 10, 20, 30, 40 and 50 wt% macromonomer in styrene were polymerized. The upper limit of conversion times was 6 h.

Post-copolymerization analysis was as shown in *Scheme 1*. After polymerization, the contents of each ampoule were diluted in chloroform and the remaining styrene monomer determined from the absorbance at 290 nm using a DMS 90 u.v./vis. spectrophotometer. The chloroform was removed and the polymer precipitated into methanol. AIBN remained in solution. The filtered polymer was vacuum dried at 40°C. This material was weighed and a sample taken to determine the MOP consumption by ^{1}H n.m.r. The ^{1}H n.m.r. spectra of the bulk copolymer and the mass of polymer obtained were used to measure the recovery losses after polymerization. Solubility tests showed the macromonomer to have some solubility in methanol. Accordingly the MOP consumption figures were corrected for lost macromonomer I by assuming that no MOP conversion would have occurred in the material lost. This is supported by the observation that if a MOP group reacts and attaches to another MOP or styrene the product becomes less soluble in methanol.

The bulk copolymers were separated by cold Soxhlet extraction with AR grade hexane, as siloxanes are highly soluble in hexane and polystyrene is not. Smith *et al.*[18] and Li and Huang[19] have used this technique to separate unreacted siloxane macromonomer from styrenic and acrylic siloxane graft copolymers and polyethylene siloxane graft copolymers, respectively.

Linear PDMS polymers with molecular weights as high as 116 500 g mol^{-1} were hexane soluble while crosslinked PDMS and polystyrene of molecular weight <4800 g mol^{-1} were insoluble. The hexane soluble fraction may have contained a copolymer having relatively short PS chains ($\leqslant 20$ monomer units in length), siloxane homopolymer with a low degree of crosslinking or low molecular weight homopolystyrene. The hexane insoluble fraction was rich in PS but may have also contained macromonomer which had been highly crosslinked. After extraction, the samples were dried and weighed. Weight losses were generally $\leqslant 1\%$ of the initial bulk polymer.

The hexane insoluble and soluble fractions were analysed by ^{1}H n.m.r. to determine the amount of unreacted MOP groups in each. Some difficulty was encountered with analysis of the hexane insoluble fraction at high conversion due to its crosslinked nature. In some instances it was analysed as a swollen gel in chloroform. This produced some peak broadening for the polystyrene component.

Molecular weight analysis

The hexane insoluble fraction at lower conversion times was analysed in tetrahydrofuran (THF) using both RI and u.v. (260 nm) detectors. Material from higher conversion times would not fully dissolve. The RI detector only showed peaks due to the PS component of the hexane insoluble fraction as the RI of PDMS is identical to that of THF at 20°C. This was confirmed by the peak shape of the RI and u.v. peaks being identical. The hexane soluble fraction, being low in PS and high in siloxane, was analysed in toluene using only a RI detector. Differences in RI of the polymers and solvents allowed separation of the components.

Measurement of the phase separation during reaction

An indication of the rate and degree of phase separation was given by the clouding of the reaction mixture during the copolymerization. A Varian model 635 u.v./vis. spectrophotometer operated at 530 nm was used to measure the transmittance of the recaction mixture at 60°C in rectangular cross-section glass ampoules with highly polished faces. The low light intensity and long wavelength used should have had minimal effect on the initiation rate of AIBN. The percentage transmittance (%T) of each ampoule filled with styrene was measured before each reaction mixture was added and the ampoule sealed after rigorous removal of dissolved oxygen.

Phase separation during polymerization was measured by optical microscopy using a Mettler FP-84 optical differential scanning calorimeter as a hot stage of a Nikon Optiphot microscope. Samples were placed in glass d.s.c. pans with highly polished lids and bases. Polymerization was performed at 60.0 ± 0.1°C. Photographs were taken of the polymerizing mixtures using a Nikon FMP shutter system fitted with a Polaroid camera. To minimize oxygen inhibition, the reaction mixtures were flushed with nitrogen before being placed in the d.s.c. pan and the differential scanning calorimeter was slowly flushed with nitrogen during polymerization.

RESULTS

Phase separation during polymerization: transmission measurements

The cloud point curves (*Figure 1*) indicate that the only samples which show total miscibility with styrene are 10 and 20 wt% macromonomer. Higher concentration samples showed haze at the start of polymerization.

The change in %T indicates an alteration in phase

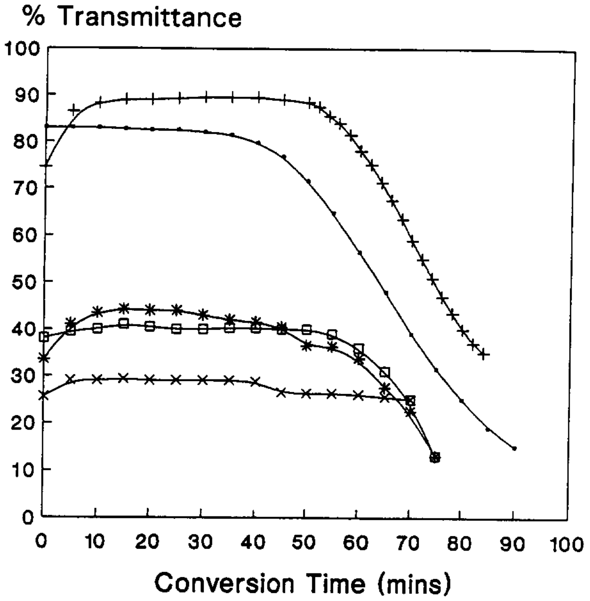


Figure 1 Clouding curves for the macromonomer–styrene–AIBN mixtures for feeds from 10 to 50 wt% macromonomer: (■) 10; (+) 20; (*) 30; (□) 40; (×) 50 wt%

properties of the reaction mixture as polymerization occurs. At 60°C this occurs at 40, 45, 50 and 60 min for the 10, 30, 40 and 20 wt% macromonomer, respectively.

No significant decrease in %T was found for the 50 wt% samples for the conversion times studied, even though at 70 min (25%T) the sample was gelled. However, at 20%T the 10 wt% sample was still very fluid in contrast to the gels or near gels shown by the 30–50 wt% macromonomer samples at the same %T.

Optical microscopy

Optical microscopy investigations showed phase separation occurring on a micro scale throughout the sample rather than the macroscopic consequences of the phase separation shown by cloud point measurements. By focusing at various depths through the sample (~1.5 mm deep) it was found that for all compositions and times there was a fairly even degree of phase separation throughout, with no indication of effects due to the interface with the glass d.s.c. cell.

Optical microscopy showed that at the start of the reaction the 10 and 20 wt% samples did not appear phase separated, whereas the 30, 40 and 50 wt% samples were phase separated before any reaction had begun.

The 10 wt% samples first displayed phase separation at 55 min by formation of small ($\leqslant 1.0\,\mu m$) spherical domains in the matrix. The size and extent of the domains increased dramatically with time. Coalescence of the phase separated domains was observed. The increase in the amount of phase separated material correlated with the decrease in the %T shown by the cloud point curves (*Figure 1*). This was expected as the phase separated domains would increase the amount of scattered light.

The 20 wt% samples appeared initially to have a slightly higher light transmission than the 10 wt% samples. After 30 min at 60°C, phase separation was visible, increasing dramatically after 60 min. This is in accordance with the clouding curve for the 20 wt% sample.

The 30, 40 and 50 wt% samples were all phase separated at 25°C, with the extent of phase separation increasing from 30 to 40 wt% and then decreasing slightly for 50 wt%. The continuous phase of the 50 wt% sample was very hazy. This may indicate phase inversion, as on a mole basis there are more dimethylsiloxy units present than styrene at 50 wt% macromonomer in the feed. After 5 min reaction time (including heating to 60°C) all samples showed a slight decrease in phase separation. The phase behaviour of the 30, 40 and 50 wt% mixtures agrees with the cloud point results, i.e. lower initial %T than the 10 and 20 wt% samples due to scattering from the phase separation and a slight increase in the %T after initial heating due to increased solubility.

Styrene and MOP group conversions

The styrene consumption during copolymerization is shown in *Figure 2*. The styrene homopolymerization curve under the same conditions is also shown to indicate the effect of the coreactant. The results show that styrene is consumed at a faster rate when macromonomer is present and this rate increases with the amount in the feed.

The MOP conversion (*Figure 3*) shows an initially high

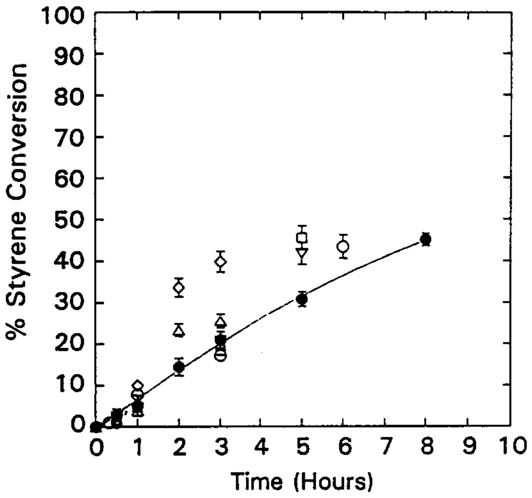


Figure 2 Percentage styrene conversion as determined by u.v. analysis for feeds from 10 to 50 wt% macromonomer (AIBN = 0.67 mol% total unsaturation): (●) HomoPS; (○) 10; (▽) 20; (□) 30; (△) 40; (◇) 50 wt%

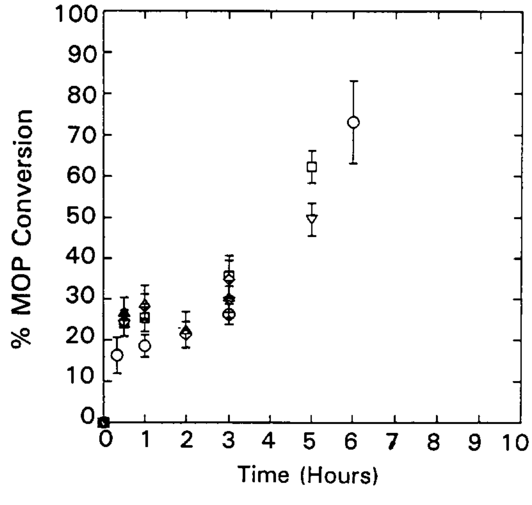


Figure 3 Percentage MOP conversion as determined by ^{1}H n.m.r. analysis for feeds from 10 to 50 wt% macromonomer (AIBN = 0.67 mol% total unsaturation): (○) 10; (▽) 20; (□) 30; (△) 40; (◇) 50 wt%

Table 1 Copolymerization of styrene and siloxane macromonomer I: 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	1.4 ± (2.1 ± 0.2)	– –	– –	– –	– –
0.5	– –	0.1 ± 0.1 –	2.8 ± 0.1 (52.4 ± 1.1)	0.0 –	0.0 –
1	6.2 ± 1.0 (82.7 ± 1.0)	0.5 ± 0.1 (41.8 ± 1.3)	5.4 ± 0.2 (48.0 ± 1.3)	0.0 –	9.9 ± 0.3 (39.8 ± 0.5)
2	– –	– –	– –	(14.3 ± 0.3 (43.9 ± 1.4)	17.6 ± 0.4 (36.0 ± 1.4)
3	17.8 ± 0.2 (86.5 ± 1.6)	16.1 ± 0.3 (70.4 ± 1.1)	20.9 ± 0.8 (56.6 ± 1.5)	23.2 ± 0.9 (44.0 ± 1.4)	24.7 ± 0.2 (38.9 ± 1.4)
5	– –	41.5 ± 0.5 (79.5 ± 5.0)	44.5 ± 3.0 (61.4 ± 1.4)	– –	– –
6	42.4 ± 0.5 (86.4 ± 1.6)	– –	– –	– –	– –

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

[b] Macromonomer in feed

value at low conversion times (~25% in 1 h). The MOP conversion increases slowly up to 3 h and then increases significantly. This most likely results from a decrease in the rate of termination of radical chains due to the formation of a crosslinked gel. No trends were noted with increasing the weight per cent macromonomer in the feed except the slightly higher MOP conversion for the 40 and 50 wt% feed for low conversion times (30 min–1 h).

Compositional analysis of hexane insoluble and hexane soluble copolymers

The yield of polymer expressed as a weight per cent of the total feed is shown in *Table 1* separated into hexane insoluble (comprising copolymer, crosslinked siloxane and high molecular weight PS) and hexane soluble (comprising polymerized siloxane macromonomer, unreacted macromonomer and low molecular weight PS) fractions. The corresponding compositions expressed as weight per cent PS in these fractions are also shown.

The amount of hexane insoluble copolymer increases with polymerization time, up to ~40% of the total feed after 5 h. At conversion times up to 1 h for the 40 and 50 wt% samples there was virtually no hexane insoluble copolymer. At longer times for these feeds the macromonomers have crosslinked and/or polymerized with enough styrene to make an appreciable amount of hexane insoluble copolymer.

The hexane soluble fraction is initially much larger than the hexane insoluble fraction. At longer conversion times the weight per cent hexane soluble material decreases as some of the hexane soluble material is converted into hexane insoluble copolymer. This occurs by polymerization of MOP groups in the hexane soluble material which results in either longer PS chains becoming attached to the copolymer, and/or an increase in the crosslink density of the material.

DISCUSSION

Conversion–time curves for copolymerization of the macromonomer

The increase in the percentage styrene conversion with macromonomer present (*Figure 2*) over that of homopolymerization may be due to the 'gel effect'[20]. That is, the rate of polymerization has increased due to the rate of termination decreasing by a greater extent than the product of the rate of propagation and the initiator efficiency.

The AIBN concentration in each sample was 0.67 mol% based on the total unsaturation. The number of moles of AIBN added for different macromonomer loadings are shown in *Table 2*. With increasing loadings of macromonomer in the feed, the mole per cent AIBN relative to styrene increases by up to 6.6%. The presence of homopolysiloxane in some hexane soluble material indicates that AIBN is present and decomposing in the siloxane phase. However, *Figure 2* shows the per cent styrene conversion with the macromonomer present, especially at higher loadings, is greater than for homopolymerization at conversion times when gelation has not occurred. This indicates that the mole per cent AIBN in the styrene phase is most likely equal or slightly greater than 0.67 when the macromonomer is present. Presumably this is the result of AIBN reaching its solubility limit in the siloxane-rich phase.

The initially high value of MOP conversion (*Figure 3*) at low times (~25% in 1 h) could reflect the higher polymerization rate coefficient of methacryl groups compared to styrene ($(k_p^{\mathrm{MMA}}/k_p^{\mathrm{Sty}} \approx 3.2)$)[17,21]. The increased MOP conversion after 3 h is most likely due to the formation of a crosslinked gel resulting in a decrease in the rate of termination of radical chains[20].

Structure elucidation of hexane insoluble copolymers

Initially the hexane insoluble copolymer contains a much higher weight per cent siloxane than present in the feed. This is due to the faster conversion of MOP groups than styrene so for each MOP reacting with the copolymer, 3727 g mol^{-1} is added. Since the hexane insoluble copolymer is insoluble in solvents which PDMS or polystyrene have high solubility, it can be concluded that the copolymer is most likely a three-dimensional network. The small number of MOP groups remaining per macromonomer also suggests that the material is

Table 2 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	1.8±0.1 (3.2±0.2)	– –	– –	– –	– –
0.5	– –	12.3±0.2 (17.9±1.0)	10.6±0.2 (0.0±0.1)	23.0±0.1 (5.6±0.2)	21.1±0.1 (0.0±0.1)
1	1.3±0.1 (2.1±0.2)	9.8±0.2 (27.5±0.8)	10.6±0.3 (0.0±0.1)	21.8±0.1 (9.3±0.2)	17.7±0.5 (3.5±0.2)
2	– –	– –	– –	14.6±0.3 –	16.1±0.3 (1.3±0.1)
3	4.7±0.2 (3.4±0.2)	8.8±0.3 (21.3±0.6)	7.3±0.3 (1.5±0.1)	8.7±0.3 –	16.2±0.5 (0.1±0.1)
5	– –	7.0±0.5 (6.2±0.2)	8.0±0.5 (0.0±0.1)	– –	– –
6	2.4±0.5 (7.4±0.2)	– –	– –	– –	– –

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

[b] Macromonomer in feed

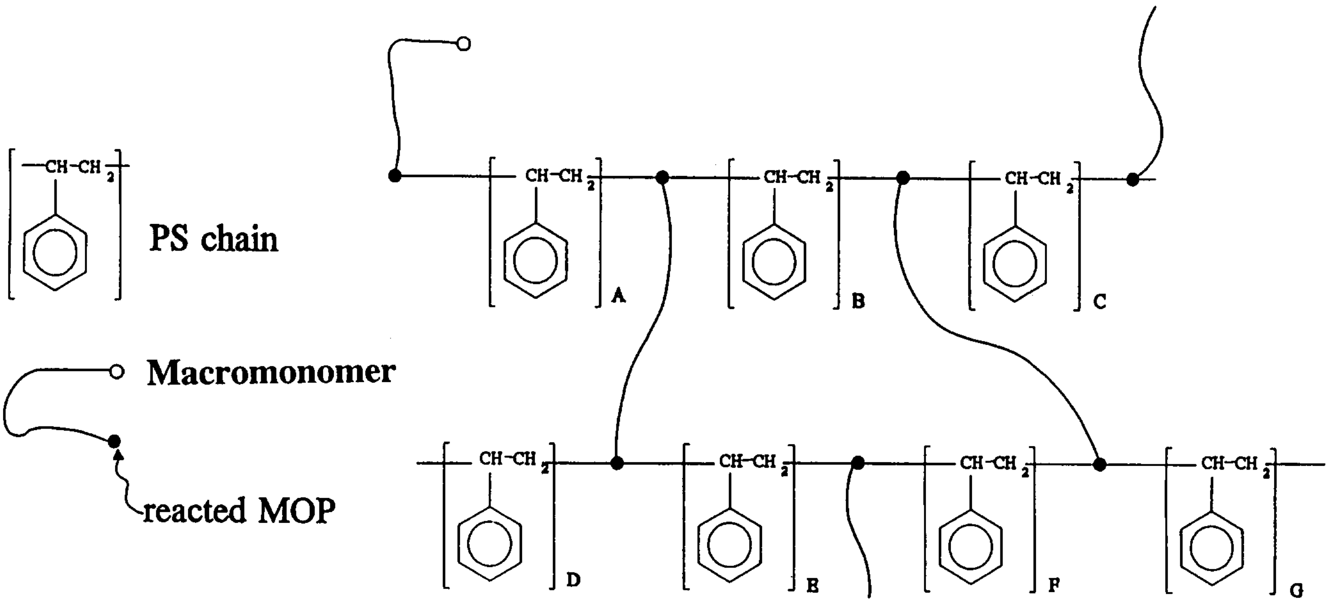


Figure 4 Proposed structure for the hexane insoluble copolymer

very highly crosslinked especially at longer reaction times (> 2 h). The proposed structure of the copolymer is given in *Figure 4*.

The structure and composition of the hexane insoluble copolymer at any time depends upon the instantaneous feed of styrene and of unreacted and partially reacted macromonomer (hexane soluble material).

The formation of a gel after quite short reaction times (< 2 h, depending on feed composition) would restrict the ability of the MOP groups to attach to a growing radical chain. This means that after gelation the reaction of MOP groups may occur more through initiation, rather than attaching to a propagating chain.

At high conversion times, the composition of the copolymer remains relatively constant at or around the feed composition. Remaining unreacted MOP groups in the hexane insoluble copolymer are not expected to increase the weight per cent copolymer appreciably, just the degree of crosslinking. However, if a MOP group contained in some hexane soluble copolymer reacts with a propagating PS chain, more hexane insoluble copolymer would be formed.

Structure elucidation of hexane soluble copolymers

Compositional analysis (*Table 1*) shows that the hexane soluble samples from macromonomer feed compositions of 10, 30, 40 and 50 wt% have a much lower styrene content (⩽ 10 wt%) than the corresponding hexane insoluble samples. In contrast the hexane soluble fractions from macromonomer feed concentration of 20 wt% samples have a styrene content much closer to that of the corresponding hexane insoluble material.

G.p.c. analysis of the hexane soluble material indicates that generally the molecular weights are higher than that of the macromonomer. The g.p.c. peak shape gives no indication of an appreciable amount of homopolystyrene

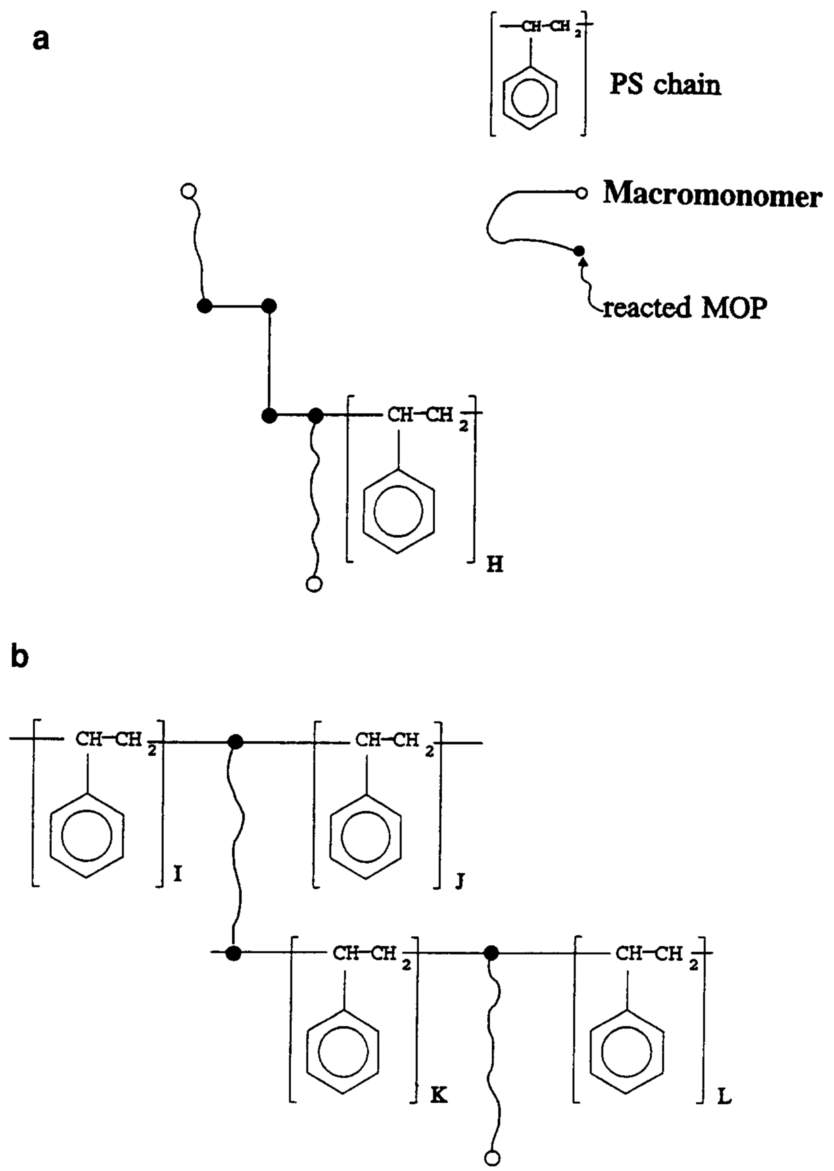


Figure 5 (a) Proposed structure for the hexane soluble copolymer from samples initially containing 10, 30, 40 and 50 wt% macromonomers in the feed. (b) Proposed structure for the hexane soluble copolymer of the sample initially containing 20 wt% macromonomers in the feed

being present in any of the hexane soluble samples. PS of molecular weight $<4800\,\mathrm{g\,mol^{-1}}$ is soluble in hexane under the Soxhlet extraction conditions used.

^{1}H n.m.r. data showed that generally, slightly more than one MOP group per macromonomer has reacted. This, combined with the above-mentioned g.p.c. results, indicates that the macromonomer has homopolymerized (i.e. dimerized, trimerized, etc.) in the samples with 10, 30, 40 and 50 wt% macromonomer feed concentration and short polystyrene chains may either be attached to the linked macromonomers or join them together (*Figure 5a*). Some of the hexane soluble samples were found to consist of 100% siloxane (30 wt% macromonomer feed). The most surprising result is the high PS content of the 20 wt% macromonomer feed samples. The slightly lower molecular weights indicate that fewer macromonomers have joined (either to each other or linked by polystyrene chains), than with the other macromonomer feeds (*Figure 5b*).

PS appears to be attached only as copolymer as there was no indication of homopolystyrene formation.

Phase chemistry during polymerization

The copolymer composition will be affected by the phase chemistry of the siloxane–styrene system during the course of polymerization. From compositions of the copolymer fractions, optical microscopy and cloud point results, it may be possible to construct a ternary phase diagram for the macromonomer I containing system as has been done for acrylonitrile–butadiene–styrene (ABS) and high impact polystyrene (HIPS)[22]. However, as the exact composition of each phase is unknown it is only possible to consider the broad consequences of the phase chemistry of the ternary system (styrene, macromonomer and copolymer) assuming that one phase is rich in styrene and poor in the macromonomer (producing the hexane insoluble copolymer) and the other is poor in styrene and rich in the macromonomer (producing the hexane soluble copolymer).

Cloud point and optical microscopy results for 20 wt% macromonomer feed show that the light transmission (%T) is still high after the first indication of phase separation (at 30 min). This indicates a smaller difference between the RI of the two phases of similar composition than at the other feeds. This is supported by the hexane soluble and hexane insoluble copolymers being similar in composition at lower conversion, suggesting phases closer in composition than for the other feeds.

Reasons for phase separation during polymerization

There are a number of possible reasons for a miscible mixture of low siloxane content phase separating during polymerization:

1. the joining of macromonomers to form a longer PDMS polymer or crosslinked network;
2. the formation of a copolymer containing polystyrene;
3. the consumption of styrene (which acts as a solvent for the system);
4. or any combination of (1) to (3).

Analysis of the copolymer composition at the cloud points indicates that phase separation of the binary styrene–macromonomer mixture is either related to the styrene consumption or the incorporation of a larger proportion of polystyrene in the hexane insoluble copolymer.

As 7% of the styrene was consumed when phase separation occurred for the 10 wt% feed sample, styrene consumption alone would not have caused the phase separation as the 20 wt% feed sample which contains 80 wt% styrene was not initially phase separated. This suggests that the formation of copolymer containing appreciable amounts of PS results in the separation of material rich in macromonomer from the bulk mixture.

Aven and Cohen[23] found that addition of small amounts of PS to a THF solution containing 15 vol% PDMS results in phase separation. The addition of PDMS to PS by blending also results in phase separation[24].

Katz and Zewi[10] and Tenhu and Heino[14] have shown clouding for the copolymerization of styrene with difumarate and MOP functionalized PDMS in bulk. The clouding indicated phase separation caused by the formation of PS chains of sufficient molecular weight to be highly insoluble in the PDMS macromonomers.

Tsukahara *et al.*[15] proposed for phase separation to occur the total monomer concentration (C_t) (in g ml^{-1}, of macromonomer and styrene) must exceed the overlap concentration C_{av} (the concentration at which the components are miscible in each other). *Table 3* shows overlap concentrations[15] calculated for this system for various molecular weights of the PS chain using equations for the radius of gyration of each component. *Table 4* shows the C_t for the macromonomer–styrene mixtures for 10 to 50 wt% feed. The rate of phase separation should increase with siloxane concentration. It is felt that the C_t and C_{av} data cannot be directly compared as the calculations take no account of (1) the effect of MOP groups on C_{av} and (2) the effect of increasing the weight per cent macromonomer in the feed (decreasing weight per cent styrene) on C_{av} when the styrene is not fully solvating the macromonomers and phase separation is occurring.

Table 3 Overlap concentrations for PS of various chain lengths with low molar mass macromonomer

No. of styryl units	PS molecular weight (g mol^{-1})	Overlap concentration[a] (g ml^{-1})
25	2604	0.64
50	5208	0.54
100	10415	0.47
200	20830	0.44
500	52073	0.41

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

Table 4 Total monomer concentration for macromonomer–styrene mixtures at various feeds

Feed (wt% macromonomer I)	Total monomer concentration (g ml^{-1})
10	0.87
20	0.89
30	0.90
40	0.92
50	0.93

CONCLUSIONS

The copolymers of low molar mass siloxane macromonomer and styrene were found to be crosslinked insoluble networks. This is consistent with the findings of Tenhu and Heino[14] for PS–PDMS copolymers containing difunctional macromonomers with molecular weights ranging from 200 to 2000 g mol^{-1}. ^{1}H n.m.r. analysis of swollen copolymer gels showed that these siloxane–PS copolymers contained only small amounts of unreacted MOP groups remaining on the macromonomers. Analysis of the low molecular weight (hexane soluble) fraction of the copolymer showed that the macromonomer could homopolymerize.

It was found 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.

ACKNOWLEDGEMENTS

This work was supported by a Generic Technology Industrial Research and Development grant from the New Materials Technology Committee, Industry Research and Development Board, Department of Industry Technology and Commerce. The authors also wish to thank Flexichem (South Australia) for supplying the siloxane macromonomers used in this study.

REFERENCES

1 Lynch, W., 'Handbook of Silicone Rubber Formulation', Van Nostrand and Reinhold, New York, 1978
2 Litvinov, V. M. and Zhdanov, A. A. *Polym. Sci. USSR* 1987, **29**, 1133
3 Zhdanov, A. A., Slonimskii, G. L., Levin, V. Yu., Martirosov, V. A., Gritsenko, O. T., Mikhlin, V. E. and Chernyavskaya, N. A. *Polym. Sci. USSR* 1987, **29**, 1651
4 Berrod, G., Vidal, A., Papirer, E. and Donnel, J. B. *J. Appl. Polym. Sci.* 1981, **26**, 833
5 Saam, J. C., Mettler, C. M., Falender, J. R. and Dill, T. J. *J. Appl. Polym. Sci.* 1979, **24**, 187
6 Yorkgitis, E. M., Tran, C., Eiss, N. S., Hu, T. Y., Yilgor, L., Wilkes, G. L. and McGrath, J. E. *Adv. Chem. Ser.* 1984, **208**, 137
7 Riffle, J. S., Yilgor, I., Tran, C., Wilkes, G. L., McGrath, J. E. and Banthia, A. K. *Am. Chem. Soc. Symp. Ser.* 1983, **122**, 21
8 Chujo, Y., Shinshino, T. and Yamashita, Y. *Polym. J.* 1984, **16**(6), 495
9 Suzuki, T. and Okawa, T. *Polymer* 1988, **29**, 2095

10 Katz, D. and Zewi, G. *J. Polym. Sci., Polym. Chem. Edn* 1978, **6**, 597

11 Rogler, W., Markert, H., Stapp, B. and Zapf, F. *Polym. Prepr.* 1988, **29**, 528

12 Yang, W. M. and Peppas, N. A. *Polym. Bull.* 1983, **9**, 255

13 Williams, T. R. *J. Appl. Polym. Sci.* 1986, **31**, 1293

14 Tenhu, H. and Heino, E.-L. *J. Appl. Polym. Sci.* 1992, **44**, 55

15 Tsukahara, Y., Hayashi, N., Jiang, X. L. and Yamashita, Y. *Polym. J.* 1989, **21**, 377

16 Duplock, S. K., Swincer, A. G., George, G. A. and O'Shea, M. S. *Inorg. Organomet. Polym.* 1991, **1**, 581

17 Rao, V. L. and Babu, G. N. *Eur. Polym. J.* 1989, **6**, 605

18 Smith, S. D., York, G., Dwight, D. W., McGrath, J. E., Stejskal, J. and Kratochvil, P. *Polym. Prepr.* 1987, **28**, 458

19 Li, L. and Huang, B. *Makromol. Chem.* 1989, **190**, 2373

20 O'Driscoll, K. F. and Huang, J. *Eur. Polym. J.* 1990, **26**, 643

21 Davis, T. P., O'Driscoll, K. F., Piton, M. C. and Winnik, M. A. *J. Polym. Sci., Polym. Lett. Edn* 1989, **27**, 181

22 Platt, A. E. in 'Comprehensive Polymer Science' (Eds G. Allen and J. Bevington), Vol. 6, Pergamon Press, Oxford, pp. 437–449

23 Aven, M. R. and Cohen, C. *Macromolecules* 1990, **23**, 476

24 Clark, A. J. F., Shaver, A. and Eisenberg, A. *Polym. Eng. Sci.* 1981, **21**, 707