

# Development of novel attachable initiators for atom transfer radical polymerization. Synthesis of block and graft copolymers from poly(dimethylsiloxane) macroinitiators

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The synthesis of poly(styrene–dimethylsiloxane) block and graft copolymers is described. Commercially available difunctional poly(dimethylsiloxane) (PDMS) containing either vinylsilyl or hydrosilyl terminal species was reacted with the corresponding hydrosilyl or vinylsilyl attachable initiators containing the benzyl chloride species. The attachment of the initiators to PDMS was achieved by hydrosilylation in the presence of a platinum(0) catalyst. The terminal benzyl chloride groups were then used as initiators for atom transfer radical polymerization (ATRP) to produce block copolymers. Using this technique, triblock copolymers consisting of a PDMS centre block and polystyrene terminal blocks were synthesized. A similar process was also used to produce graft copolymers of polystyrene from a PDMS backbone. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(dimethylsiloxane); atom transfer radical polymerization; styrene)

## INTRODUCTION

After living anionic and cationic polymerizations were achieved, 'living' radical polymerization has been one of the most targeted goals for synthetic polymer chemists. In the past few years, two new methods to realize 'living' radical polymerization techniques were reported. These are stable free radical polymerization (SFRP)<sup>1</sup> using stable nitroxide radicals such as TEMPO, and atom transfer radical polymerization (ATRP) utilizing transition metal complexes such as copper<sup>2,3</sup>, ruthenium<sup>4</sup>, nickel<sup>5</sup>, etc. In either of these processes, the key to control of chain length is an equilibrium between active free radicals and dormant species where the steady state concentration of radicals remains low thereby limiting termination reactions to high monomer conversions.

ATRP catalysed by copper halides complexed with 2,2'-bipyridine (bipy) derivatives for the polymerization of various styrenes<sup>6–9</sup>, methacrylates<sup>3,10,11</sup>, acrylates<sup>2,12</sup>, dienes and acrylonitrile<sup>13</sup> has been developed in our and other laboratories. The individual reaction steps are listed in *Figure 1*. The figure shows that while the rate constants of initiation and propagation,  $k_i$  and  $k_p$  respectively, are identical to conventional free radical polymerization, the key to control is the equilibrium between active and dormant species for the two processes defined by  $k_{a1}$ ,  $k_{d1}$  for initiation and  $k_{a2}$ ,  $k_{d2}$  for propagation. Termination by coupling and disproportionation occurs as in conventional free radical polymerization for a given monomer but its contribution is reduced due to a lower stationary concentration of growing radicals. The polymerization provides well-defined polymers with low polydispersities ( $1.05 < M_w/M_n$ )

and degrees of polymerization predetermined by the ratio of concentrations of reacted monomer and introduced initiator ( $DP = \Delta[M]/[I]_0$ ). ATRP is initiated by alkyl halides, and therefore, any polymer which has a sufficiently active alkyl halide end-group could initiate ATRP to afford block copolymers.

On the other hand, some polymers which contain terminal or pendant vinyl groups are either commercially available or easily prepared. Examples are vinyl-terminated polyisobutylene<sup>14</sup> and vinyl functional polysiloxanes<sup>15</sup>. Many functional groups can be attached to the vinyl group by hydrosilylation.

Poly(dimethylsiloxane) (PDMS) block and graft copolymers are expected to possess unique physical properties making them viable candidates for materials such as thermoplastic elastomers, compatibilizers for silicone rubbers and surfactants for supercritical carbon dioxide. Several synthetic methods for PDMS copolymers have been reported<sup>16–26</sup>. The best results were obtained using living anionic polymerization. However, these methods required stringent purification and stoichiometric conditions. Block and graft copolymers have been prepared using free radical polymerization. For example, PDMS containing internal tetraphenylethylene moieties were used for the synthesis of segmented multiblock copolymers with various vinyl monomers<sup>21,22</sup>. While the use of macroinitiators for free radical polymerization appeared to be very promising conventional methods introduced problems such as functionalization of polymer end groups, incomplete initiator efficiency and homopolymer formation<sup>23,24</sup>.

These problems are avoided by ATRP from PDMS macroinitiators, which are prepared by hydrosilylation of an attachable initiator to vinyl or hydrosilyl functionalized PDMS with a platinum(0) catalyst as shown in *Figure 2*.

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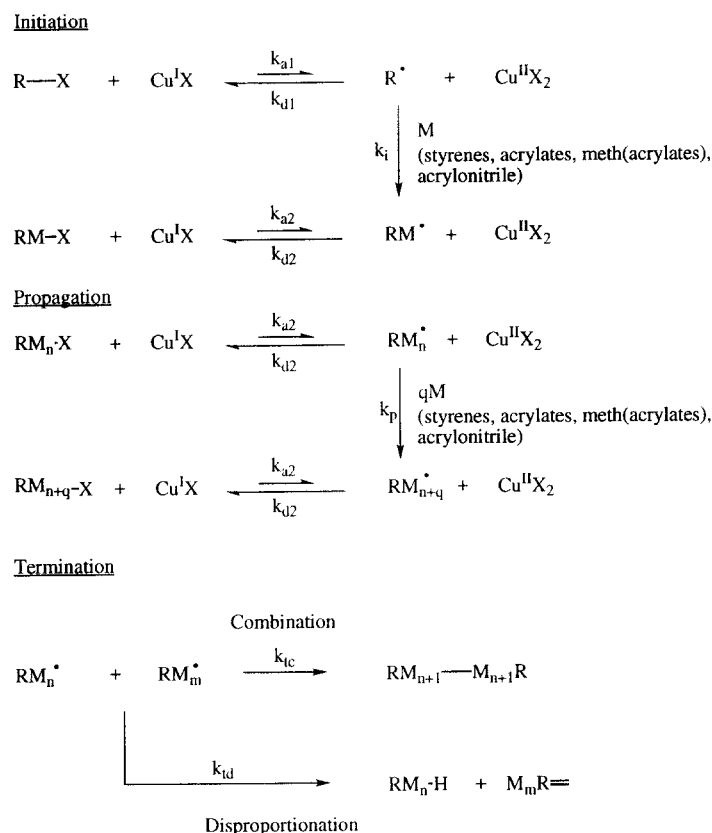


Figure 1 Reaction scheme for initiation, propagation and termination steps in atom transfer radical polymerization (ATRP)

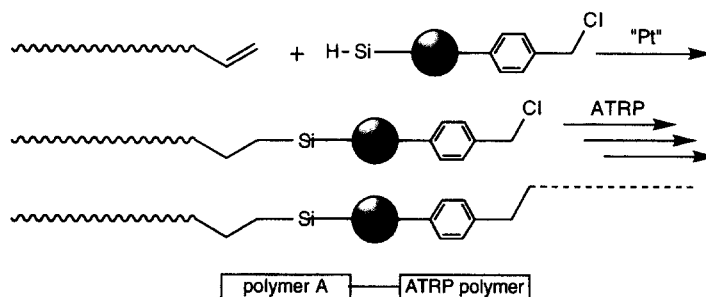


Figure 2 Reaction scheme for the synthesis of PDMS macroinitiators

Hydrosilations of this type are very selective, quantitative reactions. Initiation of ATRP of styrene from the corresponding macroinitiator is efficient yielding well-defined blocks.

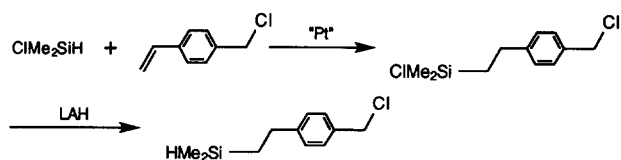
In this paper, development of novel attachable ATRP initiators is described. The resulting macroinitiators are used in simple and convenient methods to synthesize block and graft PDMS copolymers.

## EXPERIMENTAL

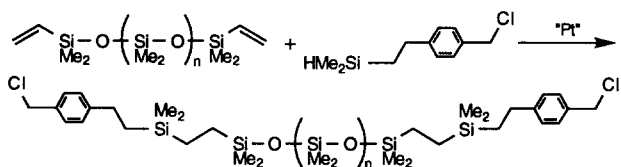
**Materials.** Styrene and 4-vinylbenzyl chloride (4-VBC, or *p*-chloromethyl styrene) (pure *p* isomer and *m,p* mixture) from Acros were passed through an Al<sub>2</sub>O<sub>3</sub> column and bubbled with argon. Benzene was distilled over CaH<sub>2</sub>. Ph<sub>2</sub>O from Acros was dried over molecular sieves. Xylene was dried over sodium. Anhydrous ethyl ether, CuCl, HSiMe<sub>2</sub>Cl, 1,4-dimethoxybenzene and LiAlH<sub>4</sub> were used as received. All of the PDMS starting materials were obtained

from UCT, GE and Gelest. 2,2'-Bipyridine (bipy) from Acros was recrystallized from *n*-hexane. The Pt[{(CH<sub>2</sub>=CH)Me<sub>2</sub>Si}<sub>2</sub>O]<sub>2</sub> complex (Karstedt's catalyst) in xylene was prepared by published procedures<sup>27,28</sup>.

*Synthesis of 2-(4-chloromethylphenyl)ethyldimethylsilane.* HSiMe<sub>2</sub>Cl (14.4 mL, 130.0 mmol) was slowly added to a mixture of 4-VBC (*m,p* mixture) (14.2 mL, 100.0 mmol), anhydrous ethyl ether (50 mL) and Pt[{(CH<sub>2</sub>=CH)Me<sub>2</sub>Si}<sub>2</sub>O]<sub>2</sub> complex xylene solution (5.0 × 10<sup>-2</sup> mmol) at room temperature under air. The mixture was stirred at room temperature for 1 h. Disappearance of the vinyl group was confirmed by <sup>1</sup>H n.m.r. To the reaction mixture was added LiAlH<sub>4</sub> (2.47 g, 65.0 mmol) at 0°C. The mixture was stirred at 0°C for 1 h. 100 mL of *n*-hexane was added, and ether was removed in vacuo at 0°C. An additional 100 mL of *n*-hexane was added at which time a precipitate appeared. After filtration through a short Al<sub>2</sub>O<sub>3</sub> column the solvent was evaporated leaving an oil. The product, 2-(4-chloromethylphenyl)-ethyldimethylsilane, was



**Figure 3** Reaction scheme for the synthesis of the benzyl chloride functionalized attachable initiator



**Figure 4** Reaction scheme for the formation of macroinitiators from vinyl functionalized PDMS

confirmed by  $^1\text{H}$  n.m.r. and used without further purification.  $^1\text{H}$  n.m.r. revealed two regioisomers of the product with *endo/exo* = 1:0.17.

$^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.3–6.9 (m, 4H), 4.5 (s, 2H), 3.9–3.7 (m, 1H, *endo/exo*), 2.6 (m, 2H, *endo*), 2.3 (m, 1H, *exo*), 1.3 (m, 3H, *exo*), 0.9 (m, 2H, *endo*), 0.1 (d, 6H,  $J = 3.66$  Hz), 0.0 (d, 3H,  $J = 3.66$  Hz),  $-0.1$  (d, 3H,  $J = 3.67$  Hz)

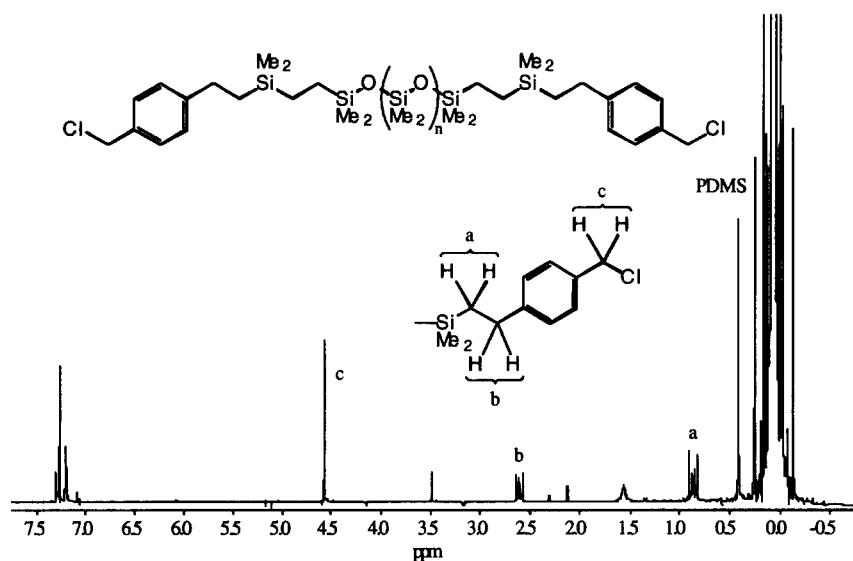
**Hydrosilylation of 2-(4-chloromethylphenyl)ethyldimethylsilane with vinyl terminated PDMS.** A mixture of vinyl terminated poly(dimethylsiloxane) ( $\text{Si}-\text{CH}=\text{CH}_2$  ca.  $9.6 \times 10^{-5}$  mol  $\text{g}^{-1}$  10.00 g), 2-(4-chloromethylphenyl)ethyldimethylsilane ( $2.307 \times 10^{-3}$  mol; 0.491 g), Karstedt's catalyst in xylene ( $9.614 \times 10^{-6}$  mol) and benzene (10.0 mL) were stirred under air at  $70^\circ\text{C}$  for 2 h. Disappearance of the vinyl group of the PDMS was confirmed by  $^1\text{H}$  n.m.r. The reaction mixture was precipitated into methanol to remove excess 2-(4-chloromethylphenyl)ethyldimethylsilane. An analogous method was applied to vinyl pendant PDMS.

**Hydrosilylation of 4-VBC with hydrodimethylsilyl terminated PDMS.** A mixture of hydrodimethylsilyl terminated poly(dimethylsiloxane) ( $\text{Si}-\text{H}$  ca.  $7.7 \times 10^{-4}$  mol  $\text{g}^{-1}$  20.00 g), 4-VBC (*m,p* mixture; 3.29 mL,  $2.31 \times 10^{-2}$  mol), Karstedt's catalyst in xylene ( $3.1 \times 10^{-5}$  mol) and benzene (20.0 mL) were stirred under air at  $50^\circ\text{C}$  for 1 h. Disappearance of the hydrosilyl group of the PDMS was confirmed by  $^1\text{H}$  n.m.r. The reaction mixture was precipitated into methanol to remove excess 4-VBC.

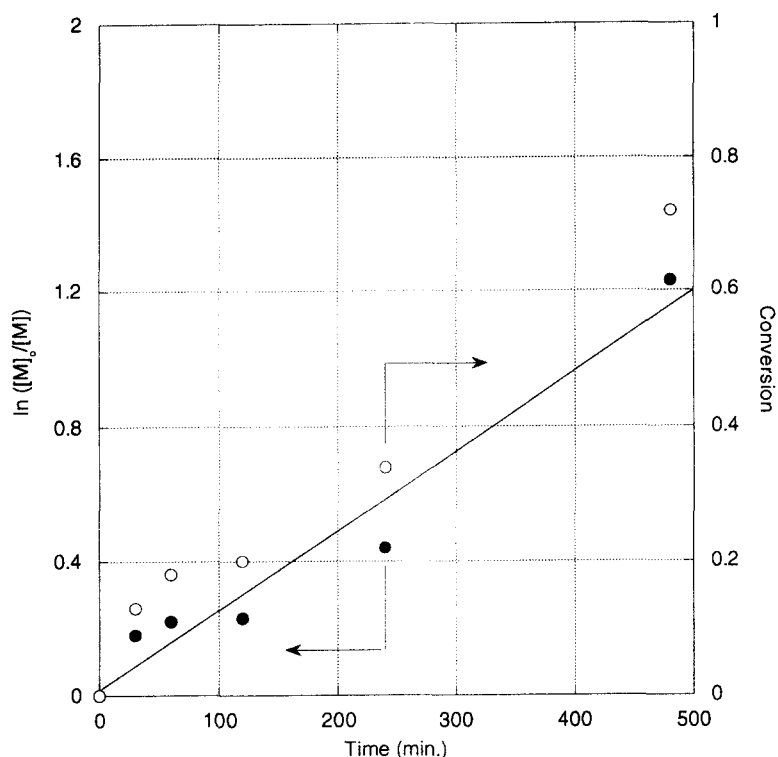
**Polymerization of styrene initiated by PDMS macroinitiator in solvent.** The polymerization was carried out in a previously dried flask equipped with a magnetic stirring bar under argon. The polysiloxane macroinitiator (4.8 g), CuCl (0.22 g), 2,2'-bipyridyl (1.02 g) and phenyl ether (5.0 g) were put into the flask, and then the flask was degassed three times by repeated freeze/vacuum/thaw cycles. Styrene (10.0 mL) was transferred to the flask under argon using proper Schlenk techniques. The mixture was stirred at  $130^\circ\text{C}$  under argon. Conversion of the polymerization was determined by g.l.c. or  $^1\text{H}$  n.m.r. measurement of the sampled reaction mixture. After the heating was stopped, the reaction mixture was purified by filtration through a short  $\text{Al}_2\text{O}_3$  column followed by precipitation into methanol from THF.

In some polymerizations, 1,4-dimethoxybenzene, anisole or xylene was used instead of phenyl ether. Furthermore, when dNbipy was substituted for bipy a homogeneous catalyst system was obtained.

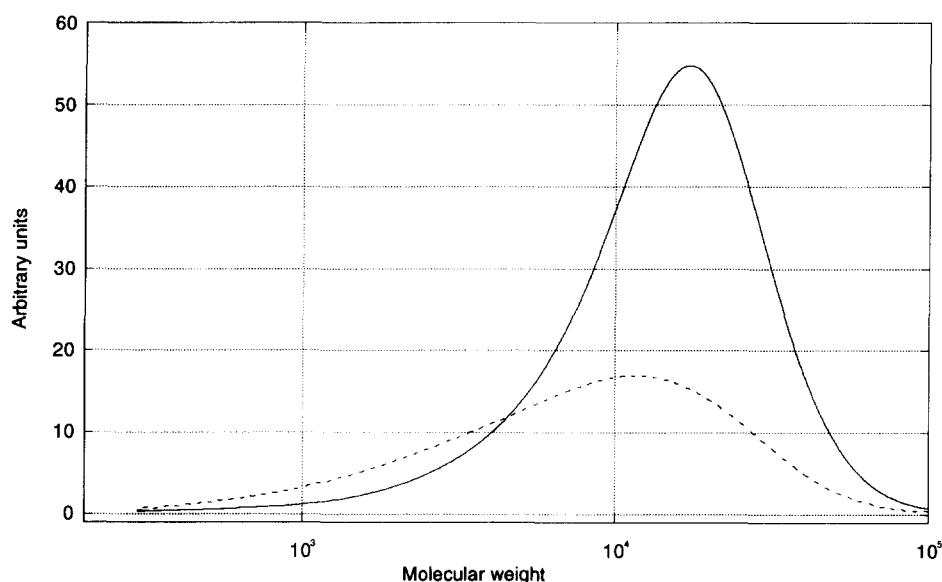
**Bulk polymerization of styrene initiated by a PDMS macroinitiator.** The PDMS macroinitiator (10.00 g), CuCl (0.137 g), and dNbipy (1.127 g) were placed into a previously dried flask equipped with a magnetic stirring bar under argon. The flask was degassed three times. Using proper Schlenk techniques the flask was charged with styrene (30.0 mL). The mixture was stirred at  $130^\circ\text{C}$  under argon. Progress of the polymerization was monitored by g.l.c. measurement of the sampled reaction mixture. At completion the reaction mixture was purified by filtration



**Figure 5**  $^1\text{H}$  n.m.r. spectrum of the telechelic poly(dimethylsiloxane) macroinitiator. Residual solvent peaks are present in the spectrum



**Figure 6** First order kinetic plot for the ATRP of styrene from a difunctional polysiloxane macroinitiator in phenyl ether with CuCl/bipy catalyst



**Figure 7** g.p.c. traces of the difunctional polysiloxane macroinitiator (---,  $M_n = 9800$ ,  $M_w/M_n = 2.40$ ) and the reaction mixture (—,  $M_n = 20\,700$ ,  $M_w/M_n = 1.70$ ) after 480 min without purification

through a short  $\text{Al}_2\text{O}_3$  column followed by precipitation into methanol from THF.

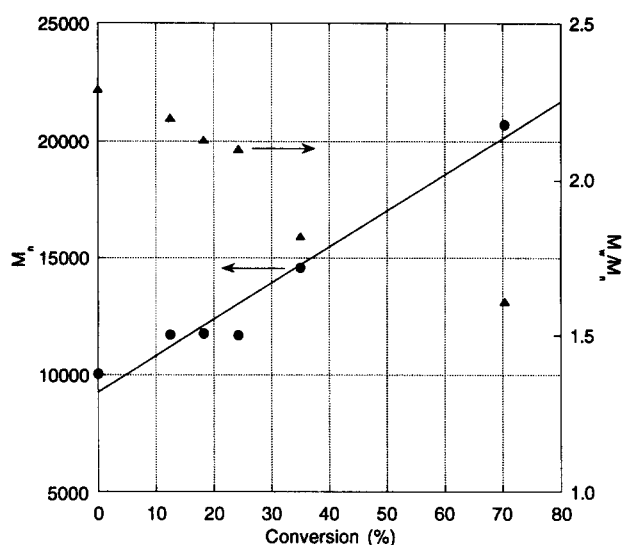
**Measurements.** Gel permeation chromatography (g.p.c.) measurements in THF were carried out using a Waters 510 liquid chromatograph pump equipped with four Phenogel columns (100 Å, 1000 Å linear and guard) in series with a Waters 410 differential refractometer and a Waters 991 UV detector. Molecular weight analysis was achieved with PSS software; calibration based on narrow molecular weight polystyrene standards. Monomer conversion was measured on a Shimadzu GC-14A gas chromatograph equipped with a wide-bore capillary column (DB-wax, J&W Sci.) or by  $^1\text{H}$  n.m.r. on a

300 MHz Bruker spectrometer using either Bruker or Tecmag data acquisition software.  $^1\text{H}$  n.m.r. spectra were run in deuterated chloroform against a TMS reference.

## RESULTS AND DISCUSSION

### Synthesis of the attachable initiator: 2-(4-chloromethylphenyl)ethyl-dimethylsilane

Hydrosilation of chlorodimethylsilane to 4-VBC, Figure 3, was performed with Karstedt's catalyst in ethyl ether under air, because hydrosilation, in general, is accelerated by oxygen. In one pot, subsequent reduction of the chlorosilyl group to a hydrosilyl moiety was carried



**Figure 8**  $M_n$  and  $M_w/M_n$  dependence on conversion for the ATRP of styrene with difunctional polysiloxane macroinitiator in phenyl ether with CuCl/bipy catalyst

out using lithium aluminium hydride (LAH) at 0°C. Although LAH can reduce benzyl chloride, this reaction did not occur under these conditions. When converting a vinyl group of PDMS to an initiating species, avoiding reduction is very important. Therefore, the excess LAH and the residue were removed by precipitation in *n*-hexane and subsequent filtration through a short Al<sub>2</sub>O<sub>3</sub> column. During the hydrosilylation, another regioisomer, i.e., a compound with a silyl group on the  $\alpha$  carbon atom to the phenyl group is formed as a minor product. <sup>1</sup>H n.m.r. showed the *endo/exo* ratio of these two isomers to be 1/0.17. The product was used in the next reaction without further purification.

#### Hydrosilylation of 2-(4-chloromethylphenyl)ethyldimethylsilane to vinyl dimethylsilyl terminated poly(dimethylsiloxane)

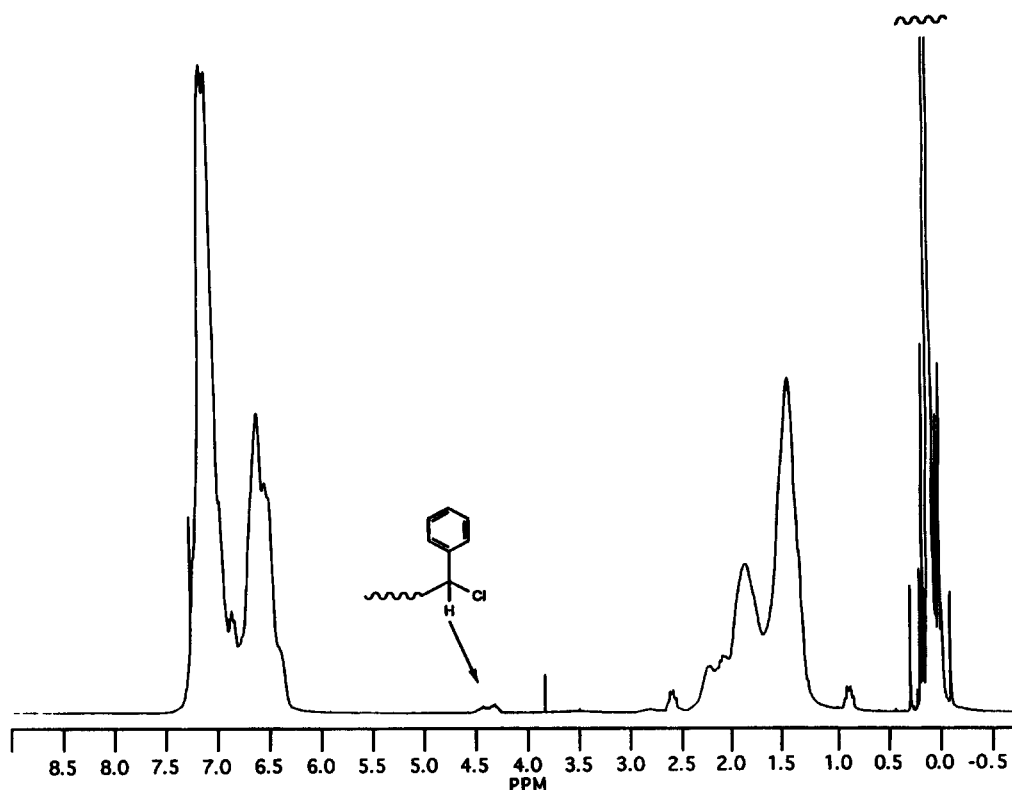
Figure 4 illustrates the hydrosilylation of 2-(4-chloromethylphenyl)ethyldimethylsilane to vinyl dimethylsilyl terminated poly(dimethylsiloxane) by Karstedt's catalyst. Excess 2-(4-chloromethylphenyl)ethyldimethylsilane was used relative to the vinyl group of poly(dimethylsiloxane) in order to achieve quantitative transformation. After completion of the reaction, the excess was removed by precipitation in methanol. No significant side reactions were observed in this system.

The <sup>1</sup>H n.m.r. spectrum of the poly(dimethylsiloxane) macroinitiator is shown in Figure 5. The observed peaks at 4.55 (s), 2.55–2.65 (m), and 0.82–0.92 (m) ppm were assigned to the two chlorobenzyl protons, the two protons in the *para* position to the chlorobenzyl group, and two methylene protons which are between silicon and the benzyl carbon, respectively. No resonances for the vinyl groups were observed. Furthermore, no peaks derived from the *exo* regioisomer of the attachable initiator were detected indicating that no more than 3% of the macroinitiating species was derived from that minor regioisomer. This can be explained by an excess of the macroinitiator which contained a low concentration of the *exo* isomer present throughout the reaction.

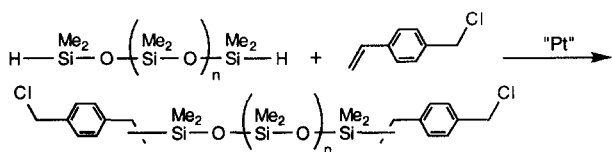
#### Polymerization of styrene initiated by difunctional polysiloxane macroinitiators

Polymerization of styrene initiated by the difunctional PDMS macroinitiator was carried out with a CuCl/bipy catalyst in phenyl ether at 130°C. The macroinitiator and growing triblock copolymer were soluble. However, the catalyst exhibited poor solubility.

The first order kinetic plot of the polymerization is shown



**Figure 9** <sup>1</sup>H n.m.r. spectrum of poly(styrene-*block*-dimethylsiloxane-*block*-styrene) copolymer prepared by ATRP.  $M_n$ (g.p.c.) = 11 000,  $M_w/M_n$ (g.p.c.) = 1.15



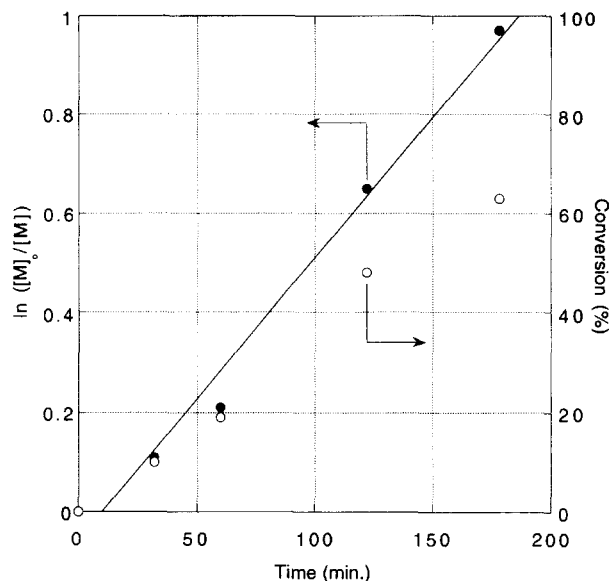
**Figure 10** Reaction scheme for the formation of macroinitiators from hydrosilyl functionalized PDMS

in Figure 6. In ATRP, the first order plot is usually linear due to a constant concentration of growing radicals throughout the polymerization. The polymerization was stopped after 480 min due to the high viscosity of the reaction mixture. At this stage, the conversion of styrene monomer was 70%.

g.p.c. traces of the difunctional polysiloxane macroinitiator and the sample at 480 min are shown in Figure 7. The growing triblock copolymer peak remained monomodal throughout the reaction, indicating that all of the attachable initiator which did not react with the PDMS had been removed prior to polymerization. Furthermore, the polymer peak continuously shifted to higher molecular weights with monomer conversion. The molecular weight of the macroinitiator was  $M_n = 9800$ ,  $M_w/M_n = 2.40$ . After 480 min the measured values had increased to  $M_n = 20\,700$ ,  $M_w/M_n = 1.60$ .

The plot of number average molecular weight,  $M_n$ , and polydispersity,  $M_w/M_n$ , dependence on conversion in this polymerization is shown in Figure 8. A linear increase of  $M_n$  versus monomer conversion was observed. The polydispersity decreased with the progress of the polymerization demonstrating that the reaction was controlled and the polystyrene blocks had low polydispersities typical of radical polymerization by an atom transfer process<sup>7</sup>.

The <sup>1</sup>H n.m.r. spectrum of the final product of poly(styrene-*block*-dimethylsiloxane-*block*-styrene) copolymer is shown in Figure 9. It reveals that the polymer consists of polystyrene and poly(dimethylsiloxane). The molar ratio of styrene to dimethylsiloxane units was 0.84. Furthermore, conservation of the polymer endgroup, a prerequisite for controlled/‘living’ polymerizations, is demonstrated by



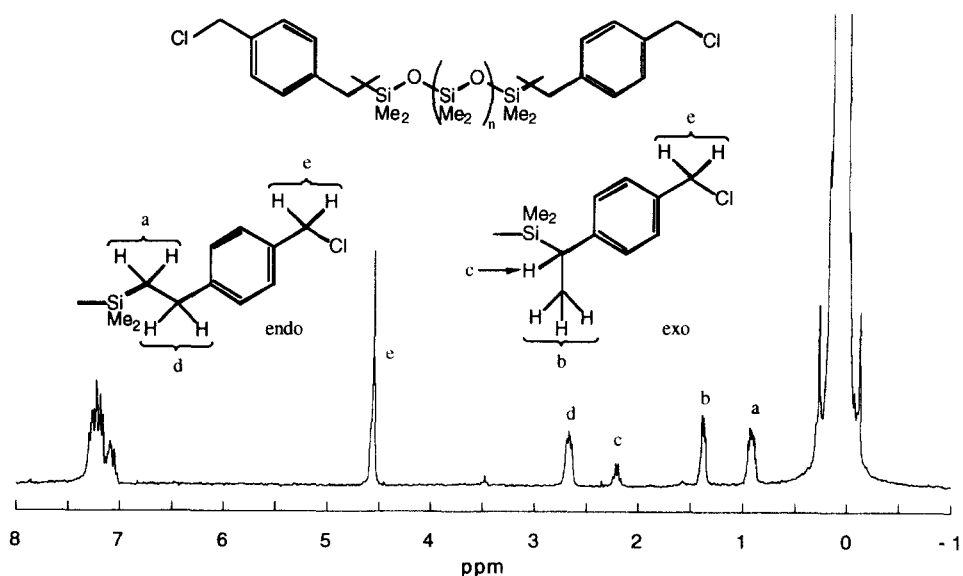
**Figure 12** First order kinetic plot for the ATRP of styrene in bulk at 130°C from a difunctional polysiloxane macroinitiator ( $M_n = 3000$ ) prepared from hydrodimethylsilyl terminated PDMS

conversion of the primary benzyl chloride from the macroinitiator at 4.4 ppm to the secondary one on the copolymer at 4.5 ppm. The precipitated polymer was isolated as a white powder.

*Alternative preparation of macroinitiators: hydrosilation of hydrodimethylsilyl terminated poly(dimethylsiloxane)*

Hydrosilation of hydrodimethylsilyl terminated PDMS with *p*-CMS proceeded as shown in Figure 10. An excess of *p*-CMS was used relative to the hydrosilyl group of PDMS in order to achieve complete transformation. After completion of the reaction, the excess was removed by means of precipitation into methanol. No significant side reactions were observed.

The <sup>1</sup>H n.m.r. spectrum of the PDMS macroinitiator is shown in Figure 11. No vinyl proton peaks were observed indicating that formation of the product was quantitative.



**Figure 11** <sup>1</sup>H n.m.r. spectrum of a difunctional PDMS macroinitiator. Structural assignment of the peaks corresponding to the two regioisomers is illustrated above

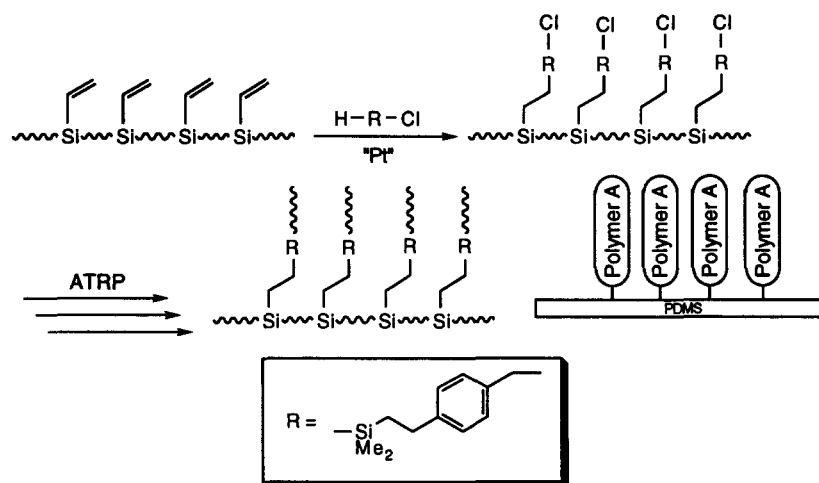


Figure 13 Reaction scheme for the formation of and ATRP from macroinitiators from pendant vinyl functionalized PDMS

The hydrosilylation gave two regioisomers with low selectivity: *endo/exo* = 1/0.6. In the figure the *endo* and *exo* protons, labelled a, d and c, b, respectively, were clearly resolved in contrast to the absence of similar peaks in Figure 5. The reason is that for the product shown in Figure 5 the reactivity of the silyl hydride attached to a secondary carbon in one of the two regioisomers of the attachable initiator is lower compared to the other regioisomer which has connectivity to a less hindered primary carbon atom. The reactivities of the primary and secondary carbons of 4-VBC are sufficiently close that similar quantities of the two regioisomers are observed in the  $^1\text{H}$  n.m.r. spectrum (Figure 11).

Polymerization using the macroinitiator prepared from hydrodimethylsilyl terminated PDMS gave similar results to the macroinitiator from the vinyl analogue. A first-order kinetic plot of the polymerization is shown in Figure 12. Following a short induction period a nearly linear kinetic curve was produced.

The molecular weights of the PDMS macroinitiator and the purified triblock copolymer were  $M_n = 3000$ ,  $M_w/M_n = 1.35$  and  $M_n = 9900$ ,  $M_w/M_n = 1.16$  respectively. The weight ratio of polystyrene/PDMS measured by  $^1\text{H}$  n.m.r. was 2.4, a value in good agreement with the g.p.c. result.

#### Preparation of PDMS graft copolymers from pendant-functionalized PDMS macroinitiators

The method used to prepare telechelic PDMS macroinitiators was applied to pendant vinyl functionalized PDMS (Figure 13). Pendant vinyl functionalized PDMS was converted to a pendant ATRP macroinitiator by the attachable initiator method analogous to that described for vinyl terminal PDMS (vide supra). Styrene was polymerized with the macroinitiator in bulk. The  $^1\text{H}$  n.m.r. spectrum indicates that the graft copolymer contained less than 5% unreacted benzyl chloride groups. The molecular weights of the PDMS macroinitiator and purified graft copolymer were  $M_n = 6600$ ,  $M_w/M_n = 1.76$  and  $M_n = 14\,800$ ,  $M_w/M_n = 2.10$  respectively. The weight ratio of polystyrene/PDMS measured by  $^1\text{H}$  n.m.r. was 1.18, in good agreement with value obtained from g.p.c. The increase in polydispersity is attributed to a variable number of initiating sites on the PDMS chains.

#### CONCLUSIONS

Novel attachable initiators which contained both a benzyl

chloride and either a hydrosilyl or vinyl group were developed for atom transfer radical polymerization. Poly(-dimethylsiloxane) macroinitiators were prepared by hydrosilylation of an attachable initiator onto vinyl or hydrosilyl functionalized PDMS. ABA triblock copolymers were then synthesized by means of ATRP. The attachable initiator methodology can be applied to other vinyl functional polymers to give a variety of block and graft copolymers by ATRP.

#### ACKNOWLEDGEMENTS

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