Direct Evidence for the Interaction of the Mechanisms of Thermally Initiated and Atom Transfer Radical Polymerization

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Introduction. Autopolymerization of styrene[1–5] remains relatively unimportant in standard free radical polymerization, but Matyjaszewski, Fukuda, and Hawker have noted that it is of great importance at the elevated temperatures used in living free radical polymerizations (LFRP) mediated by nitroxyls such as TEMPO.[6–8]

Autopolymerization of styrene in ATRP systems has been observed by Angot et al.[9] and Matyjaszewski et al.[10] during syntheses of star polymers of styrene at high monomer concentrations and at temperatures of 100 °C or higher. In both cases, sides peaks at lower molecular weights were observed in the size exclusion chromatograms of the products that were attributed to linear polystyrene arising from the thermal initiation of the monomer.

In a recent paper we published the synthesis of a poly-(methyphenylsilane)-*graft*-polystyrene copolymer.[11] This was achieved by the bromomethylation of poly(methylphenylsilane) (PMPS),[12] with the resulting bromomethylated poly(methylphenylsilane) (BrMePMPS)[13] being used as a macromolecular initiator for the bulk ATRP of styrene at 110 °C using Cu(I)Br and bipyridine (bipy) as a catalyst system.[14,15]

Although thermal initiated polymerization has been noted in both LFRP and ATRP reactions, its interaction with these systems has only been shown for LFRP.[16] In this paper we show how a detailed study of this grafting reaction has yielded valuable information concerning the interaction of the mechanisms of ATRP and the underlying autopolymerization.

Results and Discussion. PMPS[12] and BrMePMPS[13] were synthesized according to literature procedures. The polystyrene grafts were grown by ATRP.[11,17] The course of the reaction was followed by ^{1}H NMR spectroscopy and size exclusion chromatography. The reaction time until gelation for the ATRP reaction was found to vary greatly with graft chain length, from 7 h for a calculated degree of polymerization (calculated $\overline{DP}$) of ~70 to 72 h for a calculated $\overline{DP}$ of ~200. It should also be noted that the reaction time required for a grafting reaction to high molecular weight is significantly longer than for the equivalent homopolymerization using a Cu(I)Br (bipy) catalyst system.[14] The plot of M_n versus conversion for the low molecular weight grafting reaction (calculated $\overline{DP}$ ~ 70) is linear, indicating that the polymerization has living character (Figure 1). The near perfect overlay of the size exclusion chromatograms of a typical low molecular weight graft copolymer recorded at 334 nm (characteristic of the PMPS σ-conjugated silicon backbone) and at 254 nm using a UV detector demonstrates that all of the material present contains
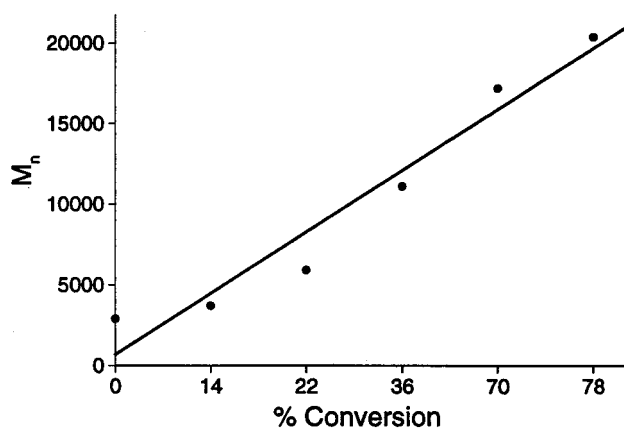

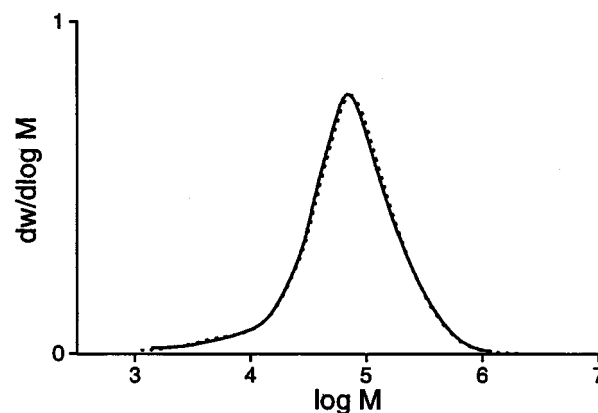**Figure 1.** A plot of M_n versus % conversion for the synthesis of a low molecular weight graft copolymer (calculated $\overline{DP}$ ~ 70).

Figure 2. An overlay of the size exclusion chromatograms (SEC) for a low molecular weight graft copolymer (calculated $\overline{DP}$ ~ 70) acquired by UV detection at 334 (···) and 254 nm (—).
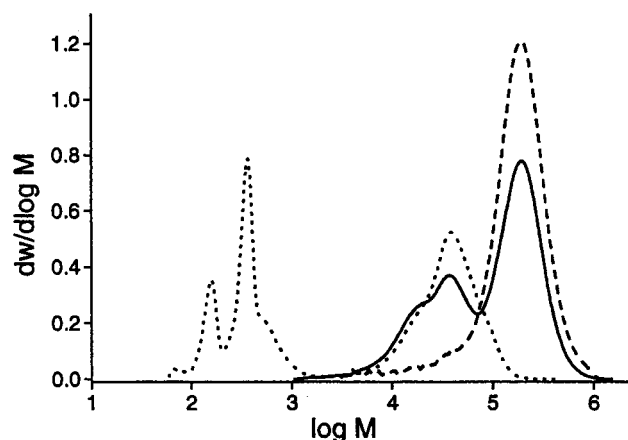

Figure 3. An overlay of the SEC for a high molecular weight graft copolymer (calculated $\overline{DP}$ ~ 200) acquired at 254 (—) and 334 nm (- - -) and after photolysis (···).

catenated silicon atoms (Figure 2). In contrast, the typical overlay for a high molecular weight copolymer system (calculated $\overline{DP}$ ~ 200), shown in Figure 3, displays a secondary peak with a shoulder at lower molecular weight in the 254 nm chromatogram, which is not present in the 334 nm chromatogram. This is

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attributable to polystyrene that is not attached to catenated silicon atoms. It is thus apparent that there is a side reaction producing polystyrene that is not bound to a polysilane chain.[18] Given the high temperature and the extended reaction times, we have drawn the conclusion that it is polystyrene produced following autoinitiation through a Mayo-type thermal mechanism.[3,4]

To investigate further the formation of the low molecular weight fraction in the course of the overall polymerization, several such products were photolyzed in order to release the polystyrene grafts,[19] as can be seen from Figure 3. Low molecular weight material ($M_n \sim 100-1000$) is formed, which is consistent with the degradation of the parts of the polysilane backbone to which grafts were not attached. In addition, a single, almost monomodal peak is observed at the same position as the secondary peak of the parent system. From the close overlay of the low molecular weight tails of these peaks in the two chromatograms it is evident that this represents a greater amount of polymer than the nongrafted polystyrene that was present before photolysis. The low polydispersity index, 1.4, for this peak including its still perceptible shoulder[20] indicates that the thermal and ATRP reactions produce polymer chains of very similar lengths.[21] Such a value is not unreasonable for high molecular weight polymer formed through ATRP. It follows that the growth of the autoinitiated polystyryl chains must also be controlled within the ATRP mechanism.

Copper(II) bromide will convert polystyryl radicals to their dormant form whether or not they originate from thermal or Cu(I)Br initiated processes. This would be analogous with the reverse ATRP process noted by Matyjaszewski.[22] Under the conditions of a normal ATRP polymerization, Cu(I)Br and RBr are present in equimolar amounts, in this case the latter species being the $-PhCH_2Br$ groups attached to the polysilane backbone. $Cu(II)Br_2$ should be present in only very small amounts. However, the Cu(I)Br used as the catalyst in these reactions was only 98% pure with the major impurity being thought to be $Cu(II)Br_2$. To test whether this was sufficient to moderate the thermally initiated polymerization, a reaction was carried out under identical conditions to the ATRP reaction, except that the brominated polysilane was excluded. Following isolation, the product proved to be a high molecular weight ($M_n \sim 250\,000$), broad distribution ($M_w/M_n = 2.5$) polymer. There had been no obvious moderation of the polymerization by any Cu(I) species produced within the system. It follows, therefore, that the only rationale for the photochemical observations is an interaction of the thermal and ATRP polymerizations through a common intermediate and that this must be the propagating free radical. In order for the autoinitiated chains to come under the ATRP control, a sufficient excess of $Cu(II)Br_2$ would have to be available within the reaction system. A mechanism for the production of such an excess has been noted previously.[23] Any occurrence of irreversible bimolecular termination involving radicals from the Cu(I)Br initiated process would make available the $Cu(II)Br_2$ required for bringing thermally initiated radicals under the control of the ATRP. While the effect on the molecular weight distribution in the low molecular weight grafting reaction is imperceptible, given the significant concentrations of propagating free radicals formed through autoinitiation and the far longer reac-

Scheme 1. Probable Mechanism for Atom Transfer Radical Polymerization
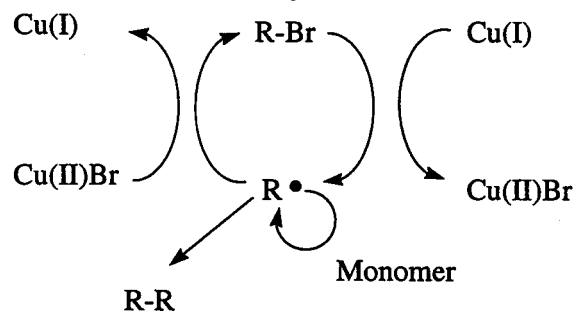
tion times, the effect is far more obvious in the high molecular weight grafting reaction. These processes are indicated in Scheme 1, within which no distinction is drawn between radicals, R•, originating within the Cu(I) or Mayo-type processes. Such processes are entirely analogous to the persistent radical effect described and modeled by Fischer[24] for the TEMPO moderated bulk polymerization of styrene and extended to ATRP reactions by Matyjaszewski et al.[25,26]

In conclusion, while the effects of the autopolymerization of styrene have been observed previously,[9,10] we believe that this fortuitous study has produced the most cogent evidence to date of the interaction of the mechanisms of ATRP and the underlying thermal polymerization through a persistent radical effect. Although we have only demonstrated the effect for a single metal-mediated system, we believe that it is quite general in all such systems involving high reaction temperatures.

Supporting Information Available: A typical polymerization procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Simon, E. *Ann.* **1839**, *31*, 265.
(2) Dostal, H.; Mark, H. *Trans. Faraday Soc.* **1936**, *32*, 54.
(3) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289.
(4) Mayo, F. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1961**, *22*, 55.
(5) Chong, Y. K.; Rizzardo, E.; Solomon, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 7761.
(6) Greszta, D.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 7661.
(7) Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T. *Macromolecules* **1996**, *29*, 6393.
(8) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373.
(9) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218.
(10) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526.
(11) Jones, R. G.; Holder, S. J. *Macromol. Chem. Phys.* **1997**, *198*, 3571.
(12) Jones, R. G.; Budnick, U.; Holder, S. J.; Wong, W. K. C. *Macromolecules* **1995**, *26*, 8036.
(13) Holder, S. J.; Swain, A. C.; Jones, R. G.; Went, M. J.; Benfield, R. E. *Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 312.
(14) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(15) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(16) Dourges, M.-A.; Charleux, B.; Vairon, J.-P. *Macromolecules* **1999**, *32*, 2495.

(17) PMPS: M_n = 11 700, M_w = 165 700, and M_w/M_n = 14. BrMePMPS: M_n = 5200, M_w = 8500, and M_w/M_n = 1.6. BrMe substitution = 33% of phenyl groups by ^{1}H NMR. Low $\overline{DP}$ graft copolymer: M_n = 9700, M_w = 37 200, and M_w/M_n = 3.8. High $\overline{DP}$ graft copolymer (includes both peaks): M_n = 60 800, M_w = 150 300, and M_w/M_n = 2.4. SEC's were acquired against linear polystyrene standards with a UV detector and as such do not take into account hydrodynamic differences between the linear and graft copolymers. A typical polymerization procedure is given as Supporting Information.

(18) It should also be noted that the monomodal distribution for the low $\overline{DP}$ copolymers and the multimodal distribution for high $\overline{DP}$ copolymers did not depend on the level of substitution in the parent BrMePMPS. These distributions were also observed for copolymers with about 40% and 20% bromomethylation, indicating that the extended reaction times were not due to crowding of initiator sites leading to inefficient initiation. A fuller discussion of initiator efficiency and the relative activity of the grafting sites and chains will be published in a full paper at a later date.

(19) Polysilanes undergo UV photodegradation to low molecular weight fragments.

(20) Thought to be a small polystyrene fraction formed through bimolecular termination of propagating free radicals.

(21) The presence of low molecular weight initiating species could possibly account for this result, but the precursor polymers were reprecipitated three times and a monomodal distribution for the lower molecular weight copolymers would seem to refute this argument.

(22) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7692.

(23) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

(24) Fischer, H. *Macromolecules* **1997**, *30*, 5666.

(25) Shipp, D. A.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2948.

(26) Matyjaszewski, K. *Macromolecules* **1998**, *31*, 4710.