Macromolecules **2000,** *33,* 1505−1507

One-Step Formation of Functionalized Block Copolymers

Didier Benoit,[†] Craig J. Hawker,*,[†]
Elbert E. Huang,[‡] Zhiqun Lin,[‡] and
Thomas P. Russell[‡]

IBM Almaden Research Center, NSF Center for Polymeric Interfaces and Macromolecular Assemblies,
650 Harry Road, San Jose, California 95120; and
Department of Polymer Science and Engineering,
University of Massachusetts, Amherst, Massachusetts 01003

Received October 15, 1999

The field of block copolymers has experienced renewed interest in recent years with the development of new synthetic strategies and potential technological uses for these nanostructured materials.[1] Of particular interest has been the elucidation of living free radical polymerization techniques,[2] such as nitroxide-mediated[3] and ATRP procedures,[4] where attention has been devoted to the polymerization of functionalized monomers which do not polymerize via other pathways.[5] This permits the synthesis of a variety of new and novel functionalized block copolymers. One commercially important and highly functionalized monomer, which has so far proved elusive in terms of controlled polymerization by a variety of living techniques, is maleic anhydride (**1**). In this communication, the controlled copolymerization of maleic anhydride (**1**), by nitroxide-mediated living free radical procedures is reported and subsequently used in the development of a novel, one-step synthesis of functionalized block copolymers.

In comparison to traditional block copolymer syntheses, the development of a general, one-step strategy for the preparation of functionalized block copolymers would represent a significant advance. To accomplish this goal, we exploited a unique feature of living free radical procedures, chains being initiated at the same time and growing at approximately the same rate. As a consequence, random copolymers prepared from monomers with different reactivity ratios[6] by either traditional or living free radical procedures, while similar on a macroscopic level (i.e., comparable tacticity and triad ratios) may be significantly different on a molecular level. For traditional free radical systems, there will be a distribution of chain structures, with chains initiated at low conversion having a different monomer composition than those initiated later in the process. In direct contrast, all chains prepared by living free radical procedures should be approximately the same with each chain growing at the same rate and experiencing the same change in monomer feed ratios.[7] Therefore, if a living free radical system can be developed for monomer combinations with dramatically different reactivity ratios, such as maleic anhydride and styrene, the alternating nature of this copolymerization may be exploited and a new one-step strategy for novel functionalized block copolymers developed.

To demonstrate this new concept in block copolymer synthesis, the controlled polymerization of a 9:1 mixture of styrene and maleic anhydride is demonstrated. Under normal free radical conditions, a 9:1 mixture of styrene and maleic anhydride will lead to a heterogeneous mixture of homopolystyrene and various styrene/maleic anhydride copolymers. Significantly different behavior may be expected for the living free radical copolymerization of styrene/maleic anhydride mixtures. In this case, all chains will be homogeneous due to the rapid initiation and living nature of the polymerization with only the monomer composition along these homogeneous chains varying. During the early stages of polymerization, preferential incorporation of maleic anhydride will occur, and upon depletion of the maleic anhydride, the monomer feed will consist of essentially pure styrene. In contrast to the normal free radical case in which pure homopolystyrene chains are produced at this stage, chain growth of a polystyrene block occurs in the living free radical case to give a poly[(styrene-*r*-maleic anhydride)-*b*-polystyrene] block copolymer.

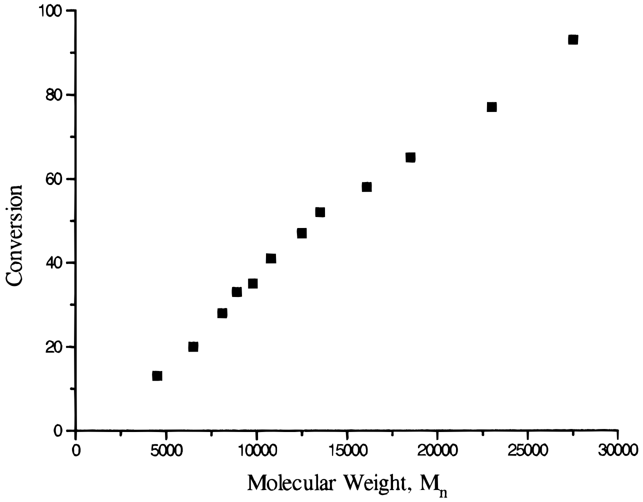


Figure 1. Evolution of experimental molecular weight, M_n, with conversion for the polymerization of a 9:1 mixture of styrene and maleic anhydride (**1**)**,** in the presence of **2** and **3** at 120 °C for 12 h.

Initially, the living free radical polymerization of a 9:1 mixture of styrene and maleic anhydride was studied at 120 °C in the presence of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as the mediating nitroxide. Unfortunately nonliving behavior was observed under a variety of different conditions with little or no control over molecular weights and polydispersity. Similar results were obtained for a range of Cu-, Ni-, or Fe-based ATRP systems, which demonstrates the difficulty in obtaining living free radical systems involving maleic anhydride. To overcome this difficulty, a recently reported α-hydrido-based alkoxyamine, **2**, was examined.[8] Interestingly, at 120 °C the rate of polymerization of a 9:1 mixture of styrene and maleic anhydride was dramatically higher than for pure styrene with >90% conversion being obtained after 1 h. While the material obtained was polydisperse (PD = 1.4−1.7), the living character was enhanced when compared to TEMPO. This high rate of polymerization, coupled with the increased polydispersity, suggests that the presence of additional nitroxide-mediating agent may be required to give true living character, a concept similar to that previously reported[8] for the homopolymerization of acrylate monomers. A small excess (5 mol %) of free

---

[†] NSF Center for Polymeric Interfaces and Macromolecular Assemblies.
[‡] University of Massachusetts.

10.1021/ma991721p CCC: $19.00

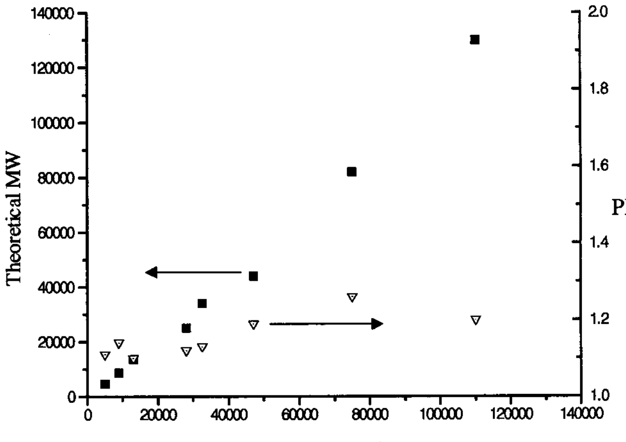


Figure 2. Relationship between theoretical molecular weight; polydispersity and experimental molecular weight, M_n, for the polymerization of a 9:1 mixture of styrene and maleic anhydride (**1**), in the presence of **2** and **3** at 120 °C for 12 h.

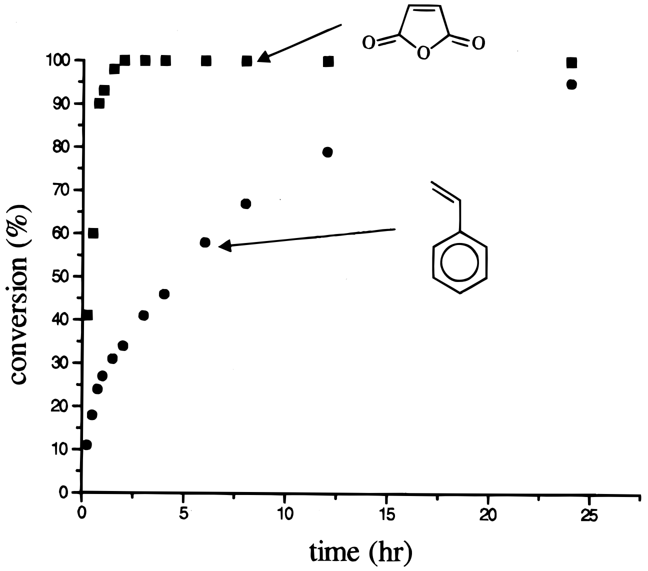


Figure 3. ^{1}H NMR determined monomer conversions for styrene and maleic anhydride (**1**), as a function of time during polymerization at 120 °C in the presence of **2** and **3**.

nitroxide, **3**, was therefore added to the reaction mixture. As can be seen in Figure 1, this produced a linear relationship between molecular weight and conversion. Significantly, the polydispersities of the products obtained at high conversion was low (1.1−1.2) and the molecular weights could be controlled up to 100 000 (Figure 2).

Examining the monomer conversion as a function of time by ^{1}H NMR spectroscopy provided insight into the compositional nature of the chains. As can be seen in Figure 3, the polymerization is initially fast with preferential consumption of maleic anhydride. After 1.5 h, no detectable amounts of maleic anhydride could be observed in the reaction mixture, while the conversion of styrene was ca. 25−30%. At this point, the monomer feed is pure styrene, and so further polymerization involves growth of a pure polystyrene block leading to a block copolymer, **4**, consisting of an initial ca. 1:2 copolymer of maleic anhydride and styrene, respectively, followed by a block of polystyrene which is roughly twice the molecular weight of the initial anhydride functionalized block (Scheme 1). Confirmation of the preferential incorporation of maleic anhydride and the block copolymer nature of **4** was also obtained by isolation of the polymers at different conversions and determination of the comonomer ratio by ^{1}H NMR and IR spectroscopy.

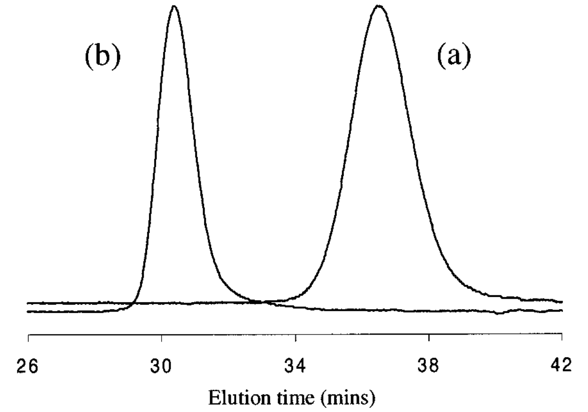
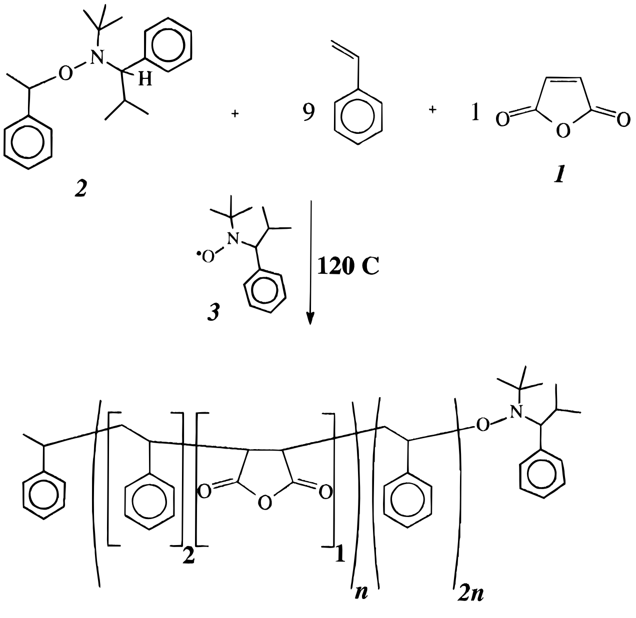


Figure 4. Comparison of GPC traces for (a) the initial poly(styrene-*r*-maleic anhydride), **5**, and (b) the poly(styrene-*r*-maleic anhydride)-*b*-polystyrene block copolymer, **6**, obtained after chain extension with styrene.

Scheme 1



4

The living nature of these maleic anhydride based copolymerizations was further demonstrated by chain extension experiments. From the above reaction mixture, an initial prepolymer, **5**, was isolated after a polymerization time of 1 h. As expected, this was shown to be a ca. 1:2 copolymer of maleic anhydride and styrene (M_n = 5000; PD = 1.19). After purification, **5** was redissolved in pure styrene and heated at 120 °C under nitrogen for 12 h to give the block copolymer, **6**. As can be seen in Figure 4, comparison of the GPC traces for **5** and **6** shows essentially complete reinitiation with no significant amount of **5** remaining. From these results, it can be concluded that the copolymerization of styrene and maleic anhydride is a living process in the presence of the alkoxyamine, **2**, and the nitroxide, **3**, which leads to the production of functionalized block copolymers in a single step.

Examination of the physical properties of the block copolymer, **4**, by a variety of different techniques support a microphase separated diblock structure. The DSC traces for the one-step block copolymers revealed two glass transition temperatures at 105 °C, which corresponds to the polystyrene block, and at 155 °C which corresponds to the maleic anhydride/styrene block. These values are in agreement with those observed for the chain-extended block copolymer, **6**, and the literature value[9] of 155 °C for a 1:2 copolymer of maleic anhydride and styrene prepared by normal free radical procedures. The microphase separation of the copolymer was further evidenced by atomic force microscopy on thin films and bulk small-angle X-ray scattering experiments. Both sets of data revealed discrete domains with a correlation length of 15 nm.

In conclusion, we have demonstrated that living free radical procedures can now be extended to reactive monomers such as maleic anhydride (**1**), by the use of a mixture of α-hydrido alkoxyamine, **2**, and nitroxide **3**. In copolymerizations with styrene, the living nature of the polymerization is preserved, which leads to preferential consumption of maleic anhydride and the one-step production of functionalized block copolymers, whose molecular weights can be readily controlled up to 100 000 while retaining low polydispersities.

Acknowledgment. Financial support from the National Science Foundation (DMR-9808677, MRSEC Program, CPIMA; DMR-9809365, MRSEC Program, University of Massachusetts), Department of Energy, Office of Basic Energy Sciences, and NIST/ATP Cooperative Agreement No. 70NANB8H4013 is gratefully acknowledged.

References and Notes

(1) Schops, M.; Leist, H.; DuChesne, A.; Wiesner, U. *Macromolecules* **1999**, *32*, 2806. Schmidt, S. C.; Hillmyer, M. A. *Macromolecules* **1999**, *32*, 4794. Russell, T. P. *Curr. Opin. Colloid Surf. Sci.* **1996**, *1*, 107.

(2) Matyjaszewski, K. Controlled Radical Polymerization. *ACS Symp. Ser.* **1998**, *685*. Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373.

(3) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245. Li, I. Q.; Howell, B. A.; Koster, R. A.; Priddy, D. B. *Macromolecules* **1996**, *29*, 8554. Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11314. Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. *Macromolecules* **1997**, *30*, 324.

(4) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866. Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6708. Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970. Granel, C.; DuBois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576.

(5) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381. Gabaston, L. I.; Furlong, S. A.; Jackson, R. A.; Armes, S. P. *Polymer* **1999**, *40*, 4505. Weimer, M. W.; Scherman, O. A.; Sogah, D. Y. *Macromolecules* **1998**, *31*, 8425. Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 3531. Li, D.; Brittain, W. J. *Macromolecules* **1998**, *31*, 3852.

(6) Laurier, G. C.; O'Driscoll, K. F.; Reilley, P. M. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 17.

(7) Matyjaszewski et al. have employed a similar concept for copolymers with gradually changing monomer compositions, termed gradient copolymers, see Greszta, D.; Matyjaszewski, K. *Polym. Prep.* **1996**, *37* (1), 569. Arehart, S.; Greszta, D.; Matyjaszewski, K. *Polym. Prep.* **1997**, *38* (1), 705. Greszta, D.; Matyjaszewski, K.; Pakula, T. *Polym. Prepr.* **1997**, *38* (1), 709. See also: Annighofer, F.; Gronski, W. *Colloid Polym. Sci.* **1983**, *263*, 15.

(8) Benoit, D.; Chaplinski, V.; Braslau, R. Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904.

(9) Traugott, T. D. *Encycl. Polym. Sci.* **1989**, *16*, 72.

MA991721P