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Low-Polydispersity Star Polymers with Core Functionality by Cross-Linking Macromonomers Using Functional ATRP Initiators

Haifeng Gao and Krzysztof Matyjaszewski*

*Department of Chemistry, Carnegie Mellon University, 4400
Fifth Avenue, Pittsburgh, Pennsylvania 15213*

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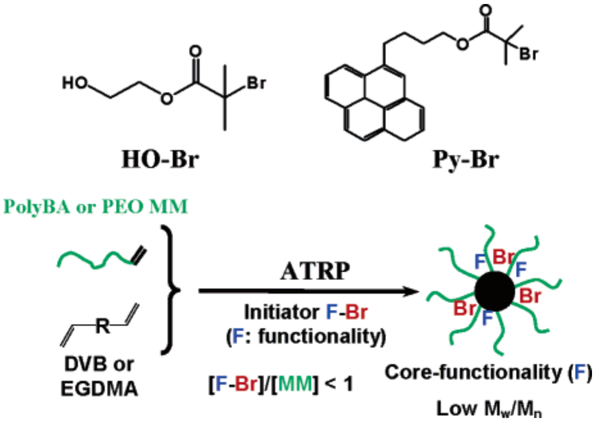
Star polymers, containing multiple arms connected at the central core, are among the simplest forms of branched topologies.[1] Continuously expanding research on star polymers has two driving forces: one is the growing demand for nanoscale polymeric materials with controlled architecture, predetermined chemical compositions, and multiple functionalities,[2−4] and the other is a multitude of new synthetic apportunities offered by living anionic polymerization,[5] living cationic polymerization,[6] metathesis,[7] and controlled/living radical polymerization (CRP).[8,9] Atom transfer radical polymerization (ATRP)[10−12] is one of the most popular CRP techniques and has been broadly applied to star synthesis employing three different synthetic strategies: "core-first"[13−15] by growing arms from a multifunctional initiator, "coupling-onto"[16,17] by attaching preformed arms onto a multifunctional core, and the "arm-first" method[18−20] by cross-linking a preformed macroinitiator (MI) using a divinyl compound.

Introduction of various functional groups into the star polymers, either in the core of the star or at the star periphery, significantly expands potential applications for star polymers, for example, in biodiagnosis, optical imaging, and drug delivery systems.[21] However, none of the three methods currently used for star synthesis allow simple and efficient introduction of functionalities into the star core.

In the star polymers synthesized by the "arm-first" method, the dormant alkyl halide chain-end groups are preserved in the star core. These sites can be employed to reinitiate polymerization of another monomer and form miktoarm (or heteroarm) star polymers.[22−24] However, for functionalities, such as hydroxy, amino, and more special groups (e.g., absorbing light or emitting fluorescence), postpolymerization modification of these "embedded" alkyl halide groups is complicated and inefficient. An alternative strategy to introduce functionalities into the star core is to use functional cross-linkers and/or functional monovinyl comonomers during the star core formation process.[25,26] However, the resulting star polymers have a broad molecular weight distribution (MWD) due to star−star coupling reactions.[27,28]

Recently, we developed a new method for synthesis of star polymers with high molecular weight, high star yield, and low polydispersity via copolymerization of linear macromonomers (MM) with a divinyl cross-linker using low molar mass ATRP initiators (MM method).[29] In this method, the number of initiating sites (derived from the initiator) and number of arms (derived from MM) per star molecule are independently controlled. A low molar ratio of initiator to MM decreases the number of initiating sites in the star core, reduces the possibility of star−star coupling reactions and decreases star polydispersity. Moreover, MMs, initiators, and cross-linkers can be added in several steps, increasing the flexibility of star synthesis. An extra advantage of this new MM method for star synthesis is that additional functional groups can be easily introduced into the star core via functional initiators. The synthesis and application of functional ATRP initiators are much easier and more efficient than the displacement of the embedded alkyl halide chain ends in the preformed star core.

Scheme 1. Synthesis of Core-Functionalized Star Polymers via ATRP Using the MM Method



In this Communication, core-functionalized star polymers with high star yield and narrow MWD were synthesized by using the MM method. To demonstrate the simplicity of the process, two kinds of functionalities, pyrene groups and hydroxyl groups, were introduced into the star core through the use of functional ATRP initiators (Scheme 1). The initiators were added either at the beginning of the polymerization or during the polymerization reactions. Copolymerization of hydrophobic poly(*n*-butyl acrylate) (polyBA) MM ($M_n = 5300$ g/mol determined by GPC, containing an acrylate chain-end group) and divinylbenzene (DVB) produced hydrophobic star polymers (polyBA)$_n$−polyDVB(F), where *n* is the average number of polyBA arms per star molecule and polyDVB and F represent the core composition and core functionality, respectively. Similarly, amphiphilic (PEO)$_n$−polyEGDMA(F) star polymers with hydrophobic core and hydrophilic arms were synthesized by copolymerization of water-soluble poly(ethylene glycol) methyl ether methacrylate (PEO MM, $M_n \sim 1100$ g/mol) and ethylene glycol dimethacrylate (EGDMA) using the ATRP technique.

(PolyBA)$_n$−polyDVB(pyrene) star polymers were synthesized using a pyrene-containing ATRP initiator (Py-Br) to initiate the copolymerization of polyBA MM and DVB. When the initial molar ratio of reagents, $[\mathrm{MM}]_0/[\mathrm{Py\text{-}Br}]_0/[\mathrm{DVB}]_0$, equaled 1/0.2/3, the conversion of DVB reached 100% within 20 h, while the molecular weight of the star polymers continued to grow until 77 h (Figure 1). The star formation process can be divided into two stages. In the first stage, until 19 h, both star−linear MM reactions and star−star coupling reactions occurred. During the second stage, from 19 to 77 h, star−star coupling reactions stopped due to the steric congestion of the arms of the star polymers, and only star−linear MM reactions occurred. This was based on the observation that there was a continuous consumption of linear MMs but much slower increase in the apparent molecular weight of the star polymers. After 77 h, the apparent molecular weight of the star polymers was $M_n = 54.7$ kg/mol and the star yield, based on MM consumption, was ca. 79%. Further increase the reaction time did not result in any

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* Corresponding author. E-mail: km3b@andrew.cmu.edu.

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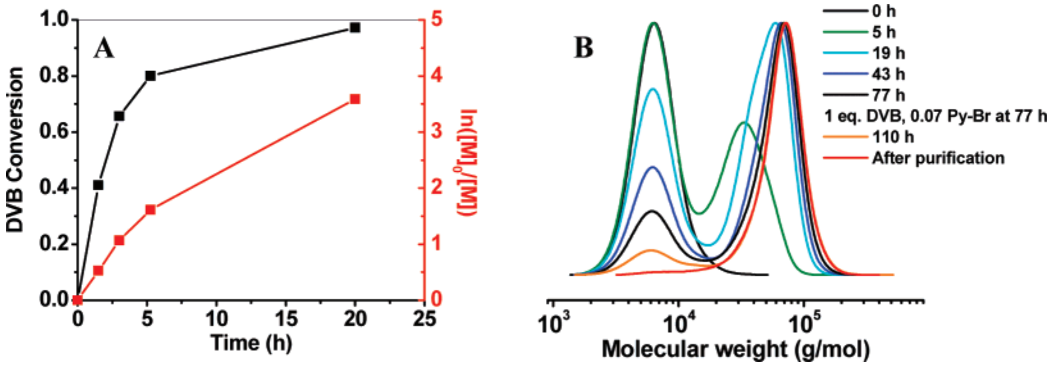

Figure 1. (A) Dependence of DVB conversion and $\ln([M]_0/[M])$ on reaction time and (B) evolution of GPC traces during synthesis of core-functionalized (polyBA)$_n$−polyDVB(pyrene) star polymers by the MM method. Experimental conditions: $[\text{polyBA MM}]_0/[\text{Py-Br}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 1/(0.2 + 0.07)/(3 + 1)/0.2/0.2$; $[\text{polyBA MM}]_0 = 0.06$ M; in anisole at 80 °C; linear polystyrene standards were used for calibration of the THF GPC.

increase of the molecular weight or yield of the star polymers because they reached their saturation size.

Addition of another batch of DVB and pyrene-containing initiator expanded the size of the star core and introduced more pendent vinyl groups and initiating sites into the star core. This expansion decreased core congestion and made further star−linear polymer reactions possible. With appropriate amounts of additional DVB and Py-Br, it is possible to allow further star−MM reactions but limit star−star coupling reactions. After the addition of 1 equiv of DVB and 0.07 equiv of Py-Br at 77 h, the star polymers began to grow again. Star growth stopped after 110 h when the core of the star once again reached the saturation size. The apparent molecular weight of the star polymers increased to 61.0 kg/mol, larger than 54.7 kg/mol, indicating that essentially no star−star coupling reactions occurred between 77 and 110 h. At the same time, the absolute molecular weight of the star polymers ($M_{\text{w,MALLS}}$), measured by the MALLS detector, was ca. 180.0 kg/mol, and the MWD remained as narrow as $M_w/M_n = 1.17$. The star yield reached 93% after 110 h, and the average arm number per star was determined to be ca. 31.

Similarly, hydroxyl-core-functionalized star polymers, (polyBA)$_n$−polyDVB(OH), were successfully synthesized by using HO-containing ATRP initiator (HO-Br) (Figure 1S in the Supporting Information).

The (polyBA)$_n$−polyDVB(pyrene) star polymers were purified by precipitation in cold MeOH to remove free polyBA linear chains and pyrene-containing molecules. The GPC curve in Figure 1B indicates that the purified product contained only pyrene-encapsulated star polymers. In Figure 2, the purified (polyBA)$_n$−polyDVB(pyrene) star polymers in THF showed strong absorption peaks between 300 and 360 nm, which indicate the presence of pyrene groups covalently bonded to the star core, since free pyrene-containing molecules had been removed from the star molecules by precipitation. The absorption peaks had the same position and shape as those from the free Py-Br small initiator in THF, suggesting a similar environment around the pyrene groups. When concentration of (polyBA)$_n$−polyDVB(pyrene) star was the same as that of a control (polyBA)$_n$−polyDVB star, any difference in the absorption spectra is due to absorption peaks of pyrene groups (with the same wavelength maxima as free Py-Br initiator in THF). On the basis of the UV−vis calibration curve of Py-Br in THF (Figure 2S, Supporting Information), the weight fraction of pyrene in the star polymers was determined as $f_{\text{pyrene}} = 0.016$ g/g. If all of the added Py-Br initiators were incorporated into the star polymers, a weight fraction of pyrene groups in star polymers would be 0.020 g/g. This indicates that the encapsulation efficiency of the pyrene initiators into stars was ca. 80%. In the final (polyBA)$_n$−polyDVB(pyrene) star polymers, the average number of arms per star is 31, as discussed above, and the average number of pyrene groups per star molecule is ca. 6.7.

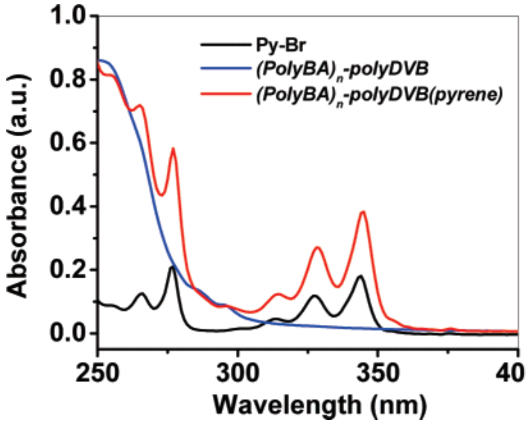

Figure 2. UV−vis spectra of Py-Br, (polyBA)$_n$−polyDVB, and (polyBA)$_n$−polyDVB(pyrene) star polymers in THF.

Pyrene-containing initiators, Py-Br, can also be added into the reaction system during the polymerization. In such a way, the pyrene groups should be mainly located on the surface of the star core. It was found that when the Py-Br initiator was added at a later stage, the star polymers also showed strong UV absorption peaks between 300 and 360 nm. On the basis of the calibration curve, over 75% of the added Py-Br initiators were encapsulated into the star polymers, which contained an average number of 2.4 pyrene groups per star molecule (Figures 3S and 4S in the Supporting Information).

Pyrene functional groups were also introduced into the core of amphiphilic (PEO)$_n$−polyEGDMA star polymers prepared by the MM method using a Py-Br functional ATRP initiator. When the initial molar ratio of $[\text{PEO MM}]_0/[\text{Py-Br}]_0/[\text{EGDMA}]_0$ was 1/0.1/1, the star yield reached 95% after 26 h, and the polydispersity of the star polymer was as low as $M_w/M_n = 1.20$ (Figure 3A). Compared to the previous (polyBA)$_n$−polyDVB(pyrene) star polymers, the (PEO)$_n$−polyEGDMA(pyrene) star polymers formed faster and had higher star yield without an extra addition of cross-linker and initiator. Such a difference was mainly due to the lower steric hindrance, originated from “thinner” PEO chains, which facilitated the incorporation of more arms into one star molecule. After dialysis against MeOH to remove the linear PEO chains and the free pyrene-containing molecules, the (PEO)$_n$−polyEGDMA(pyrene) star polymers was

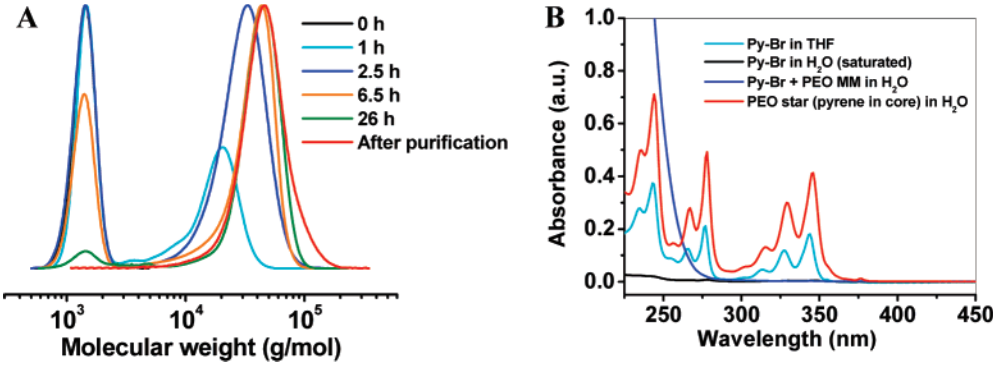

Figure 3. (A) GPC traces and (B) UV−vis spectra of core-functionalized $(PEO)_n$−polyEGDMA(pyrene) star polymers by the MM method. Experimental conditions: $[PEO\ MM]_0/[Py\text{-}Br]_0/[EGDMA]_0/[CuBr]_0/[dNbpy]_0 = 1/0.1/1/0.1/0.2$; $[PEO\ MM]_0 = 0.23$ M; in toluene at 60 °C; linear poly(methyl methacrylate) standards were used for calibration of the THF GPC.

characterized by UV−vis spectroscopy. In THF solution, the star polymers show similar absorption peaks between 300 and 360 nm, as those observed for free Py-Br initiator. In contrast, the $(PEO)_n$−polyEGDMA star polymers without pyrene core functionality had none of these peaks (Figure 5S). On the basis of the calibration curve, 74% of the added Py-Br initiator molecules were encapsulated into the $(PEO)_n$−polyEGDMA-(pyrene) star polymers, and the average number of pyrene groups was 13.5 per star molecule.

The amphiphilic $(PEO)_n$−polyEGDMA(pyrene) star polymers had a core−shell structure, containing a hydrophobic cross-linked polyEGDMA core and hydrophilic PEO arms. Thus, the core was used for encapsulation of hydrophobic pyrene groups, while the hydrophilic arms stabilized the star polymers in water. It is seen in Figure 3B that a solution of the $(PEO)_n$−polyEGDMA(pyrene) star polymers in water showed strong UV absorption peaks between 300 and 360 nm. The location and shape of these peaks overlapped with those of Py-Br in THF, indicating that the pyrene groups in the polyEGDMA core had a similar hydrophobic environment as the free Py-Br in THF. In contrast, the free Py-Br in water showed no detectable absorption peaks due to its extremely low solubility in water. These results show the successful encapsulation of pyrene groups in the amphiphilic $(PEO)_n$−polyEGDMA(pyrene) star polymers. This also indicates that the functional star molecules can potentially be used as an amplified fluorescent probe in the field of bioimaging.

In summary, core-functionalized star polymers were synthesized by copolymerization of linear MMs with a divinyl cross-linker using a low molar mass functional ATRP initiator. Because of a low molar ratio of initiator to MM, star−star coupling reactions were suppressed, resulting in the formation of low-polydispersity star polymers in high yield. Two different functionalities, pyrene groups and hydroxyl groups, were successfully introduced into the star core with high encapsulation efficiency. The pyrene core-functionalized star polymers showed strong UV absorption in both organic solvents and aqueous media due to the solubilization of the star core by hydrophilic arms.

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Supporting Information Available: Procedures for preparation and characterization of $(polyBA)_n$−polyDVB(F) and $(PEO)_n$−polyEGDMA(pyrene) star polymers and the GPC plots. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747.
(2) Kreutzer, G.; Ternat, C.; Nguyen, T. Q.; Plummer, C. J. G.; Mnson, J.-A. E.; Castelletto, V.; Hamley, I. W.; Sun, F.; Sheiko, S. S.; Herrmann, A.; Ouali, L.; Sommer, H.; Fieber, W.; Velazco, M. I.; Klok, H.-A. *Macromolecules* **2006**, *39*, 4507.
(3) Ooya, T.; Lee, J.; Park, K. *J. Controlled Release* **2003**, *93*, 121.
(4) Wang, F.; Bronich, T. K.; Kabanov, A. V.; Rauh, R. D.; Roovers, J. *Bioconjugate Chem.* **2005**, *16*, 397.
(5) Szwarc, M. *Nature* **1956**, *178*, 1168.
(6) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.
(7) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413.
(8) Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization. From Synthesis to Materials; ACS Symp. Ser.* **2006**, *944*.
(9) Matyjaszewski, K., Davis, T. P., Eds. *Handbook of Radical Polymerization*; Wiley: Hoboken, NJ, 2002.
(10) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(11) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(12) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(13) Ueda, J.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557.
(14) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218.
(15) Matyjaszewski, K.; Miller, P. J.; Fossum, E.; Nakagawa, Y. *Appl. Organomet. Chem.* **1998**, *12*, 667.
(16) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 4960.
(17) Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 11360.
(18) Xia, J. H.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4482.
(19) Zhang, X.; Xia, J. H.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 2340.
(20) Baek, K. Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 215.
(21) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2002**, *35*, 1493.
(22) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857.
(23) Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 5995.
(24) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 7216.
(25) Baek, K. Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 7629.
(26) Terashima, T.; Kamigaito, M.; Baek, K. Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2003**, *125*, 5288.
(27) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 3154.
(28) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 633.
(29) Gao, H.; Ohno, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 15111.

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