Star Polymers via Cross-Linking Amphiphilic Macroinitiators by AGET ATRP in Aqueous Media

Wenwen Li and Krzysztof Matyjaszewski*

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

Received May 30, 2009; E-mail: km3b@andrew.cmu.edu

Star polymers with multiple arms connected to a central core have attracted considerable research interest since their initial preparation by living anionic polymerization in the 1950s.[1] Their three-dimensional (3D) globular compact structure results in a unique set of physical properties, such as high functionality and low viscosity as compared to their linear analogues with similar molecular weight. This generates several potential applications for star polymers, including drug delivery, cosmetics, coatings, membrane, or lithography.[2,3] During the past decade, star polymers with a well-defined structure, molecular weight, and multiple functionalities have been successfully prepared using controlled radical polymerization (CRP)[4] techniques, such as atom transfer radical polymerization (ATRP),[5] which do not require stringent reaction conditions but still provide good control.

The synthesis of star polymers using CRP techniques can be divided into three synthetic strategies: (1) "core-first";[6] (2) "arm-first";[7] and (3) "coupling onto".[8] The "arm-first" method, by cross-linking linear arm precursors with cross-linking agents, is the most convenient method to synthesize star polymers with a large number of arms (>100 per star molecule), considering the larger size of the cross-linked core and reduced steric hindrance compared to the other two strategies. This technique also allows the facile preparation of star polymers with random or gradient copolymer arms or miktoarm star polymers.[3] Up to now, star polymer synthesis using the "arm-first" method was mostly conducted in a homogeneous dilute system.[7] However, when amphiphilic star polymers are targeted, heterogeneous polymerization provides an alternative synthetic route, since the block copolymer arm precursors can be preassembled into micelles in selective solvents and then cross-linked.[9]

In this communication, we report the synthesis of amphiphilic star polymers with low polydispersity (PDI) and high molecular weight in highly diluted aqueous media by an activator generated by electron transfer atom transfer radical polymerization (AGET ATRP),[10] using the "arm-first" method. The basic concept employed for the star synthesis is to preform cross-linker swollen micelles and then to cross-link the preassembled structures (Scheme 1).

Scheme 1. Synthesis of Star Polymers via Cross-Linking the Amphiphilic Arms in Aqueous Dispersed Media
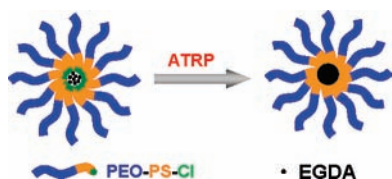
To form micelles swollen with the cross-linker and catalyst, the amphiphilic macroinitiator (MI) was first dissolved in CH_2Cl_2 together with a cross-linker and catalyst in air-stable Cu(II) form, resulting in a homogeneous organic solution, which was subse-

quently mixed with water and subjected to sonication. Micelles were obtained after the slow removal of CH_2Cl_2 by evaporation from the resulting stable emulsion after sonication.

Table 1 summarizes the results of star synthesis in aqueous dispersed media using poly(ethylene oxide)-*b*-polystyrene (PEO-PS-Cl) as the MI and ethylene glycol diacrylate (EGDA) as the cross-linker. The initial molar ratio of PEO-PS-Cl and EGDA was changed from 1:18 to 1:40. In all cases, star polymers with high molecular weight and very low PDI were obtained within 2 h, as evidenced by the appearance of a new and very narrow GPC peak at high molecular weight. For example, at the initial molar ratio of PEO-PS-Cl and EGDA 1:18, star polymers with apparent number-average molecular weight 108 kg/mol, absolute molecular weight 1154 kg/mol, and PDI 1.04 were obtained after 5 h (Figure 1a).

Table 1. Star Synthesis with PEO-PS-Cl As Arm Precursor in Water[a]

| entry	DP[a]	MW_{MI}[b] (kg/mol)	$M_{n,RI}$[c] (kg/mol)	$M_{w,MALLS}$[d] (kg/mol)	PDI[e]	N_{arm}[f]
S1	18	7.9	108	1154	1.04	96
S2	30	7.9	104	1504	1.04	100
S3	40	7.9	114	1694	1.03	101

[a] Polymerization conditions: [MI]:[EGDA]:[CuBr$_2$/bis(2-pyridylmethyl)-octadecylamine]:[ascorbic acid] = 1:DP:1.2:0.5, [hexadecane] = 3.6 wt % based on cross-linker, 70 °C. [b] Molecular weight of MI determined by NMR. [c] Number-average molecular weight of star polymers determined by THF GPC with RI detector, calibration with linear polystyrene as standard. [d] Weight-average molecular weight of star polymers determined by THF GPC with MALLS detector, dn/dc = 0.095 ± 0.004 mL/g. [e] PDI = $M_{w,RI}/M_{n,RI}$ determined by THF GPC with RI detector. [f] Number-average value of the number of arms per star molecule (N_{arm}) was calculated based on eq S1 (Supporting Information).

In contrast, if the star polymers were synthesized in a homogeneous organic medium using the same ratio of reagents ([MI]:[EGDA] = 1:18) and the same copper complex by normal ATRP, star polymers with a much lower molecular weight (apparent MW: 79 kg/mol, absolute MW: 245 kg/mol) and relatively higher PDI 1.20 were obtained. This could be caused by a different star formation process. During the arm-first star synthesis in homogeneous conditions, the final star polymers are formed through two contributing reactions: star–star reactions and star–linear polymer reactions. Both of these reactions increase the star molecular weight. However, after the star molecules reach a certain size, steric hindrance suppresses both these reactions, as it is difficult to insert more arms into the core of a congested star molecule. This affects the star molecular weight and star yield.

The star formation process is different in aqueous dispersed media. Due to the formation of preorganized micelles, star–star or star–linear chain reactions are not required for the formation of the star. Ideally, each micelle is converted to an individual star molecule, so the star molecular weight should depend on the initial size of the micelles, i.e., the number of linear polymers incorporated

into the micelles. Steric hindrance is avoided, and therefore, uniform and higher molecular weight stars are expected. The diluted aqueous media further reduce the possibility for star−star coupling reactions and decrease polydispersity. However, the diluted conditions should not affect the molecular weight of star polymers, since the number of arms was already determined by the preformed micelles. Since the same amounts of MI, water, and CH_2Cl_2 were used in all reactions with the same sonication time, the cross-linker containing droplets with similar size should be obtained after sonication. After evaporation of CH_2Cl_2, the cross-linker and catalyst swollen micelles with similar size and similar number of incorporated linear polymers should be obtained. This also explains why the arm number of star molecules does not change significantly as the ratio of MI to cross-linker is adjusted (from 1:18 to 1:40, Table 1).

To confirm the star formation process in aqueous dispersed media, dynamic light scattering (DLS) was used to determine the size of the preassembled micelle structures and formed star polymers during the polymerization process (Figure 1b). Before the polymerization was started, well-defined small micelles with average diameter ca. 20 nm were observed by DLS. This size essentially did not change during the reaction, indicating that each of these small micelles was converted to an individual star molecule. Thus, the micelle size determined the star size. In contrast, no micelles or larger aggregates were found in DMF, indicating that the system was homogeneous in organic solvent.
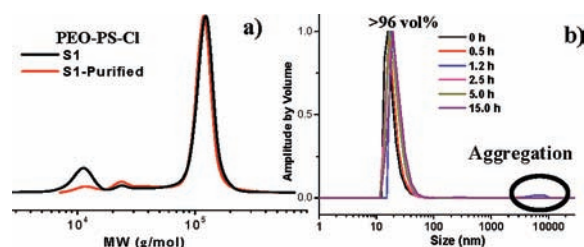
Figure 1. (a) GPC traces and (b) DLS plots for the star polymers formed in aqueous dispersed media with PEO-PS-Cl as arm precursor (S1).

Although star polymers with high MW and low PDI were obtained in aqueous dispersed media using PEO-PS-Cl as arm precursor, the star yield was limited and did not increase after 5 h. The area percentage of the final star polymer peak in the GPC traces was ∼85%, according to the multipeak splitting using a Gaussian function. The unreacted linear MI was removed by preparative GPC. The limited star yield could be caused by several reasons, including the loss of chain end functionality, incomplete incorporation of MIs into micelles, or formation of aggregates. Since the reaction was conducted in water at high temperature (70 °C), the halogen chain end of PEO-PS-Cl could be hydrolyzed, and the MI could lose its chain-end functionality and not initiate the polymerization. Since styryl bromides hydrolyze ca. 30 times faster than styryl chlorides,[11] for a comparison, PEO-PS block copolymers with Br chain ends were synthesized and used for star synthesis in water under similar conditions. The star polymers with high MW (absolute MW > 1000 kg/mol) and low PDI (<1.1) were formed, and the star yield was indeed lower (ca. 70%, Table S1, Supporting Information). The twice higher amount of nonincorporated Br-MI could be caused by the more significant hydrolysis of the Br chain end. It should be noted that a small population of larger aggregates (<4%, based on DLS volume intensity) existed in the system from the beginning

of the reaction. Thus, it is possible that some block copolymers were not incorporated into the micelles, also affecting the star yield (Figure 1b).

Thus, star polymers with low PDI and high MW were prepared by AGET ATRP in aqueous dispersed media using a simple "arm-first" method and linear amphiphilic block copolymer PEO-PS-Cl as arm precursors. The amphiphilic block copolymers formed micelles in water and were then cross-linked with divinyl cross-linkers. Due to the formation of cross-linker swollen micelles before the polymerization was initiated, star−star or star−linear reactions were not required for star formation, and the suppression of star−star coupling reactions resulted in star polymers with low PDI ($M_w/M_n < 1.1$). Moreover, since the number of arms was predetermined by the formed micelles, star polymers with absolute molecular weight over 1000 kg/mol were obtained. Introduction of various site-specific functionalities into the star polymers is currently under investigation.

Supporting Information Available: Procedures for preparation of (PEO-PS)$_n$-polyEGDA star polymers in aqueous dispersed media and homogeneous systems, calculation of the number-average value of the number of arms per star molecule (N_{arm}). This material is available free of charge via the Internet at http://pubs.acs.org.

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