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Synthesis of Star-Shaped Polystyrene by Atom Transfer Radical Polymerization Using an “Arm First” Approach

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Star-shaped or star polymers have attracted much attention in research over the years due to their unique three-dimensional shape and highly branched structure.[1] The synthesis of star polymers generally involves living polymerization techniques, and this has been extensively investigated in anionic, cationic, and ring-opening metathesis polymerizations.[2−7] Recently controlled/“living” radical polymerization has been used to prepare various well-defined polymers and complex architectures.[8,9] One such method is atom transfer radical polymerization (ATRP).[10,11]

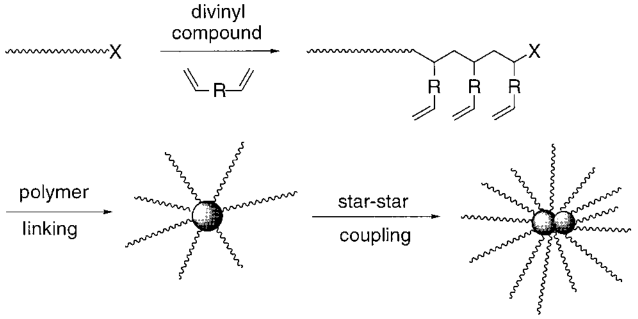
ATRP involves the reversible activation of dormant alkyl halides to form radicals via halogen abstraction by transition metal complexes.[12] The dynamic equilibrium between the alkyl halides and radicals is greatly shifted toward the dormant alkyl halides. The low concentration of radicals suppresses the contribution of radical termination reactions and maintains a constant number of propagating polymer chains.

ATRP has been applied toward the synthesis of star polymers. For example, our group reported the synthesis of star polystyrene (PSt) and poly(methyl acrylate) (PMA) using either organic[13] or siloxane and cyclotriphosphazene-derived inorganic multifunctional initiators.[14] Sawamoto and co-workers reported the synthesis of star poly(methyl methacrylate) (PMMA) by ruthenium-mediated ATRP using tri-, tetra-, hexa- and octafunctional dichloroacetate initiators.[15,16] Similarly, Gnanou and co-workers reported the synthesis of star PSt using octafunctional calixarene derivatives.[17]

The method employed in the above studies involves the use of multifunctional initiators and is generally termed the “core first” technique. The “arm first” technique employs the coupling of preformed macroinitiators by a multifunctional coupling reagent and has been extensively studied in living anionic and cationic polymerizations.[3,5,6] The proposed mechanism for the star polymer formation in the presence of a divinyl coupling reagent is presented in Scheme 1. Initially, a few units of the divinyl coupling reagents are added to the macroinitiator chain ends to form short block copolymers. The block copolymers containing the divinyl units then start to react with each other to form cross-linked cores, and this leads to the formation of star polymers. Finally, star−star coupling can occur, leading to the formation of higher molecular weight stars. In this paper, we report the synthesis of star polystyrenes (PSt) by the “arm first” technique via ATRP using a preformed PSt macroinitiator in the presence of a divinyl coupling reagent.

The polystyrene macroinitiator used in this study was obtained by the polymerization of styrene using 1-phenylethyl bromide as the initiator and copper bromide complexed by 2,2′-bipyridine (bpy) as the catalyst in bulk at 110 °C.[18] After the reaction, the macroinitiator was isolated by dissolving the polymer solution in THF, passing the mixture through an alumina column to remove the catalyst, and precipitation in methanol. The isolated PSt macroinitiator had the predicted molecular weight and low polydispersity (M_n = 3200, M_w/M_n = 1.16). The end functionality of the PSt macroinitiator was probed by chain extension to a new block of PSt or PMA. For both block copolymers, the presence of a small shoulder in the size exclusion chromatography (SEC) traces corresponding to the macroinitiator indicates that a small fraction of the PSt macroinitiator lost the bromine functionality (Figure 1). This reflects the inevitable radical termination reactions during the macroinitiator synthesis by a radical polymerization process. Similar results were also observed by Fukuda and co-workers.[19]

Scheme 1



Three commercially available divinyl reagents, divinylbenzene (DVB), 1,4-butanediol diacrylate (BDA), and ethylene glycol dimethacrylate (EGDMA), were reacted with the PSt macroinitiator by ATRP with CuBr complexed by bpy as the catalyst in anisole at 110 °C.[20] These three divinyl reagents were chosen so that the effect of the coupling moiety (styrenic, acrylic, and methacrylic) on the star formation can be studied. Under the reaction conditions, DVB led to the formation of a soluble star polymer without gelation after 30 h. In contrast, an insoluble polymer was obtained after 14 h in the presence of BDA and within 20 min with the use of EGDMA. In addition, DVB provided star formation with higher yield than BDA as shown by the presence of a smaller amount of residual PSt macroinitiator in the star polymer from SEC. These results indicate the importance of choosing an appropriate divinyl coupling reagent. As methacrylic monomers typically produce a higher concentration of radicals under ATRP conditions, EGDMA as the coupling reagent led to extensive polymer cross-linking and star−star coupling to form an insoluble gel. For BDA, the addition of styrenic radicals to acrylic monomers is relatively slow, while propagation among acrylic monomers is fast. This may lead to the formation of mixed block copolymers with some polymer chains containing long divinyl units and others without divinyl units. DVB has a high affinity to radical addition and a low self-propagation rate which favors star formation for PSt macroinitiators under ATRP conditions.

Star-shaped PSt formation using DVB as the coupling reagent was studied in further detail. First, different ligands were used to complex the copper catalyst. When

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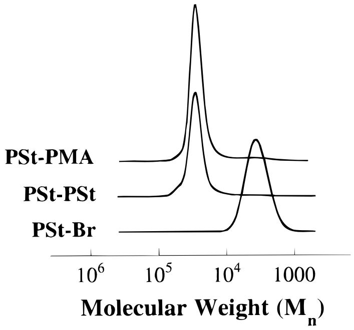

Figure 1. Synthesis of block copolymers with styrene and MA using polystyrene as the macroinitiator. $[\text{PSt-Br}]_0 = [\text{CuBr}]_0 = [\text{PMDETA}]_0/13 = [\text{styrene}]_0/192 = [\text{MA}]_0/232 = 0.047$ M; temperature = 110 °C (styrene) or 90 °C (MA); time = 2.75 h.

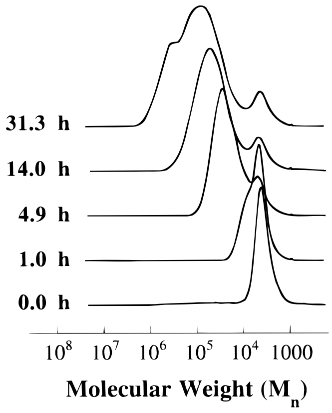

Figure 2. Synthesis of star-shaped polystyrene in the presence of divinylbenzene using CuBr/bpy as the catalyst. $[\text{PSt-Br}]_0 = [\text{CuBr}]_0 = [\text{bpy}]_0/3 = [\text{DVB}]_0/10 = 0.07$ M in anisole at 110 °C.

bpy was used as the ligand (Figure 2), after 1 h, there was some broadening in the molecular weight distribution without a significant increase in molecular weight, indicating the formation of PSt−DVB block copolymers. The DVB units in the block copolymer then started to react with each other forming star polymers. After 5 h, most of the PSt macroinitiators have participated in the star polymer formation. Longer reaction times resulted in an increasing amount of star−star coupling and the formation of star polymers with higher molecular weights. However, it did not decrease the amount of the residual PSt macroinitiator. The presence of the PSt macroinitiator shoulder in the SEC chromatogram of the star polymer even after 30 h indicates the incomplete star formation. When *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) was used as the ligand, the formation of star polymers was much faster (Figure 3). However, the PSt macroinitiator was still present in the final product. The faster star polymer formation with PMDETA as the ligand than bpy could be ascribed to the lower redox potential of the copper−PMDETA complex as previously reported.[21]

The effect of the DVB to PSt macroinitiator ratio was also investigated (Figure 4). It was found that a ratio of DVB to PSt macroinitiator between 5 and 15 was optimal for the star formation. A lower DVB to PSt ratio led to a lower yield of star polymers while higher ratios of DVB to PSt (e.g., DVB/PSt = 20) led to the formation of an insoluble gel in 2.8 h without significant improvement of the yield.

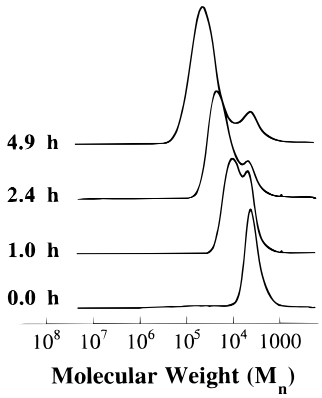

Figure 3. Synthesis of star-shaped polystyrene in the presence of divinylbenzene using CuBr/PMDETA as the catalyst. $[\text{PSt-Br}]_0 = [\text{CuBr}]_0 = [\text{PMDETA}]_0 = [\text{DVB}]_0/10 = 0.07$ M in anisole at 110 °C.

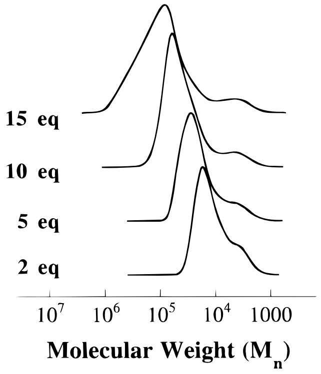

Figure 4. Effect of the divinylbenzene to polystyrene macroinitiator ratio on the synthesis of the star-shaped polystyrene. $[\text{PSt-Br}]_0 = [\text{CuBr}]_0 = [\text{PMDETA}]_0 = [\text{DVB}]_0/x = 0.07$ M in anisole at 110 °C ($x = 2$, 5, 10, or 15); reaction time = 5.5 h.

In summary, star-shaped polystyrenes were prepared by the coupling of polystyrene macroinitiators in the presence of divinylbenzene using copper-mediated ATRP. The yield of star polymers was ca. 85−90%. However, the presence of PSt macroinitiator in the final product indicates that the "arm first" technique is not a very efficient method for the synthesis of star polymers by ATRP under the reaction conditions investigated. This reflects in part the inherent problem of radical termination reactions in the radical polymerization. A fraction of the polymer chains always terminate even in a controlled radical polymerization process which leads to partially functionalized macroinitiators. Several factors pertinent to star formation, including the choice of ligand and the ratio of DVB to PSt, were studied and used to optimize the star formation process.

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(18) In a typical experiment, a dry round-bottom flask with a magnetic stir bar was charged with CuBr (0.13 g, 0.94 mmol), 2,2′-bipyridine (0.44 g, 2.8 mmol), styrene (10 mL, 0.087 mol), and diphenyl ether (10 mL). The flask was fitted with a rubber septum and degassed by three freeze−pump−thaw cycles. The flask was then immersed in an oil bath thermostated at 110 °C. The polymerization was initiated by the addition of degassed 1-phenylethyl bromide (0.13 mL, 0.94 mmol). After 6.5 h, the polystyrene macroinitiator was obtained by precipitation into methanol.

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(20) In a typical experiment, a dry glass tube with a magnetic stir bar was charged with CuBr (10.0 mg, 0.07 mmol), ligand (0.07 or 0.14 mmol), polystyrene macroinitiator (0.2 g, 0.06 mmol), DVB, and anisole (∼1 mL). The glass tube was degassed by three freeze−pump−thaw cycles and sealed under vacuum. The glass tube was then immersed in an oil bath thermostated at 110 °C. After a certain time, the glass tube was taken out and broken. The sample was dissolved in THF to measure conversion (GC) and molecular weight (SEC).

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