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Low Polydispersity Star Polymers via Cross-Linking Macromonomers by ATRP

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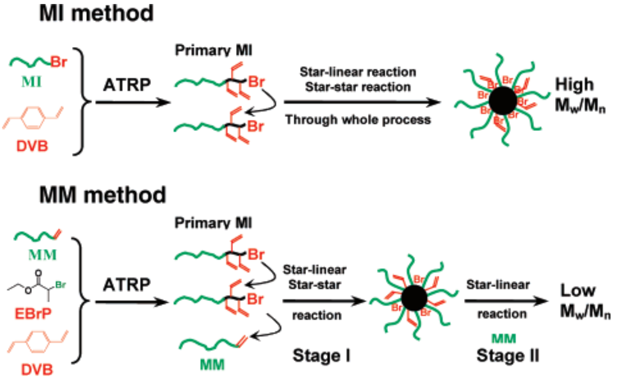
In this communication, we describe high yield synthesis of star polymers with low polydispersity by copolymerization of linear macromonomers (MM) with a divinyl compound using low molar mass ATRP initiators. The number of initiating sites in the star core was decreased by using low ratio of concentration of initiator to MM, which effectively limited the extent of star−star reactions and resulted in star polymers with low polydispersity.

The growing demand for nanoscale soft materials with uniform size and multiple functionalities motivated development of many new procedures that combine architectural control with incorporation of various functional groups, such as dendrimers and hyperbranched macromolecules.[1] As a branched nanoscale material, star polymers with well-defined structure and multiple arms/functionalities have potential applications in drug delivery, coatings, and lithography.[2] Synthesis of star polymers is most often accomplished by living anionic polymerization[3] or controlled/living radical polymerization.[4] Atom transfer radical polymerization (ATRP)[5] was used for the synthesis of star polymers by growing arms from a multifunctional initiator (classic "core-first" method)[6] and also attaching arms to the well-defined core.[7] However, the classic "arm-first" method,[8] based on cross-linking of a linear macroinitiator (MI) with a divinyl compound, is the easiest way to synthesize star polymers containing multiple arms and functionalities. It also allows preparation of various miktoarm star polymers.[9] Unfortunately, the resulting star polymers generally have a statistical distribution of the number of arms and a relatively broad molecular weight distribution (MWD, $M_w/M_n > 1.5$). The final product is also contaminated by the residual unreacted starting linear polymers. Therefore, it is essential to purify the product by tedious fractionation procedures in order to obtain a star polymer with a higher purity and narrower MWD.

During the arm-first star synthesis by cross-linking MI chains, two different reactions contribute to the formation of the star polymers (Scheme 1). One is a star−star reaction including a radical−radical coupling reaction and a radical−vinyl group reaction between two star molecules. The second one is a star−linear polymer reaction. The linear MI chain, defined as "primary MI", contains an initiating site and potentially a few dangling vinyl groups at one chain end. Both reactions increase the star molecular weight, but star−star reactions broaden MWD of the final product. Star−star reactions between two star cores (radical−radical or radical−vinyl) require the participation of radicals from the star core. In contrast, in the star−MI reactions, the radicals can also originate from the linear MIs. These reactions are less affected by steric congestion since MI can more easily approach a star core. During the synthesis of star polymers by cross-linking linear MIs, star−star reactions occur throughout the star formation process because the number of initiating sites (dormant form of radicals) in the star core is equal to the number of arms per star.[10] Thus, lower ratio of initiating sites to arms per star could reduce the star−star coupling process and increase their uniformity.

Scheme 1. Comparison of Star Synthesis by MI Method and MM Method



In this communication, we report for the first time the synthesis of star polymers via copolymerization of a linear MM with a divinyl compound using low molar mass ATRP initiators. A poly(*n*-butyl acrylate) (polyBA) MM ($M_n = 5300$ g/mol determined by GPC, containing an acrylate chain-end group) and divinylbenzene (DVB) were copolymerized by ATRP using ethyl 2-bromopropionate (EBrP) as an initiator and CuBr/tris(2-(dimethylamino)ethyl)amine (Me_6TREN) as a catalyst. Compared to the previously described arm-first star synthesis using cross-linking of linear MIs (MI method), the current process based on cross-linking of linear MMs (MM method) employs a small molecule initiator (e.g., EBrP) to initiate the copolymerization of polyBA MM and DVB. In the MI method, both initiating sites and arms in the star molecule are from MI, resulting in their identical numbers in each star (by default). In this new MM method, the numbers of initiating sites and arms (derived separately from initiator and MM) are independently controlled. Therefore, the number of initiating sites per star molecule may be much smaller than the number of arms when a low molar ratio of EBrP to MM was used. Lower number of initiating sites in the star core decreases the possibility of star−star reactions and results in the formation of star polymers with narrower MWD (Scheme 1). Moreover, the MM, initiator, and cross-linkers can be added in several steps, increasing the flexibility of star synthesis.

Star polymers $(\text{polyBA})_n$−polyDVB, where polyDVB represents the core of the star and n is the average number of polyBA arms per star molecule, were synthesized with an initial molar ratio of $[\text{MM}]_0/[\text{EBrP}]_0/[\text{DVB}]_0$ equal to 1/0.2/3. The conversion of DVB reached 100% after 24 h, while the yield of the star polymer continued to increase until 130 h (Figure 1). Star polymers were produced from the beginning of the reaction, as evidenced by the large shift of a new GPC elution peak to higher molecular weight. After 7.5 h, the apparent weight-average molecular weight (M_w) of the star polymer was 45.0 kg/mol and the star yield was 52% by weight. At this point, further increase of the apparent M_w significantly slowed down, although the star yield continued to increase. The star polymer stopped growing at 130 h with the

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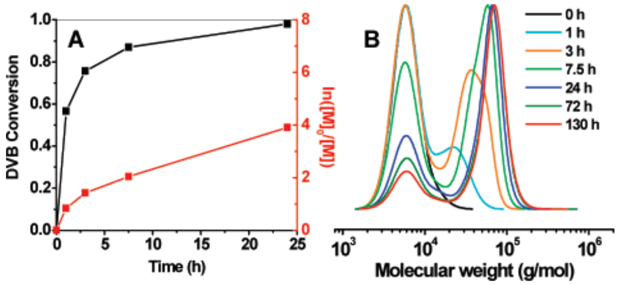
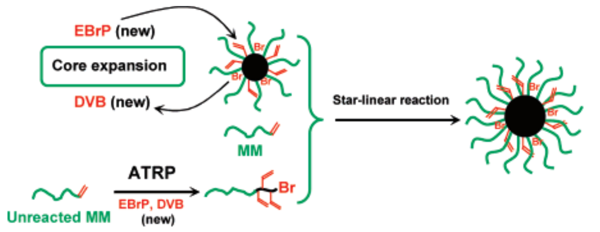


Figure 1. (A) Dependence of DVB conversion and $\ln([M]_0/[M])$ on reaction time and (B) evolution of GPC traces during synthesis of $(\text{polyBA})_n$−polyDVB star polymers by MM method. Experimental conditions: $[\text{polyBA MM}]_0/[\text{EBrP}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0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

Scheme 2. Synthesis of Star Polymers by Multistep Addition of EBrP and DVB in the MM Method



apparent M_w of 61.3 kg/mol and star yield as 77%. It is reasonable to expect that, during the initial 7.5 h, both star−star reactions and star−MM reactions occurred (Stage I, Scheme 1). However, after 7.5 h, due to the congestion around the core of star polymers, the star−star reactions stopped and only star−MM reactions were possible, evidenced by the essentially unchanged elution peak of the star polymer in the GPC analysis (Stage II, Scheme 1). At 130 h, the star polymer became so congested that the star−linear polymer reactions also stopped and the star polymers stopped growing. The star polymer produced at 130 h had a narrow MWD ($M_w/M_n = 1.15$) due to the early limitation of star−star coupling reactions at 7.5 h.

In contrast, the star polymer produced by cross-linking a linear polyBA-Br MI ($M_n = 4800$ g/mol) using DVB ($[\text{MI}]_0/[\text{DVB}]_0 = 1/3$) had a much broader MWD ($M_w/M_n = 1.55$) and showed a multi-modal peak distribution in the GPC analysis because star−star coupling reactions occurred throughout the entire polymerization period (Scheme 1 and Figure 1S in Supporting Information). This result indicates that by using lower amounts of initiator in the reaction star−star reactions were stopped at an earlier stage of the copolymerization and led to star polymers with narrower MWD.

The size of the star polymer reached saturation and prevented additional star−MM reactions when the star core became so congested that both the initiating sites and vinyl groups within the star core were unable to participate in further reactions with linear polymer chains. At this stage, only small molecules, such as free DVB and EBrP, could access the core and react with the initiating sites and vinyl groups in the star core. Thus, addition of another batch of DVB and EBrP at this stage could introduce more pendent vinyl groups and initiating sites to the star core while expanding its size and functionality. This expansion decreased core congestion and made further star−linear polymer reactions possible again. With appropriate amounts of additional DVB and EBrP, it is possible to allow star−MM reactions but to limit star−star reactions. Therefore, the newly added DVB and EBrP can increase the star yield and star molecular weight while avoiding any broadening of MWD (Scheme 2). The star−MM reaction stops again when the star polymer reaches its new saturated size. In order to further increase the star molecular weight and star yield, a second batch of DVB and EBrP was added and the star polymer began growing again. This process can be repeated until the star yield reaches essentially 100% incorporation of initially added MM.

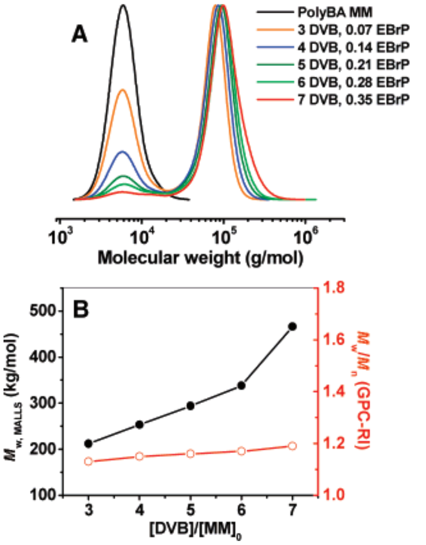


Figure 2. Influence of several-step addition of DVB and EBrP on (A) GPC traces and (B) molecular weight and MWD of $(\text{polyBA})_n$−polyDVB star polymers in MM method. Experimental conditions: $[\text{polyBA MM}]_0/[\text{EBrP}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 1/(0.07 + 0.07 \times 4)/(3 + 1 \times 4)/0.2/0.2$; $[\text{polyBA MM}]_0 = 0.06$ M; in anisole at 80 °C.

Figure 2A shows the evolution of the GPC traces for star polymers produced after addition of four batches of DVB and EBrP during the reaction. The initial molar ratio of $[\text{MM}]_0/[\text{EBrP}]_0/[\text{DVB}]_0$ was 1/0.07/3, and each time, 1 equiv of DVB and 0.07 equiv of EBrP were added to the ongoing reaction. After each addition, the star yield increased while the apparent molecular weight of the star polymers ($M_{w,\text{RI}}$, based on linear polySt standards) shifted very slowly to higher molecular weight region. In contrast, the absolute molecular weights of star polymers, determined by MALLS detector ($M_{w,\text{MALLS}}$), increased more quickly, indicating that the star polymers became more compact with the increase in star yield. During the whole process, the MWD of the star polymers remained almost unchanged (Figure 2B). After the addition of the fourth batch of DVB and EBrP to the reaction, the star yield reached over 98% and the MM peak in the GPC traces essentially disappeared. At that moment, without any purification step to fractionate the product, the absolute M_w of star polymer was 466 kg/mol and the MWD remained as narrow as $M_w/M_n = 1.19$.

It is worth noting that MM can react not only with the core but also with the newly added DVB and EBrP to form primary MI, as shown in Scheme 2. Therefore, all new batches of DVB and EBrP were added into the system after the conversion of polyBA MM was >60% (Figure 2A). Consequently, due to the concentration effect, the newly formed MI reacted preferentially with initiating sites or vinyl groups in the preformed star core rather than with each other to generate new stars. Figures 2S and 3S indicate that, after adding more DVB and EBrP, most of the unreacted linear MIs were incorporated into the preformed stars.

Another feature of the MM method is high reproducibility. Several reactions carried out under the same experimental conditions with the same reagent ratios resulted in star polymers with the same molecular weight and the same star yield. The GPC curves of the star copolymers formed in each step completely overlapped (Figure 3). Some small differences in experimental conditions and/or

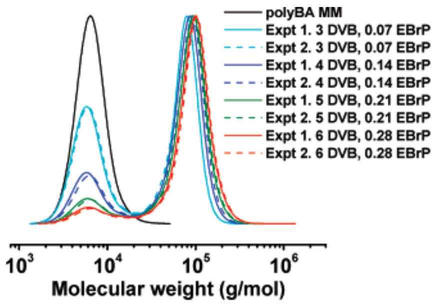


Figure 3. Comparison of the GPC results of two independent reactions with the same initial composition and experimental conditions for synthesis of (polyBA)$_n$−polyDVB star polymers in MM method. Experimental conditions: $[\text{polyBA MM}]_0/[\text{EBrP}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 1/(0.07 \times 4)/(3 + 1 \times 3)/0.2/0.2$; $[\text{polyBA MM}]_0 = 0.06$ M; in anisole at 80 °C.

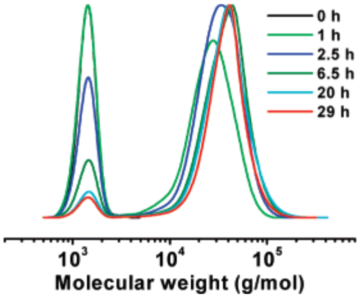


Figure 4. Synthesis of (PEO)$_n$−polyEGDMA star polymers by MM method. Experimental conditions: $[\text{PEO MM}]_0/[\text{EBiB}]_0/[\text{EGDMA}]_0/[\text{CuBr}]_0/[\text{dNbpy}]_0 = 1/0.1/1/0.06/0.12$; $[\text{PEO MM}]_0 = 0.18$ M; in toluene at 60 °C. Linear polyMMA standards were used for calibration of the THF GPC.

procedures should lead to some variation in the reaction rate and/or final MWD. However, since each new batch of DVB and EBrP was always added to the systems after the star growth (or star−linear polymer reaction) stopped, the reaction that proceeded faster would reach the maximum size of star earlier and essentially would wait for the reaction that proceeded slower to catch up. Therefore, differences in reaction rates had no influence on the reproducibility of the synthesis, resulting in complete overlap of the GPC curves in any two independent reactions. This feature indicates that the structure of the star polymers can be predetermined by selection of the initial reaction conditions, which is important for any larger scale production of star polymers with precisely controlled properties.

The concept of the new MM method was successfully illustrated by copolymerization of polyBA MM and DVB cross-linker using EBrP as ATRP initiator to synthesize (polyBA)$_n$−polyDVB star polymers with low polydispersity and high star yield. In this method, other types of MMs, cross-linkers, and initiators can also be used for synthesis of various star polymers. For example, commercially available poly(ethylene glycol) methyl ether methacrylate (PEO MM, $M_n \sim 1100$ g/mol) was used for synthesis of (PEO)$_n$−polyEGDMA star polymers by using ethylene glycol dimethacrylate (EGDMA) as cross-linker and ethyl 2-bromoisobutyrate (EBiB) as ATRP initiator. With the initial molar ratio of $[\text{PEO MM}]_0/[\text{EBiB}]_0/[\text{EGDMA}]_0$ as 1/0.1/1, the star yield reached 97% after 29 h and the polydispersity of the star polymer was as low as $M_w/M_n = 1.18$ (Figure 4). Compared to polyBA MM, the PEO MM is much "thinner", which resulted in a less congested environment around the star core and facilitated the incorporation of linear MM chains into the star polymer. As discussed before, due to the smaller amount of EBiB used, the number of initiating sites per star was only ca. 10% versus the number of arms. Less initiating sites in the star core decreased the probability of star−star reactions and produced star polymers with narrower MWD.

In summary, we report a new procedure for the high yield synthesis of uniform star polymers via copolymerization of a MM with a divinyl cross-linker, such as DVB and EGDMA, using ATRP. The star polymers have high molecular weight and narrow MWD. The molar ratio of initiator and MM determined the ratio of initiating sites and arms in the star polymer. The lower number of initiating sites in the star core decreased the extent of star−star reactions, leading to star polymers with narrower MWD. Addition of extra cross-linker and initiator during the reaction increased the star molecular weight and star yield, while the MWD of the star polymer remained very narrow.

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

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