Synthesis of Low-Polydispersity Miktoarm Star Copolymers via a Simple "Arm-First" Method: Macromonomers as Arm Precursors

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ABSTRACT: Miktoarm star copolymers with variable arm compositions, high star yield (>85%), and low polydispersity ($M_w/M_n < 1.2$) were successfully synthesized by a simple "arm-first" method, one-pot cross-linking a mixture of linear macromonomers (MMs) and/or macroinitiators (MIs), via the atom transfer radical polymerization (ATRP) technique. Characterization of the star product by liquid adsorption chromatography proved that the star polymers obtained by cross-linking different MMs and MIs were miktoarm stars containing two arm species in one molecule. The incorporation of MM into miktoarm star molecule increased the star molecular weight and the average number of arms but did not change the number of initiating sites in the star core because the initiating sites independently originated from the incorporated MIs or low molar mass ATRP initiators. By using lower amount of initiator, the molar ratio of initiating sites to incorporated arms in the miktoarm star was decreased, which effectively reduced the extent of star−star coupling reactions and resulted in the formation of miktoarm star copolymers with low polydispersity. The molar ratios of arms in the miktoarm star copolymers were in agreement with the composition of initial MMs and/or MIs mixture. During the cross-linking reaction of a mixture of two MMs, addition of extra cross-linker and low molar mass initiator increased the molecular weight and yield of the miktoarm star molecules while preserving their low polydispersity.

Introduction

Star polymers, consisting many arms connecting to a central core, represent a branched nanoscale material with compact structure, globular shape, and large surface area.[1,2] Introduction of various functional groups into the star polymers, either in the star core or at the star periphery, significantly expands the potential applications of star polymers in various areas, such as in catalysis, optical imaging, and drug delivery systems.[3–6] On the basis of the chemical compositions of the arm species, star polymers can be classified into two categories: homoarm and miktoarm (or heteroarm) star polymers. The homoarm star polymers with a symmetric structure comprise radiating arms with similar molecular weight and identical chemical composition. In contrast, miktoarm star molecule contains two or more arm species with different chemical compositions and/or molecular weights.[7] Compared to the large number of reports on synthesis of homoarm star polymers by using various controlled/"living" polymerization techniques, such as living anionic polymerization,[2,8] living cationic polymerization,[9] metathesis,[10] and controlled radical polymerization (CRP),[11–13] the synthesis of miktoarm star copolymers is more difficult and consequently covered by fewer reports.

For synthesis of miktoarm star copolymers by using CRP methods, three strategies are possible. The first one involves the use of a multifunctional miktoinitiator ("core-first" method) by combining various CRP techniques with other living polymerization methods, especially the ring-opening polymerization (ROP) technique.[14–20] Chain-end modification of preformed macroinitiator (MI) is an alternative strategy for synthesis of miktoinitiators.[21–25] In a second method, miktoarm star copolymers are synthesized by chain-end coupling reactions between multifunctional coupling agents and reactive linear chains. For instance, the recently developed "click reactions",[26] Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions between an azide and an alkyne, have been used as a highly efficient organic coupling reaction for synthesis and functionalization of star[27–30] and miktoarm star copolymers.[31–35] In the third method, miktoarm star copolymers containing a highly cross-linked core (nodule) and statistically distributed arms are synthesized by using the polymerization of divinyl cross-linker. Traditionally, the "in−out" method[7,36–38] was reported for synthesis of miktoarm star copolymers containing two kinds of arms with different chemical compositions, in which the word "in" refers to the formation of star MI by the "arm-first" method and the word "out" represents the subsequent growth of the second generation of arms from the multifunctional star MI. Because of the congested environment around the cross-linked core in the star MI, not all of the initiating sites participated in the formation of the second generation of arms, and the initiation efficiency of the star MI was less than 100%.[37,38] Thus, the number of the second generation of arms is lower than the number of the first generation of arms, and it is conceptually impossible to synthesize a miktoarm star copolymer containing more than two kinds of arms by using the "in−out" method.[39]

In order to synthesize miktoarm star copolymers with potentially any molar ratios and species of the arms, we recently reported a new method for synthesis of miktoarm star copolymers by using a simple and general "arm-first" method, i.e., one-pot cross-linking a mixture of different linear MIs by divinyl cross-linker.[40] Linear MIs with high degree of bromine chain-end functionality but different chemical compositions and molecular weights, including polyacrylate, polystyrene, polymethacrylate, and poly(ethylene oxide), were incorporated into one miktoarm star molecule by a one-step atom transfer radical polymerization (ATRP)[41–44] cross-linking reaction. The obtained miktoarm star copolymers are formulated as (polyA)$_n$-(polyB)$_p$-polyX, where polyX represents the cross-linked core of the miktoarm star copolymer; n and p are the average numbers of polyA and polyB arms per miktoarm star molecule, respectively. Within our investigation, the molar ratios of arms in the obtained miktoarm star copolymers were always in agreement with the composition of the initial MI mixture, indicating the powerful capacity of this general "arm-first" method for synthesis of miktoarm star copolymers. However, one concern of this method is that the polydispersity of the obtained miktoarm star

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Table 1. Molecular Weights and Distributions of Linear MIs and MMs

entries[a]	linear chains	$M_{n,theor}$ (kg/mol)[b]	DP[b]	$M_{n,GPC}$ (kg/mol)[c]	M_w/M_n[c]
MI-B_{36}	PolyBA-Br MI	4.80	36	4.69	1.10
MI-M_{69}	PolyMA-Br MI	6.10	69	5.76	1.06
MI-E_{45}	PEO-Br MI	2.16	45	2.06	1.03
MM-B_{42}	PolyBA MM	5.48	42	5.30	1.05
MM-B_{90}	PolyBA MM	11.7	90	10.4	1.13
MM-E_{23}	PEO-MA MM	1.10	23	1.26	1.04
MM-E_{45}	PEO-MA MM	2.08	45	2.23	1.05

[a] The code to denote each MI or MM follows the rules: B represents polyBA, M represents polyMA, and E represents PEO. The subscript number represents the degree of polymerization (DP) of the linear arm precursors. Detailed synthetic procedures and supplies for all MIs and MMs are described in the Experimental Section. [b] Theoretical molecular weight ($M_{n,theor}$) and average DP of linear polymers determined from monomer conversions or producer data. [c] Number-average molecular weight and polydispersity, measured by GPC in THF with RI detector, calibration with linear polySt as standard.

copolymers was relatively high ($M_w/M_n > 1.3$) when linear MIs were used as arm precursors.[40]

Functional star polymers with high molecular weight and low polydispersity were synthesized recently via copolymerization of linear macromonomer (MM) as arm precursor with divinyl cross-linker using low molar mass ATRP initiator (MM method).[45,46] In this method, the number of initiating sites (derived from the low molar mass initiator) and the number of arms (derived from MM) per star molecule were independently controlled. A low molar ratio of initiator to MM decreased the number of initiating sites in the star core, reduced the possibility of star−star coupling reactions, and decreased star polydispersity. Moreover, various functionalities can be easily introduced into the star cores by using different functional initiators.[46]

It is evident that the combination of the MM method and the general one-pot “arm-first” method provides a practical strategy for synthesis of miktoarm star copolymers with both variable arm compositions and low polydispersity. Herein, we report the first synthesis of high-yield and low-polydispersity ($M_w/M_n < 1.2$) miktoarm star copolymers containing a cross-linked core and multiple arms with different chemical compositions by using linear MMs to partially or completely replace linear MIs as the arm precursors.

Experimental Section

Materials. Methyl acrylate (MA, 99%), *n*-butyl acrylate (BA, 99%), and divinylbenzene (DVB, 80%) were purchased from Aldrich and purified twice by passing through a column filled with basic alumina to remove the inhibitor. For poly(ethylene oxide) methyl ether methacrylate MM (PEO MM, $M_n \sim 1100$ g/mol, Aldrich), the inhibitor was removed by passing the PEO MM solution in methylene chloride through a basic alumina column and evaporating the methylene chloride solvent. PEO MM with $M_n \sim 2080$ g/mol (50 wt % solution in water, Aldrich) was extracted by methylene chloride from water, followed by the rotary evaporation of methylene chloride. Two types of polyBA MMs containing an acrylate chain-end group but different molecular weights (MM-B_{42}: $M_{n,theor} = 5.48$ kg/mol, $M_w/M_n = 1.05$; MM-B_{90}: $M_{n,theor} = 11.7$ kg/mol, $M_w/M_n = 1.13$, Table 1) were generously provided by Kaneka (Japan) and used as received. These linear MMs were synthesized by ATRP of BA using a method similar to that reported in the open literature.[47] CuBr (98%, Acros) was purified using a modified literature procedure.[37] PEO-based monofunctional ATRP MI containing tertiary bromine chain-end functionality was synthesized by a one-step esterification reaction between PEO-OH ($M_n \sim 2000$ g/mol, Fluka) and α-bromoisobutyryl bromide.[40] Linear polyBA-Br MI and polyMA-Br MI were synthesized by ATRP of BA and MA, respectively, based on the published procedures.[40] Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized following the previously reported procedure.[48] All other reagents—ethyl 2-bromoisobutyrate (EBiB), $CuBr_2$, and solvents—were purchased from Aldrich with the highest purity and used as received without further purification.

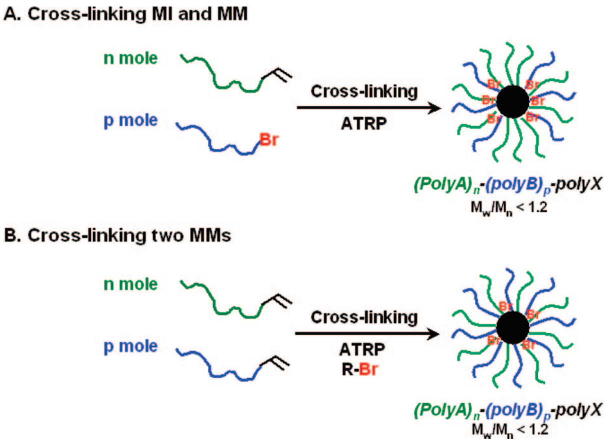
Synthesis of Miktoarm Star Copolymers via Cross-Linking a Mixture of Linear MIs and/or MMs. All experimental procedures for synthesis of various kinds of miktoarm star copolymers via one-pot cross-linking reaction of a mixture of linear MIs and/or MMs were similar. A typical procedure for synthesis of $(\text{polyBA})_n$-$(\text{polyMA})_p$-polyDVB miktoarm star copolymers by cross-linking linear polyBA MM (MM-B_{42}, $M_{n,theor} = 5.48$ kg/mol, Table 1) and polyMA-Br MI (MI-M_{69}, $M_{n,theor} = 6.10$ kg/mol, Table 1) via ATRP reactions is briefly described, started with the ratios of reagents $[\text{MM-B}_{42}]_0/[\text{MI-M}_{69}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 0.80/0.20/3.0/0.2/0.2$. A clean and dry Schlenk flask was charged with polyBA MM (1.6 g, 292 μmol), polyMA-Br MI (0.45 g, 73 μmol), DVB (0.156 mL, 1.09 mmol), Me_6TREN (19.3 μL, 73 μmol), and anisole (3.4 mL). The flask was deoxygenated by five freeze−pump−thaw cycles. During the final cycle the flask was filled with nitrogen, and CuBr (10.5 mg, 73 μmol) was quickly added to the frozen mixture. The flask was sealed with a glass stopper then evacuated and back-filled with nitrogen five times before it was immersed in an oil bath at 80 °C. At timed intervals, samples were withdrawn via a syringe fitted with stainless steel needle and immediately diluted with THF. The samples were used to measure DVB conversions and polymer molecular weights by gas chromatography (GC) and gel permeation chromatography (GPC), respectively. The reaction was stopped at 100 h by exposure to air, and the solution was filtered through a column filled with neutral alumina to remove the copper complex. The final miktoarm star polymers were obtained after precipitation into cold methanol and drying under vacuum at 60 °C for 1 day.

Characterization. Monomer conversions were determined from the concentration of the unreacted monomer in the samples periodically removed from the reactions using a Shimadzu GC-14A gas chromatograph, equipped with a capillary column (DB-Wax, 30 m × 0.54 mm × 0.5 μm, J&W Scientific). Anisole or DMF was used as internal standard for calculation of monomer conversions. The polymer samples were separated by GPC (Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å), with THF eluent at 35 °C, flow rate = 1.00 mL/min and differential refractive index (RI) detector (Waters 2410)). The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene (polySt) standards using WinGPC 6.0 software from PSS. Area fractions of both star and linear polymers were determined by multipeak splitting of the GPC curve using Gaussian function in Origin 6.0 software. The obtained GPC curves with flat baseline were imported into the WinGPC software for calculation of the apparent molecular weights and polydispersity of the star and linear polymers. The detectors employed to measure the absolute molecular weights ($M_{w,MALLS}$) were a triple detector system containing RI detector (Wyatt Technology, Optilab REX), viscometer detector (Wyatt Technology, ViscoStar), and a multiangle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology. ^{1}H NMR spectra of the polymer solutions in $CDCl_3$ were collected on Bruker Avance 300 MHz spectrometer at 27 °C. Liquid chromatography under the critical conditions (LCCC) of polyMA homopolymers[40,49] was used to analyze the star and miktoarm star copolymers.

Results and Discussion

The classic “arm-first” method,[4,50–52] based on cross-linking a linear MI and/or mixture of MIs, is a convenient strategy for synthesis of star and/or miktoarm star copolymers with high molecular weight and large number of arms. Unfortunately, the resulting (miktoarm) star polymers generally had a relatively broad molecular weight distribution because of the inevitable star−star coupling reactions, which included radical−radical coupling reaction and radical−pendant vinyl group reaction

Scheme 1. Synthesis of Low-Polydispersity Miktoarm Star Copolymers by Cross-Linking a Mixture of (A) MM and MI or (B) Two MMs via the One-Pot "Arm-First" Method



between two star molecules. The star−star coupling reactions could be decreased by using less divinyl cross-linker, e.g., lower molar ratio of cross-linker to arm precursor, although the molecular weight and averaged arm numbers of the obtained star molecules also decreased significantly. In order to synthesize star polymers with both high molecular weight and low polydispersity, a critical strategy is to decease the number of initiating sites (dormant form of radicals) per star molecule while keeping the number of arm unchanged.[45] However, this is difficult to be achieved in the traditional "arm-first" method via cross-linking linear MIs because both the initiating sites and arms in the obtained star molecules originate from the linear MIs, and every linear MI contains one chain-end initiating functionality. In contrast, by using linear MM as arm precursor for synthesis of star polymers, the incorporation of linear MM into star molecule only increased the averaged arm numbers, rather than changing the number of initiating sites, which originated from low molar mass initiators. The number of initiating sites in the star core was decreased by using lower ratio of initiator to MM, which effectively limited the extent of star−star reactions and resulted in star polymers with low polydispersity.[45] Therefore, it was expected that by using linear MMs to partially or completely replace the linear MIs as arm precursors, the miktoarm star copolymers synthesized via the one-pot cross-linking reaction could have high molecular weight as well as narrow molecular weight distribution.

To illustrate the hypothesis for synthesis of miktoarm star copolymers with high molecular weight and low polydispersity by using the one-pot "arm-first" method, several types of linear MIs and MMs with different chemical compositions and molecular weights were used for the ATRP cross-linking reactions. All linear precursors had narrow molecular weight distribution (low M_w/M_n), and the relevant information is summarized in Table 1. Simply cross-linking a mixture of MM and MI or a mixture of two MMs by a divinyl cross-linker, such as DVB, produced miktoarm star copolymers with high star yield and low polydispersity (Scheme 1).

Synthesis of (PolyBA)$_n$-(PolyMA)$_p$-PolyDVB Miktoarm Star Copolymers via Cross-Linking a Mixture of Linear MM and MI. As the first example to use linear MM as arm precursor for synthesis of low-polydispersity miktoarm stars copolymers, a mixture of linear polyBA MM (MM-B_{42} in Table 1) and polyMA-Br MI (MI-M_{69} in Table 1) with molar ratio of $[\text{MM-B}_{42}]_0/[\text{MI-M}_{69}]_0 = 0.80/0.20$ was cross-linked by using DVB as cross-linker and CuBr/Me_6TREN as catalyst (entry M-BM2, Table 2).

Before polymerization, the system was a mixture of two linear precursors, MM-B_{42} and MI-M_{69}. Because of their similar molecular weights and the relatively low resolution of the GPC technique, the mixture of MM-B_{42} and MI-M_{69} precursors showed one elution peak during GPC analysis (Figure 1B.) During the cross-linking reaction, the conversion of DVB increased with reaction time and reached essentially 100% at 21 h (Figure 1A). The GPC curves in Figure 1B indicate that as the conversion of DVB increased, the amount of linear chains (both MM and MI) incorporated into the star polymers increased. This was confirmed by the decreasing RI signal corresponding to the mixture of linear precursors and an increasing GPC peak at higher molecular weight direction. Although there was no free DVB cross-linker left after 21 h, the yield of star polymers continued to increase via the reaction of propagating radicals and pendant vinyl groups located in the linear primary chains and/or star cores until the reaction was stopped at 100 h. The obtained star product at 100 h had an apparent molecular weight, $M_{w,RI} = 64.7$ kg/mol, determined by GPC with RI detector and linear polySt as standard, which was lower than the absolute molecular weight $M_{w,MALLS} = 157.2$ kg/mol, indicating the compact structure of the star polymers. The area fraction of star product was 86%, based on the multipeak splitting of the GPC curve using Gaussian function, and the polydispersity of the star was as low as $M_w/M_n = 1.15$ (entry M-BM2, Table 2). After precipitation of the star product into cold methanol to remove the unreacted linear chains, the purified star polymers were obtained successfully (Figure 1B).

As reported previously,[40] during the cross-linking reaction of a mixture of two reactive linear chains, the obtained star product could be either a miktoarm star copolymer containing two kinds of arms in one molecule or a mixture with contaminant of homoarm star polymers. Since the polyMA-Br MI was the only initiating species in the initial mixture of polyBA MM and polyMA-Br MI, the possibility for generation of (polyBA)$_p$-polyDVB homoarm star contaminant in the final star product should be excluded, although the existence of (polyMA)$_p$-polyDVB homoarm stars was still possible. In order to determine the distribution of the two kinds of arms in the final star product, the liquid chromatography under the critical conditions (LCCC) for polyMA homopolymer,[53] which separates polymers based on their chemical compositions, was employed to characterize polyBA MM, polyMA-Br MI, and the obtained star product (Figure 2). Under this condition, the linear polyMA-Br MI showed a chromatographically "invisible" elution behavior due to the compensation of enthalpic interaction and entropic exclusion between polyMA polymers and the stationary columns.[49] Therefore, the elution volume of linear polyMA-Br MI was similar to the void volume of the columns ($V_e = 5.18$ mL). In contrast, the elution behavior of polyBA MM (MM-B_{42}, $V_e = 4.36$ mL) was in a size exclusion mode: polymers with high molecular weight eluted earlier.

Before purification, the star product M-BM2 obtained by cross-linking the mixture of polyBA MM and polyMA-Br MI showed two elution peaks. The smaller one at 4.36 mL represented the unincorporated linear polyBA MM, and the bigger one at $V_e = 3.27$ mL represented the formed star polymers. The absence of elution peak ca. 5.18 mL indicated that all polyMA-Br MIs were incorporated into the star format. The (polyMA)$_p$-polyDVB homoarm star polymers synthesized under similar conditions to M-BM2 with molar ratio of $[\text{MI-M}_{69}]_0/[\text{DVB}]_0 = 1/3$ (S-M1 in Table 2) showed an elution volume at $V_e = 4.84$ mL, different from those in M-BM2 product. The results in Figure 2 proved that there was no (polyMA)$_p$-polyDVB homoarm star contaminant in the obtained star product M-BM2. Since the possibility for (polyBA)$_p$-polyDVB homoarm star contaminant has been excluded, the obtained star product (M-BM2) was a miktoarm star copolymer containing two arm species in one star molecule. After purifica-

Table 2. Synthesis of (PolyA)$_n$-(PolyB)$_p$-PolyDVB Miktoarm Star Copolymers by the "Arm-First" Method with MI and MM[a]

entries[b]	polyA	polyB	$f_{\text{polyA}}/f_{\text{polyB}}$	A_{star}[c]	$M_{\text{w,RI}}$ (kg/mol)[d]	$M_{\text{w,MALLS}}$ (kg/mol)[e]	M_w/M_n[d]	n_A/n_B[f]	N_{arm} per star[g]	$N_{\text{arm-A}}$ per star[g]	$N_{\text{arm-B}}$ per star[g]
S-B1	MI-B_{36}		1.00/0	0.89	50.2	124.5	1.31	1.00/0	24	24	0
S-M1		MI-M_{69}	0/1.00	0.90	59.4	153.2	1.34	0/1.00	23	0	23
M-BM1	MI-B_{36}	MI-M_{69}	0.50/0.50	0.89	50.7	119.9	1.33	0.47/0.53	20	9	11
M-BM2	MM-B_{42}	MI-M_{69}	0.80/0.20	0.86	64.7	157.2	1.15	0.77/0.23	26	20	6
M-BM3	MM-B_{42}	MI-M_{69}	0.50/0.50	0.88	58.8	147.7	1.22	0.53/0.47	24	13	11
M-BM4	MM-B_{42}	MI-M_{69}	0.20/0.80	0.90	56.5	157.1	1.24	0.22/0.78	25	5	20
M-BE1	MM-B_{42}	MI-E_{45}	0.83/0.17	0.86	82.3	181.6	1.14	0.80/0.20	36	29	7
M-BE2	MM-B_{42}	MI-E_{45}	0.67/0.33	0.87	63.7	154.7	1.16	0.65/0.35	35	23	12
M-BE3	MM-B_{42}	MI-E_{45}	0.50/0.50	0.89	50.9	127.2	1.19	0.48/0.52	33	16	17

[a] Synthesis of (polyA)$_n$-(polyB)$_p$-polyDVB miktoarm star copolymers by cross-linking a mixture of linear MM and MI (Table 1). Experimental conditions: $[\text{polyA}]_0/[\text{polyB}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = f_{\text{polyA}}/f_{\text{polyB}}$ /3.0/0.2/0.2, $([\text{polyA}]_0 + [\text{polyB}]_0) = 0.065$ M, 80 °C in anisole for 100 h. [b] In "M-$\alpha\beta\gamma$", "M" represents "miktoarm star", "α" and "β" represent the corresponding linear MM and/or MI with abbreviations of B, M, E for polyBA, polyMA and PEO, respectively. Similarly, "S-$\alpha\gamma$" represents homoarm star (S) with arm composition "α". [c] Area fraction of star or miktoarm star polymers, determined by the multipeak splitting of the GPC curve using Gaussian function. [d] Weight-average molecular weight and polydispersity, measured by THF GPC with RI detector, calibration with linear polySt as standard. [e] Weight-average molecular weight, measured by THF GPC with MALLS detector. [f] Average molar fraction of arm A and arm B in the fractionated miktoarm star copolymers, determined by ^{1}H NMR, 27 °C, $CDCl_3$ as solvent. [g] Number-average value of the number of arms per star or miktoarm star molecule (N_{arm}) was calculated based on eq S1 in the Supporting Information. $N_{\text{arm-A}} = N_{\text{arm}} \times n_A$; $N_{\text{arm-B}} = N_{\text{arm}} \times n_B$.

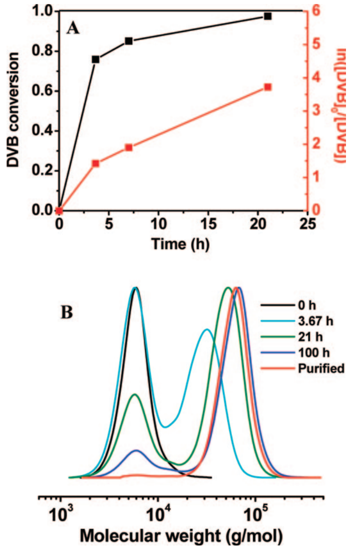


Figure 1. (A) Dependence of DVB conversion and ln([DVB]$_0$/[DVB]) on reaction time and (B) the GPC traces during the synthesis of (polyBA)$_n$-(polyMA)$_p$-polyDVB miktoarm star copolymers (entry M-BM2 in Table 2) by cross-linking polyBA MM ($M_{\text{n,theor}} = 5.48$ kg/mol, MM-B_{42}) and polyMA-Br MI ($M_{\text{n,theor}} = 6.10$ kg/mol, MI-M_{69}). Experimental conditions: $[\text{MM-B}_{42}]_0/[\text{MI-M}_{69}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 0.80/0.20/3.0/0.2/0.2$, $([\text{MM-B}_{42}]_0 + [\text{MI-M}_{69}]_0) = 0.065$ M, 80 °C in anisole; linear polySt standards for GPC calibration.

tion of the miktoarm star copolymers by precipitation into cold methanol, the peak representing the unincorporated polyBA chains was essentially absent, indicating the successful removal of linear polymer contaminant from the miktoarm star product (Figure 2).

The purified miktoarm star copolymers were characterized by ^{1}H NMR spectroscopy (Figure 3). Based on the integration of proton peaks (H_a from polyBA arm and H_c from polyMA arm) and the DP of each arm, the molar ratio of polyBA and polyMA arms in the final miktoarm star copolymer was around $n_A/n_B = 0.77/0.23$, which was close to their initial $f_{\text{polyA}}/f_{\text{polyB}} = 0.80/0.20$ molar ratio (M-BM2, Table 2). Given the absolute molecular weight of the miktoarm star copolymer was $M_{\text{w,MALLS}} = 157.2$ kg/mol, the total averaged arm number per miktoarm star molecule in M-BM2 was calculated ca. $N_{\text{arm}} = 26$, in which 20 arms were polyBA and 6 arms were polyMA (detailed calculation is described in the Supporting Information).

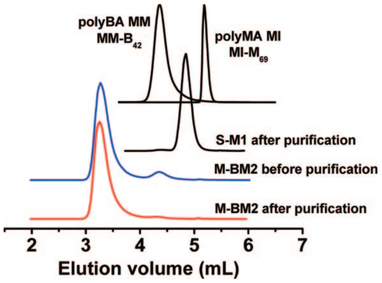


Figure 2. LCCC chromatograms of polyBA MM (MM-B_{42}), polyMA-Br MI (MI-M_{69}), (polyMA)$_p$-polyDVB homoarm star (S-M1), and (polyBA)$_n$-(polyMA)$_p$-polyDVB miktoarm star (M-BM2) before and after purification. LCCC conditions for polyMA homopolymer: two sets of silica columns with pore size of 100 and 300 Å, mobile phase as 2-butanone/cyclohexane (86/14 by volume) with flow rate as 0.5 mL/min at 32 °C.[49]

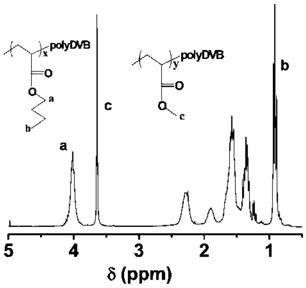


Figure 3. ^{1}H NMR spectrum of the purified (polyBA)$_n$-(polyMA)$_p$-polyDVB miktoarm star copolymers (M-BM2, Table 2). NMR conditions: 27 °C, $CDCl_3$ as solvent.

Effect of Initial Molar Ratio of MM and MI on the Polydispersity of Miktoarm Star Copolymers. By changing the initial molar ratios of linear polyBA MM (MM-B_{42}) and polyMA-Br MI (MI-M_{69}), a series of (polyBA)$_n$-(polyMA)$_p$-polyDVB miktoarm star copolymers were synthesized (Table 2). The obtained miktoarm star copolymers were purified by precipitation into cold methanol to remove the unincorporated linear chains before ^{1}H NMR analysis of the arm compositions in the miktoarm star product. It is found in Table 2 that the arm compositions in different (polyBA)$_n$-(polyMA)$_p$-polyDVB miktoarm star copolymers were in agreement with the molar ratios of MM and MI in the initial mixture. By systematically changing the molar ratios of polyBA MM and polyMA-Br MI (from 0.80/0.20 to 0.50/0.50 to 0.20/0.80, M-BM2 to M-BM4), miktoarm star copolymers with different arm compositions were obtained.

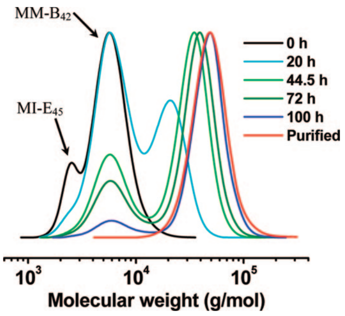


Figure 4. GPC traces during the synthesis of (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers by cross-linking polyBA MM and PEO-Br MI (M-BE2, Table 2). Experimental conditions: $[\text{MM-B}_{42}]_0/[\text{MI-E}_{45}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 0.67/0.33/3.0/0.2/0.2$, ($[\text{MM-B}_{42}]_0 + [\text{MI-E}_{45}]_0$) = 0.065 M, 80 °C in anisole; linear polySt standards for GPC calibration.

As discussed above, a major target of the current study is to obtain miktoarm star copolymers with uniform structure (e.g., low polydispersity). Compared to the star or miktoarm star copolymers synthesized by cross-linking MI or mixture of MIs (S-B1, S-M1, and M-BM1 in Table 2), the miktoarm star copolymers obtained via cross-linking mixture of polyBA MM and polyMA-Br MI had lower polydispersity because the molar ratio of initiating sites to arms in the miktoarm star copolymers was less than unity. When the molar ratio of polyBA MM and polyMA-Br MI was 0.80/0.20, the polydispersity of the miktoarm star copolymer was $M_w/M_n = 1.15$ (M-BM2). While the polydispersity of the miktoarm star copolymer increased to $M_w/M_n = 1.24$ (M-BM4), when the molar ratio of polyBA MM to polyMA-Br MI was changed to 0.20/0.80, this result was reasonable because the number of initiating sites per star molecule increased with the increasing molar ratio of MI to MM in the initial mixture, which enhanced the star−star coupling and increased the polydispersity of miktoarm star product.

PolyBA MM (MM-B$_{42}$) was also used for synthesis of (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers by combining with PEO-Br MI (MI-E$_{45}$). The evolution of GPC traces with reaction times in a typical reaction is shown in Figure 4, in which the initial molar ratios of reagents were $[\text{MM-B}_{42}]_0/[\text{MI-E}_{45}]_0/[\text{DVB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 0.67/0.33/3.0/0.2/0.2$ (M-BE2, Table 2). With the increase of reaction time, the GPC peaks representing the formed miktoarm star copolymers shifted to higher molecular weight direction with increasing area fraction. At 100 h, the yield of (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymer reached 87% by area, and the polydispersity was as low as $M_w/M_n = 1.16$ (M-BE2, Table 2). After precipitation in cold methanol, the purified miktoarm star polymers were analyzed by ^{1}H NMR spectroscopy to determine the arm composition. Based on the integration of proton peaks (H$_a$ from polyBA arm and H$_d$ from PEO arm, Figure 5) and the DP of each arm, the molar ratio of polyBA and PEO arms in the M-BE2 miktoarm star copolymer was around $n_A/n_B = 0.65/0.35$, which was in agreement to the initial molar ratio of the two arm precursors $f_{\text{polyA}}/f_{\text{polyB}} = 0.67/0.33$ (M-BE2, Table 2). By changing the molar ratios of polyBA MM and PEO-Br MI in the initial mixture (M-BE1 to M-BE3 in Table 2), a series of (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymer were synthesized. The similar trend was found that the polydispersity of the miktoarm star copolymers increased from $M_w/M_n = 1.14$ to 1.19 when the molar ratios of MM-B$_{42}$ to MI-E$_{45}$ changed from 0.83/0.17 to 0.50/0.50 in the initial mixture of arm precursors.

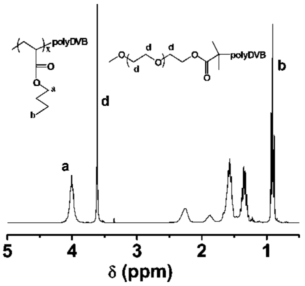


Figure 5. ^{1}H NMR spectrum of the purified (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers (M-BE2, Table 2). NMR conditions: 27 °C, CDCl$_3$ as solvent.

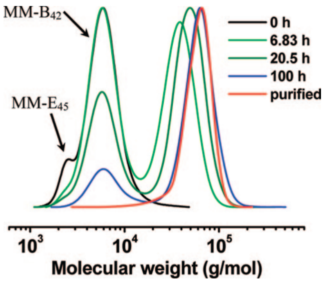


Figure 6. GPC traces during the synthesis of (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers (M-BE4, Table 3) by cross-linking polyBA MM (MM-B$_{42}$) and PEO MM (MM-E$_{45}$). Experimental conditions: $[\text{MM-B}_{42}]_0/[\text{MM-E}_{45}]_0/[\text{DVB}]_0/[\text{EBiB}]_0/[\text{CuBr}]_0/[\text{Me}_6\text{TREN}]_0 = 0.80/0.20/3.0/0.2/0.2/0.2$, ($[\text{MM-B}_{42}]_0 + [\text{MM-E}_{45}]_0$) = 0.065 M, 80 °C in anisole; linear polySt standards for GPC calibration.

The results in Table 2 indicate that miktoarm star copolymers with low polydispersity were successfully synthesized by cross-linking the mixture of linear MI and MM. The polydispersity increased with the molar ratio of MI to MM in the initial mixture. In other words, the molar ratio of linear MM to MI should be high in order to obtain a low-polydispersity miktoarm star copolymers ($M_w/M_n < 1.20$), which limited the free variation of the molar ratios of incorporated arms in the miktoarm star product. In order to synthesize low-polydispersity miktoarm stars with potentially any molar ratio of the two types of arms, totally replacing the linear MI by MM as arm precursor was necessary, in which low molar mass initiator, such as EBiB, was used for the terpolymerization of two MM species and one cross-linker by using the ATRP technique. Since the initiating sites in the star format completely originated from the low molar mass initiator, the molar ratio of initiating sites to arms in the miktoarm star copolymer was independent of the molar ratios of the two MMs in the initial mixture.

Synthesis of Miktoarm Star Copolymers via Cross-Linking Mixture of Two MMs. By copolymerization of polyBA MM (MM-B$_{42}$), PEO MM (MM-E$_{45}$), and DVB with EBiB as initiator and CuBr/Me$_6$TREN as catalyst, miktoarm star copolymers, (polyBA)$_n$-(PEO)$_p$-polyDVB, were synthesized via ATRP. The molar ratios of reagents in the reaction were $[\text{MM-B}_{42}]_0/[\text{MM-E}_{45}]_0/[\text{DVB}]_0/[\text{EBiB}]_0 = 0.80/0.20/3.0/0.2$, and GPC traces of the obtained miktoarm star copolymers are shown in Figure 6. During the reaction, both linear polyBA MM and PEO MM were consumed and incorporated into the miktoarm star polymers, as evidenced by the decreased intensity of the two linear MMs in GPC analysis. After 100 h, the reaction was stopped because further increasing the reaction time had no effect on the molecular weight of miktoarm star copolymer and the star yield. The absolute molecular weight of the miktoarm star molecule at 100 h was $M_{w,\text{MALLS}} = 210.9$ kg/mol, higher than its apparent molecular weight, $M_{w,\text{RI}} = 63.7$ kg/mol, indicating its compact structure. The polydispersity of the miktoarm star copolymers was as low as $M_w/M_n = 1.15$ (Table

Table 3. Synthesis of (PolyBA)$_n$-(PEO)$_p$-PolyDVB Miktoarm Star Copolymers by Cross-Linking Two MMs via the "Arm-First" Method[a]

entries[b]	MM-1	MM-2	[MM-1]/[MM-2]	A_{star}[c]	$M_{w,RI}$ (kg/mol)[d]	$M_{w,MALLS}$ (kg/mol)[e]	M_w/M_n[d]	n_1/n_2[f]	N_{arm} per star[g]	N_{arm-1} per star[g]	N_{arm-2} per star[g]
M-BE4	MM-B_{42}	MM-E_{45}	0.80/0.20	0.78	63.7	210.9	1.15	0.76/0.24	42	32	10
M-BE5[h]	MM-B_{42}	MM-E_{45}	0.50/0.50	0.77	50.6	230.1	1.13	0.46/0.54	57	26	31
M-BE5s[h]	MM-B_{42}	MM-E_{45}	0.50/0.50	0.96	78.4	378.5	1.19	0.48/0.52	89	43	46
M-BE6	MM-B_{42}	MM-E_{45}	0.20/0.80	0.75	34.3	202.6	1.17	0.16/0.84	66	10	56
M-BE7	MM-B_{42}	MM-E_{23}	0.50/0.50	0.82	44.7	187.1	1.16	0.45/0.55	53	24	29
M-BE8	MM-B_{90}	MM-E_{45}	0.50/0.50	0.64	78.4	325.5	1.13	0.48/0.52	49	23	26

[a] Experimental conditions: $[MM\text{-}1]_0/[MM\text{-}2]_0/[DVB]_0/[EBiB]_0/[CuBr]_0/[Me_6TREN]_0 = f_{MM\text{-}1}/f_{MM\text{-}2}/3.0/0.2/0.2/0.2$, $([MM\text{-}1]_0 + [MM\text{-}2]_0) = 0.065$ M, 80 °C in anisole. [b] In "M-BEγ", "M" represents "miktoarm star", "B" and "E" represent the corresponding polyBA MM and PEO MM, respectively. [c] Area fraction of miktoarm star copolymers, determined by the multipeak splitting of the GPC curve using Gaussian function. [d] Weight-average molecular weight and polydispersity, measured by THF GPC with RI detector, calibration with linear polySt as standard. [e] Weight-average molecular weight, measured by THF GPC with MALLS detector. [f] Average molar fraction of arm 1 and arm 2 in the miktoarm star copolymers, determined by ^{1}H NMR, 27 °C, $CDCl_3$ as solvent. [g] Number-average value of the number of arms per star or miktoarm star molecule (N_{arm}) was calculated based on eq S1 in the Supporting Information. $N_{arm\text{-}1} = N_{arm} \times n_1$; $N_{arm\text{-}2} = N_{arm} \times n_2$. [h] During this reaction, two extra batches of 1 equiv of DVB and 0.05 equiv of EBiB were added into the reaction system at 95 and 130 h, respectively, in order to increase the yield of miktoarm star copolymers. The reaction was finally stopped at 160 h. The codes M-BE5 and M-BE5s represent the miktoarm star product at 95 and 160 h, respectively.

3, M-BE4). The star yield was $A_{star} = 78\%$, based on the multipeak splitting of the GPC curve using the Gaussian function. After precipitation into cold methanol to remove the unincorporated linear chains, the purified miktoarm star product was analyzed by ^{1}H NMR spectroscopy to determine the molar ratio of the two types of arms in the miktoarm star molecule. The result indicates that the molar ratio of the polyBA and PEO arms in the miktoarm star product was around $n_1/n_2 = 0.76/0.24$, which was in agreement with the molar ratios of two MMs in the initial mixture. Based on the absolute molecular weights of the miktoarm star copolymer, the averaged arm number per miktoarm star molecule in M-BE4 was $N_{arm} = 42$, in which 32 arms were polyBA (M-BE4, Table 3).

By systematically changing the molar ratios of polyBA MM (MM-B_{42}) and PEO MM (MM-E_{45}) in the initial mixture from [MM-B_{42}]/[MM-E_{45}] = 0.80/0.20 to 0.20/0.80 (M-BE4, M-BE5, and M-BE6 in Table 3), (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers with various arm compositions and narrow molecular weight distribution were obtained. For all of the obtained miktoarm star copolymers, the polydispersities were low ($M_w/M_n \leq 1.17$), and the values were almost independent of the variation of the arm compositions. Such a result proved that by cross-linking two MMs the molar ratio of initiating sites to arms in the miktoarm star product was determined by the ratio of initiator to total MMs, instead of the ratios of two MM species in the initial mixture. By using less moles of EBiB than MM during the cross-linking reaction, low-polydispersity miktoarm star copolymers with freely varied arm compositions were synthesized successfully. In addition, the absolute molecular weights of the obtained miktoarm star polymers were similar when the molar fraction of PEO MM in the initial MM mixtures varied from 0.20 (M-BE4) to 0.80 (M-BE6). However, because of the fact that the molecular weight of MM-E_{45} ($M_{n,theor} = 2.08$ kg/mol) was smaller than that of polyBA arm ($M_{n,theor} = 5.48$ kg/mol), the averaged arm number per miktoarm star molecule increased from $N_{arm} = 42$ in M-BE4 to $N_{arm} = 66$ in M-BE6.

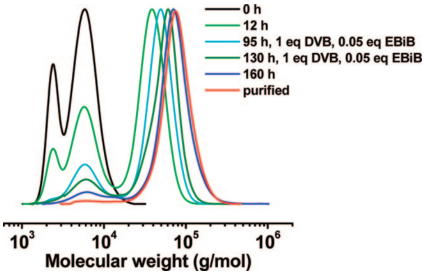


Figure 7. Synthesis of (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers with high star yield and low polydispersity by cross-linking polyBA MM (MM-B_{42}) and PEO MM (MM-E_{45}) via multistep addition of DVB and EBiB (M-BE5 and M-BE5s, Table 3). Experimental conditions: $[MM\text{-}B_{42}]_0/[MM\text{-}E_{45}]_0/[DVB]_0/[EBiB]_0/[CuBr]_0/[Me_6TREN]_0 = 0.50/0.50/(3.0 + 1.0 + 1.0)/(0.2 + 0.05 + 0.05)/0.2/0.2$, $([MM\text{-}B_{42}]_0 + [MM\text{-}E_{45}]_0) = 0.065$ M, 80 °C in anisole; linear polySt standards for GPC calibration.

(PolyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers were also synthesized by using MMs with different molecular weights (e.g., arm lengths). For example, miktoarm star copolymers (M-BE7, Table 3) with shorter PEO arms compared to M-BE5 were synthesized by cross-linking a mixture of equimolar MM-B_{42} and MM-E_{23} ($M_{n,theor} = 1.10$ kg/mol), and miktoarm star copolymers containing longer polyBA arms were synthesized by using MM-B_{90} ($M_{n,theor} = 11.7$ kg/mol) and MM-E_{45} as arm precursors. The results in Table 3 indicate that by fixing the molar ratio of $[MM\text{-}1]_0/[MM\text{-}2]_0/[DVB]_0/[EBiB]_0 = 0.50/0.50/3.0/0.2$ and the total concentration of MMs ($[MM\text{-}1]_0 + [MM\text{-}2]_0) = 0.065$ M (M-BE5, M-BE7, and M-BE8), variation of the molecular weights of linear MMs had no significant effect on the polydispersity of miktoarm star polymers because the molar ratio of EBiB to total MMs was unchanged. The increasing arm length of MMs decreased the star yield from 82% (M-BE7) to 64% (M-BE8) but increased the molecular weights of the obtained polymers. As a result, the averaged arm numbers per miktoarm star molecule were nearly constant when the molecular weights of these two MMs changed.

It should be noted that compared to the (polyBA)$_n$-(PEO)$_p$-polyDVB miktoarm star copolymers synthesized by cross-linking MM-B_{42} and MI-E_{45} (Table 2), the miktoarm stars obtained by cross-linking two MMs, MM-B_{42} and MM-E_{45}, always had a lower polydispersity, which was independent of the composition of the initial MM mixture. However, the miktoarm star copolymers synthesized by cross-linking two MMs had a lower star yield ($A_{star} < 80\%$ for M-BE4, M-BE5, and M-BE6 in Table 3), which increases the complexity of star purification and significantly hinders the application of this novel method for synthesis of low-polydispersity miktoarm star copolymers in large scale. In order to increase the star yield as well as keeping the low polydispersity, a multistep addition of low molar mass cross-linker and initiator was applied during the cross-linking reaction, which has been verified as a promising strategy for synthesis of low-polydispersity star polymers with quantitative star yield.[45] By adding another batch of DVB and EBiB during the reaction, more pendant vinyl groups and initiating sites were introduced to the star core, which expanded the core size and decreased the core congestion. With appropriate amounts of DVB and EBiB added in each batch, it was possible to increase the star molecular weight and star yield while retaining the narrow molecular weight distribution of the star polymer.[45,46]

An example, in Figure 7, shows the results for synthesis of high-yield and low-polydispersity miktoarm star copolymers, (polyBA)$_n$-(PEO)$_p$-polyDVB, via multiple step addition of cross-linker and initiator during cross-linking the mixture of MM-B$_{42}$ and MM-E$_{45}$ with equal moles. The initial composition was [MM-B$_{42}$]$_0$/[MM-E$_{45}$]$_0$/[DVB]$_0$/[EBiB]$_0$/[CuBr]$_0$/[Me$_6$TREN]$_0$ = 0.50/0.50/3.0/0.2/0.2/0.2. The GPC peak representing the formed miktoarm star copolymer shifted to higher molecular weight direction with the increasing reaction time. At 95 h, the yield of miktoarm star copolymer reached $A_{\text{star}} = 77\%$, and its absolute molecular weight was $M_{\text{w,MALLS}} = 230.1$ kg/mol (M-BE5, Table 3). In order to increase the miktoarm star yield, a second batch of 1 equiv of DVB and 0.05 equiv of EBiB was added into the reaction system at 95 h, which expanded the miktoarm star core and facilitated the incorporation of more linear chains into the miktoarm star format (Figure 7). Similarly, a third batch of DVB and EBiB was added into the system at 130 h, and the reaction was stopped at 160 h with final star yield as high as $A_{\text{star}} = 96\%$ and polydispersity as low as $M_w/M_n = 1.19$ (M-BE5s, Table 3). These results clearly indicate that by using linear MMs as arm precursors, the ratio of initiating sites to arms in one miktoarm star molecule could be decreased by using a less amount of low molar mass initiator, which decreased the star−star coupling reaction and resulted in miktoarm star copolymers with low polydispersity. Addition of extra cross-linker and initiator during the reaction increased the molecular weight and yield of the miktoarm star molecule, while keeping the low polydispersity.

Conclusions

A simple one-pot "arm-first" method was successfully applied for synthesis of miktoarm star copolymers with both variable arm compositions and low polydispersity by cross-linking a mixture of linear MMs and/or MIs using the ATRP technique. On the basis of the LCCC analysis, the obtained star product was proved to be miktoarm star copolymers containing two arm species in one molecule without any contaminant of homoarm star polymers. When a mixture of linear MM and MI was used as arm precursors, the molar ratio of initiating sites to arms in the miktoarm star molecule is less than unity because the incorporation of linear MM into star format did not increase the initiating sites in the star core. The lower amount of initiating sites in the star molecule decreased the extent of star−star coupling reactions and produced miktoarm star copolymers with low polydispersity ($M_w/M_n < 1.2$). However, the polydispersity of miktoarm star molecules increased with the molar ratio of MI to MM in the initial mixture due to the increased number of initiating sites in the miktoarm star molecules. Low-polydispersity miktoarm stars with freely varied molar ratios of the two arm species were successfully synthesized via cross-linking a mixture of different MMs using low molar mass ATRP initiator. In such a case, the initiating sites in the star format completely originated from the low molar mass initiator and the molar ratio of initiating sites to arms in the miktoarm star copolymer was independent of the molar ratios of the two MMs in the initial mixture. Addition of extra cross-linker and initiator during the reaction increased the molecular weight (up to ∼380 kg/mol) and yield of the miktoarm star molecule (up to ∼96%), while the molecular weight distribution of the miktoarm star polymers remained narrow ($M_w/M_n < 1.2$). All these results indicate that the one-pot "arm-first" method via cross-linking a mixture of linear MMs and/or MIs is a powerful strategy for synthesis of various kinds of miktoarm star copolymers with both high molecular weight and low polydispersity.

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Supporting Information Available: Detailed calculation of the average number of arms per miktoarm star molecule. 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) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. *Prog. Polym. Sci.* **2006**, *31*, 1068.
(3) Wang, F.; Bronich, T. K.; Kabanov, A. V.; Rauh, R. D.; Roovers, J. *Bioconjugate Chem.* **2005**, *16*, 397.
(4) Helms, B.; Guillaudeu, S. J.; Xie, Y.; McMurdo, M.; Hawker, C. J.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6384.
(5) 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.
(6) Fukukawa, K.-i.; Rossin, R.; Hagooly, A.; Pressly, E. D.; Hunt, J. N.; Messmore, B. W.; Wooley, K.; Welch, M.; Hawker, C. J. *Biomacromolecules* **2008**, *9*, 1329.
(7) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857.
(8) Szwarc, M. *Nature (London)* **1956**, *178*, 1168.
(9) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.
(10) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413.
(11) Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization. From Synthesis to Materials*; ACS Symp. Ser. 944; American Chemical Society: Washington, DC, 2006.
(12) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93.
(13) Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds. *Macromolecular Engineering: From Precise Macromolecular Synthesis to Macroscopic Materials Properties and Applications*; Wiley-VCH: Weinheim, 2007.
(14) Heise, A.; Trollsas, M.; Magbitang, T.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *Macromolecules* **2001**, *34*, 2798.
(15) He, T.; Li, D. J.; Sheng, X.; Zhao, B. *Macromolecules* **2004**, *37*, 3128.
(16) Celik, C.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2542.
(17) Shi, P.-J.; Li, Y.-G.; Pan, C.-Y. *Eur. Polym. J.* **2004**, *40*, 1283.
(18) Penczek, S.; Cypryk, M.; Duda, A.; Kubisa, P.; Slomkowski, S. *Prog. Polym. Sci.* **2007**, *32*, 247.
(19) Priftis, D.; Pitsikalis, M.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5164.
(20) Liu, C.; Zhang, Y.; Huang, J. *Macromolecules* **2008**, *41*, 325.
(21) Guo, Y.-M.; Xu, J.; Pan, C.-Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 437.
(22) Francis, R.; Lepoittevin, B.; Taton, D.; Gnanou, Y. *Macromolecules* **2002**, *35*, 9001.
(23) Cai, Y.; Armes, S. P. *Macromolecules* **2005**, *38*, 271.
(24) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31*, 1133.
(25) Babin, J.; Leroy, C.; Lecommandoux, S.; Borsali, R.; Gnanou, Y.; Taton, D. *Chem. Commun.* **2005**, 1993.
(26) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.
(27) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 4960.
(28) Hoogenboom, R.; Moore, B. C.; Schubert, U. S. *Chem. Commun.* **2006**, 4010.
(29) Altintas, O.; Yankul, B.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6458.
(30) Gao, H.; Min, K.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2007**, *208*, 1370.
(31) Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 11360.
(32) Altintas, O.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5699.
(33) Altintas, O.; Yankul, B.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3588.
(34) Deng, G. H.; Ma, D. Y.; Xu, Z. Z. *Eur. Polym. J.* **2007**, *43*, 1179.
(35) Wang, G.; Luo, X.; Liu, C.; Huang, J. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2154.
(36) Du, J. Z.; Chen, Y. M. *Macromolecules* **2004**, *37*, 3588.
(37) Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 5995.
(38) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 7216.
(39) Wiltshire, J. T.; Qiao, G. G. *Macromolecules* **2006**, *39*, 9018.
(40) Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2007**, *129*, 11828.

(41) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(42) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(43) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(44) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270.
(45) Gao, H.; Ohno, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 15111.
(46) Gao, H.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 399.
(47) Muehlebach, A.; Rime, F. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3425.
(48) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958.
(49) Gao, H.; Min, K.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2006**, *207*, 1709.
(50) Abrol, S.; Kambouris, P. A.; Looney, M. G.; Solomon, D. H. *Macromol. Rapid Commun.* **1997**, *18*, 755.
(51) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4482.
(52) Bosman, A. W.; Vestberg, R.; Heumann, A.; Frechet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 715.
(53) Pasch, H.; Trathnigg, B. *HPLC of Polymers*; Springer: Heidelberg, 1997.

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