7216 *Macromolecules* **2006,** *39,* 7216−7223

Synthesis of Miktoarm Star Polymers via ATRP Using the "In−Out" Method: Determination of Initiation Efficiency of Star Macroinitiators

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Received July 26, 2006; Revised Manuscript Received August 21, 2006

ABSTRACT: Miktoarm star polymers were synthesized via atom transfer radical polymerization (ATRP) using the "in−out" method. First, ATRP was applied to the synthesis of star polymers using the "arm-first" method with poly(*tert*-butyl acrylate) arms and a core formed with divinylbenzene as cross-linker. "Dormant" initiating sites were preserved in the core of the star copolymer, which was then used as a multifunctional macroinitiator (MI) for initiating an ATRP of another monomer to produce the miktoarm star polymer. Because of the congested environment in the star core, not all of the initiating sites participated in the formation of the second generation of arms, and the initiation efficiency (IE) of the star MI was less than 100%. A kinetic method was used for quantitative determination of the IE value of the star MIs. Three factors, including the arm length of star MI, the structural compactness of star MI, and the chemical compatibility of the two kinds of arms on one miktoarm star molecule, have an important effect on the IE of the star MI. It was found that the IE value of the star MI decreased with increasing arm length and structural compactness. When the two arms had the same chemical composition, the star MI had the highest IE value. The IE of the star MI varied from 5% to 54%, depending on the above three factors.

Introduction

With the development of new polymerization techniques, including living anionic polymerization[1] and controlled/"living" radical polymerization (CRP),[2,3] the synthesis of star polymers, with multiple arms connecting to one central core, has attracted considerable attention, mainly due to their compact structure and globular shape.[4] Regardless of the polymerization method, the preparation of star polymers by CRP can be categorized into two broad approaches: core-first[5−11] and arm-first.[12−25] In the arm-first technique, the linear arms of the star polymers are synthesized first followed by binding of the arms to form the core, usually achieved by using a divinyl cross-linker. The preserved initiating sites in the star core can be further employed to initiate the polymerization of another monomer to form miktoarm (or heteroarm) star polymers,[22,26] (polyA)$_n$−polyX−(polyB)$_p$, where polyX represents the cross-linked core of the miktoarm star polymer; n and p are the average number of polyA and polyB arms per star molecule, respectively. The miktoarm star polymers contain two kinds of arms with different chemical composition and/or molecular weight. Based on the synthetic procedure used for the synthesis, this method is termed the "in−out" method,[26−28] in which the word "in" refers to the arm-first method for formation of the star polymer macroinitiator (MI) and the word "out" represents the subsequent growth of the second generation of arms from the multifunctional star core.

The in−out method is a promising technique for synthesis of miktoarm star copolymers with multiple arms, multiple functional groups, and high molar mass.[22,27,28] However, several questions remain open in the synthetic procedures, which include the initiation efficiency (IE) of the multifunctional star MI during the extension of the second generation of arms, polyB, from the star core.[27] Star MIs synthesized via the arm-first method are characterized by several features.[14,29] First, the star polymer contains multiple arms and a highly cross-linked core; the steric congestion near the star core is very high, depending on the chemical nature of the arms and the number of arms per star. Second, the preserved initiating sites in the star polymer, such as alkyl halides in atom transfer radical polymerization (ATRP),[30−32] are distributed throughout the cross-linked core, with some of them embedded inside the core and the others located near the core surface. Third, possible termination reaction during the star core formation can decrease the number of initiating sites per star. On the basis of these characteristics, it is expected that, during the polymerization of another monomer using the star polymer as MI, only a fraction of the initiating sites within the star core are accessible to the catalyst complex and monomer and can participate in the initiation process. This limited accessibility of initiating sites has often been encountered during the polymerization using a multifunctional MI with a congested structure,[33] which decreases the IE value of the star MI. Thus, it is reasonable to expect that the IE of a star MI is usually less than 100% during the synthesis of miktoarm star polymers.

It is a challenge to determine the IE value of star MIs during the synthesis of miktoarm star polymers using the in−out method because the presence of a highly cross-linked core hinders the accurate analysis of star polymers using nuclear magnetic resonance (NMR) spectroscopy and/or gel permeation chromatography (GPC) technique. Recently, the synthesis of miktoarm star polymers containing a cleavable core was reported.[27] The IE value of the star MI was determined via GPC analysis of the cleaved product of the miktoarm star polymers, which was a mixture of linear triblock and diblock polymer chains. It indicated that only ca. 20% of the initiating sites in the star MIs participated in the formation of the second generation of polymer arms. Based on these results, two questions arise for further exploration. The first is how to improve the IE of the star MIs and which factors influence IE. The second question is whether a more general method can be established for quantitatively determining the IE value of star MIs, especially those containing noncleavable cores, because

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10.1021/ma061702x CCC: $33.50

the most often used cross-linkers, such as divinylbenzene (DVB) and ethylene glycol dimethacrylate, are not appropriate for facile backbone cleavage.

In this present work, star polymers containing a noncleavable core, (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) (*t*BA as *tert*-butyl acrylate), were synthesized via ATRP using the arm-first method in a one-pot process.[24] Several parameters were controlled during the synthesis of star polymers forming polymers with various structures (different arm length and star structural compactness). Using these star polymers as MIs, miktoarm star polymers were synthesized via ATRP using the in−out method. A kinetic method is reported for quantitative determination of the IE value of star MIs, which compared the relative rates of monomer consumption in the polymerization to a control ATRP reaction under the same experimental conditions as those during the miktoarm star synthesis except for the use of 1-phenylethyl bromide as the monofunctional initiator. Three factors (arm length of star MI, structural compactness of star MI, and chemical compatibility of the second generation of arms to the first generation of arms) were studied, and hence their influence on the IE value of the star MI was systematically evaluated.

Experimental Section

Materials. All monomers, including *n*-butyl acrylate (BA, 99%, Aldrich), *tert*-butyl acrylate (*t*BA, 98%, Aldrich), divinylbenzene (DVB, 80%, Aldrich), methyl acrylate (MA, 99%, Aldrich), and styrene (St, 99%, Aldrich), were purified twice by passing the monomers through a column filled with basic alumina to remove the inhibitor. CuBr (98%, Acros) was purified using a modified literature procedure.[34] All other reagents—ethyl 2-bromopropionate (EBrP), 1-phenylethyl bromide (1-PEBr), *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA), $CuBr_2$, and solvents—were purchased from Aldrich with the highest purity and used as received without further purification.

Synthesis of (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star MIs via ATRP Using the Arm-First Method. A typical procedure was briefly described, starting with the ratio of reagents $[tBA]_0/[DVB]_0/[EBrP]_0/[CuBr]_0/[PMDETA]_0 = 50/3/1/0.5/0.5$. A clean and dry Schlenk flask was charged with BA (10 mL, 0.07 mol), PMDETA (0.146 mL, 0.70 mmol), and 10 mL of anisole. The flask was degassed by five freeze−pump−thaw cycles. During the final cycle the flask was filled with nitrogen, and CuBr (0.100 g, 0.70 mmol) was quickly added to the frozen mixture. No additional special care was taken to avoid moisture condensation. The flask was sealed with a glass stopper and then evacuated and backfilled with nitrogen five times before it was immersed in an oil bath at 60 °C. The N_2-bubbled initiator EBrP (0.181 mL, 1.40 mmol) was then injected into the reaction system, via a purged syringe, through the sidearm of the Schlenk flask. At timed intervals, samples were withdrawn via a syringe fitted with stainless steel needle and diluted with THF. The samples were used to measure the monomer conversions and polymer molecular weights by gas chromatography (GC) and GPC, respectively. At ca. 80% *t*BA conversion, N_2-purged DVB (0.596 mL, 4.19 mmol) was injected into the reaction system, and the temperature of the oil bath was elevated to 80 °C. The reaction was stopped after 15 h via exposure to air and dilution with THF. The solution was filtered through a column filled with neutral alumina to remove the copper complex before the polymer was dried under vacuum at 60 °C for 2 days.

Synthesis of Miktoarm Star Polymer by the In−Out Method Using (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star as MI. (Poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers were used as MIs for ATRP of another monomer to synthesize miktoarm star polymers. To determine the influence of different factors on the IE value of the star MI, (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers with different arm length and structural compactness were employed as MIs for the polymerization of various types of monomers, including *t*BA, BA, MA, and St. The experimental procedure for synthesis of miktoarm star polymers was similar to that of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers. The theoretical number of initiating sites per star MI was equal to the average number of arms per star based on the assumption that there was no loss of the Br chain-end functionality during the synthesis of star polymer. A typical reaction mixture composition for (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(polyBA)$_p$ miktoarm star polymer is (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star MI (0.6 g, 96.1 μmol of alkyl bromide initiating sites), BA (4.13 mL, 28.8 mmol), PMDETA (40.1 μL, 192.2 μmol), anisole (4 mL), CuBr (24.8 mg, 173.0 μmol), and $CuBr_2$ (4.3 mg, 19.2 μmol). The reaction was conducted at 60 °C for 22 h. Samples were withdrawn periodically for GC and GPC measurements of monomer conversions and polymer molecular weights.

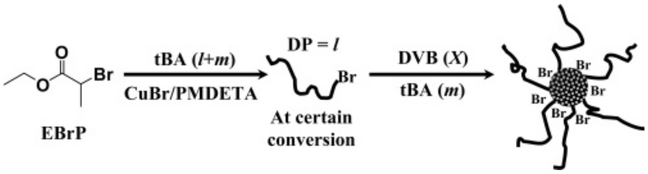
Control Reactions. To determine the IE value of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star MIs during the synthesis of miktoarm star polymers, a reference kinetic plot was established by performing a control reaction, in which the IE of the initiator was assumed to be 100%. According to the monomer used for the formation of the second arm in the miktoarm star, several control reactions were performed via ATRP of different monomers using 1-PEBr as initiator and CuBr/PMDETA as catalyst. The synthetic procedure and the concentrations of all reagents in the control reaction were the same as those employed in the synthetic reaction of miktoarm star polymers. The concentration of 1-PEBr in the control reaction was also the same as that of the alkyl bromide initiating sites in the reaction for miktoarm star. A typical control reaction composition for ATRP of BA was composed of 1-PEBr (13.1 μL, 96.1 μmol), *t*BA (4.13 mL, 28.8 mmol), PMDETA (40.1 μL, 192.2 μmol), anisole (4 mL), CuBr (24.8 mg, 173.0 μmol), and $CuBr_2$ (4.3 mg, 19.2 μmol). The reaction was conducted at 60 °C for 22 h, and samples were periodically withdrawn for GC and GPC measurements.

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 was used as internal standard for calculation of monomer conversions. The polymer samples were measured 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)). Toluene was used as the internal standard to correct the fluctuation of the THF flow rate. The apparent molecular weights and polydispersity were determined with a calibration based on linear polySt standards using WinGPC 6.0 software from PSS. The detectors employed to measure the absolute molecular weights were a RI detector (Wyatt Technology, Optilab REX) 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.

Results and Discussion

Star polymers, (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA), were synthesized via ATRP using the arm-first method in a one-pot process. During the synthesis of miktoarm star copolymers using these multifunctional stars as MIs, only a fraction of the initiating sites within the star core are accessible to the catalyst complex and monomer and can participate in the formation of the second generation of arms, which decreases the IE value of the star MI. Three factors can influence the IE value of the star MI. Two of them are the inherent nature of the star polymer, arm length, and structural compactness, and the third one is the chemical compatibility of the second generation of arms to the preformed first generation of arms in the star MI. To explore the influence of the structure of star MI on its IE value, different (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers with various arm length and structural compactness were used as MIs for syntheses of series of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(poly*t*BA)$_p$

Scheme 1. Outline for Synthesis of (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star Polymers via ATRP Using the Arm-First Method in a One-Pot Process



miktoarm star polymers. In this study, *t*BA was used as the monomer for the formation of the second arms in order to exclude the influence from the third factor of chemical compatibility between the two arms. To study the influence of the third factor on the IE value of star MI, one typical star polymer was used as MI for ATRP of different monomers, including *t*BA, BA, MA, and St. The detailed results for each ATRP reaction are discussed below.

Synthesis of (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star MIs. To synthesize (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers containing multiple initiating sites in the core, a linear poly*t*BA homopolymer was synthesized first using EBrP as initiator and CuBr/PMDETA as catalyst. At certain *t*BA conversions, instead of stopping the reaction and removing the unreacted monomer, N_2-purged DVB was injected into the polymerizing system to act as cross-linker, producing the star polymers in situ (Scheme 1). Several parameters, including the poly*t*BA arm length (*l*: average degree of polymerization (DP) of the formed poly*t*BA chain), the amount of remained *t*BA when DVB was added (*m*), the DVB addition amount (X = $[DVB]_0/[EBrP]_0$), and the resulting star core chemical composition, had a significant influence on the structures of the obtained star polymers.[24] Through properly controlling each parameter, a series of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers were synthesized with different arm length and star structural compactness ($M_{p,ab}/M_{p,app}$: the ratio of peak values between the absolute molecular weight and apparent molecular weight of the star copolymers).[35] The arm length of the star polymer was controlled by varying the initial amount of *t*BA added to the reaction and the DVB addition moment. The star structural compactness was controlled via changing the DVB addition amount at a given arm length. Table 1 lists the detailed information on the obtained (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers. Samples in entries S1−S3 had the same arm length (l = 20), while their structural compactness $M_{p,ab}/M_{p,app}$ varied from 1.24 to 2.19. Samples in entries S4−S6 and S7−S9 had the arm lengths l = 40 and 90, respectively. Their structural compactness also ranged from ca. 1.2 to 2.2. Under reasonable approximation, these nine samples covered a full range of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers with an orthogonal change in arm length (*l*: 20, 40, and 90) and star structural compactness ($M_{p,ab}/M_{p,app}$: 1.2, 1.6, and 2.2). All these star polymers were used as multifunctional MIs for syntheses of miktoarm star polymers via ATRP using the in−out method.

Synthesis of (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA)−(PolyBA)$_p$ Miktoarm Star Polymers by ATRP Using the In−Out Method. Star polymers obtained from the arm-first method preserve multiple initiating sites within the cores that can be further used as MIs for the synthesis of miktoarm star polymers by initiating the polymerization of another monomer. This technique, termed as the in−out method, is an important method that allows the synthesis of star polymers containing two types of arms with different chemical composition and/or molecular weight. Using the (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymer identified in Table 1, entry S5, as the MI, (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(polyBA)$_p$ miktoarm star polymers were synthesized by ATRP of BA monomer with the ratios of reagents $[BA]_0/[initiating\ sites]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ = 300/1/1.8/0.2/2. In Figure 1, the GPC curves of the reaction samples shifted to higher molecular weight with the increase of reaction time and BA conversion, indicating the formation of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(polyBA)$_p$ miktoarm star polymers. After 22 h, the absolute molecular weight of the star polymers increased from 88 000 to 148 500 g/mol, measured by GPC with MALLS detector.

Table 1. Summary of (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star MIs[a]

entry[a]	$l/m/X/[EBrP]_0$[b]	$M_{p,app}$[c] (g/mol)	M_w/M_n[c]	$M_{p,ab}$[d] (g/mol)	n_{arm}[e]	compactness ($M_{p,ab}/M_{p,app}$)
S1	20/5/1.2/1	17 300	1.56	21 500	6.3	1.24
S2	20/10/2/1	37 900	1.61	60 600	14.9	1.60
S3	20/10/3/1	67 700	1.84	142 900	34.1	2.19
S4	40/10/1.5/1	24 200	1.22	28 100	4.6	1.16
S5	40/10/3/1	56 300	1.38	88 000	14.1	1.56
S6	40/10/5/1	65 400	1.71	140 600	21.6	2.15
S7	90/10/3/1	58 900	1.23	70 600	5.4	1.20
S8	90/10/4/1	66 500	1.35	108 400	8.3	1.63
S9	90/10/6/1	83 400	1.46	181 000	13.5	2.17

[a] Experimental conditions: $[tBA]_0/[DVB]_0/[EBrP]_0/[CuBr]_0/[PMDETA]_0$ = $(l+m)/X/1/0.5/0.5$, $[tBA]_0$ = 3.25 M, 60 °C in anisole. The temperature was elevated to 80 °C after addition of DVB. [b] Definition: l = number-average DP of poly*t*BA arm before addition of DVB, determined from GC measurement; m = molar ratio of unreacted *t*BA monomer to initial EBrP amount when DVB was added; X = $[DVB]_0/[EBrP]_0$. [c] Peak value of the apparent molecular weight and polydispersity, measured by GPC in THF with RI detector, calibration with linear polySt as standard. [d] Peak value of the absolute molecular weight, measured by GPC in THF with MALLS detector. [e] Number-average value of the number of arms per star molecule (n_{arm} = $M_{p,ab}(star) \times arm_{wt\%}/M_{p,arm}$). $M_{p,arm}$ was measured by GPC in THF with RI detector, calibrated with linear polySt standard.

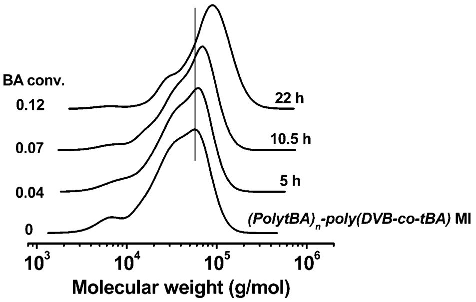
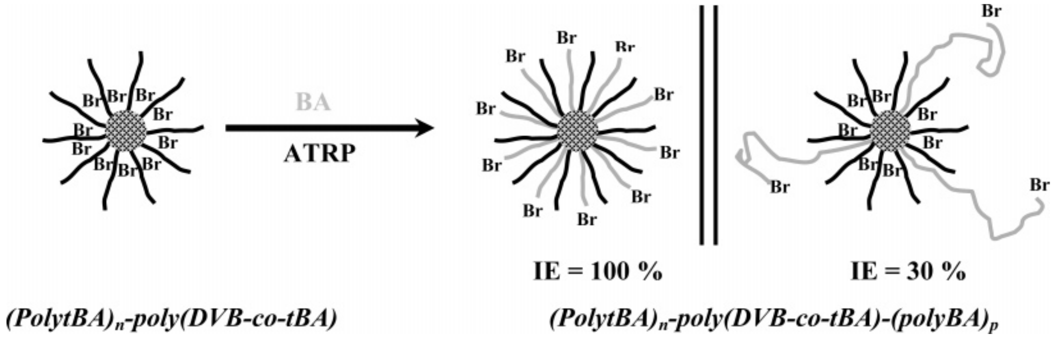


Figure 1. GPC traces of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(polyBA)$_p$ miktoarm star polymers synthesized via ATRP of BA using (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers as MIs. Experimental conditions: $[BA]_0/[initiating\ sites]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ = 300/1/1.8/0.2/2, $[BA]_0$ = 3.30 M, 60 °C in anisole.

During the synthesis of miktoarm star polymers using multifunctional star polymers as MIs, the IE of the star MI is very important because it directly affects the morphology of the miktoarm star polymers obtained in the reaction. For example, if the IE of star MI were 100%, the number of the second generation of arms in the miktoarm star should be the same as that of the first generation of arms, and if the IE were less than 100%, the number of the second arms would be less than that of the first arms. This hypothesis is illustrated in Scheme 2. During the synthesis of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(polyBA)$_p$ miktoarm star polymers, the conversion of BA was ca. 12% after 22 h (Figure 1). If the IE of star MI were 100%, the average DP of the second generation of arms should be around 36, comparable to that of the first generation of arms preformed in the star MI. However, if the IE were less than 100%, e.g. 30%, the average DP of the second generation of

Scheme 2. Illustration of Two Different Morphological Situations of the (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA)−(PolyBA)$_p$ Miktoarm Star Polymers Due to Different IE Values of the (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) MI



arms becomes ca. 120 and the average number of the polyBA arms per miktoarm star was only 30% of the first generation of arms, poly*t*BA.

Determination of the IE for (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star MI during the Synthesis of Miktoarm Star Polymers. A kinetic method was developed to quantitatively determine the IE value of the star MI during the synthesis of miktoarm star polymers. The kinetics of a classic ATRP reaction is defined by several parameters, as shown in eq 1, in which [Cu(I)/L] and [Cu(II)/L] are the concentrations of Cu(I)/L and Cu(II)/L complexes, respectively. The slope of the semilogarithmic plot (k^{app}) is proportional to [P−X], the concentration of the propagating polymer chains with bromine at chain end. In a normal ATRP reaction with small molecule (alkyl bromide) as initiator, the IE value of the initiator can be assumed close to 100% when certain amount of $\mathrm{CuBr_2}$ is added initially in the ATRP reaction. All initiators are small molecules with high mobility and full access by the catalyst complex and monomer. Furthermore, the initially added $\mathrm{CuBr_2}$ ensures that the ATRP equilibrium can be established as soon as the polymerization begins and the initial nonstationary period in ATRP could be minimized. Figure 2 shows the semilogarithmic kinetic plot and molecular weight evolution for ATRP of BA using 1-PEBr as initiator. 10% of $\mathrm{CuBr_2}$ vs total copper was added initially in the reaction. It is seen that the first-order kinetic plot was linear, indicating a constant concentration of radicals during the polymerization. The experimental molecular weights determined by GPC were in a very good agreement with the predicted values, which confirmed that all added initiators were rapidly consumed and participated in the chain propagation process. The total concentration of added initiating sites ($[\mathrm{R{-}X}]_0$) was proportional to the slope of the semilogarithmic plot in the control reaction ($[\mathrm{R{-}X}]_0 = [\mathrm{P{-}X}] \sim k^{\mathrm{app}}_{\mathrm{control}}$).

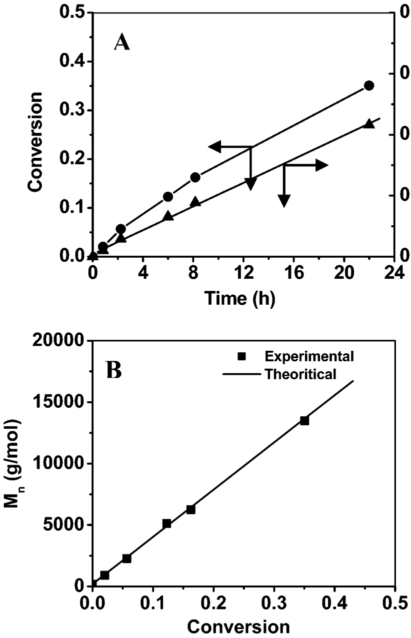


Figure 2. (A) Dependence of BA conversion and $\ln([\mathrm{M}]_0/[\mathrm{M}])$ on reaction time and (B) the molecular weight evolution for ATRP of BA. Experimental conditions: $[\mathrm{BA}]_0/[\text{1-PEBr}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{PMDETA}]_0 = 300/1/1.8/0.2/2$, $[\mathrm{BA}]_0 = 3.30$ M, 60 °C in anisole.

$$\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]} = k_{\mathrm{p}}K_{\mathrm{ATRP}}\frac{[\mathrm{P{-}X}][\mathrm{Cu(I)/L}]}{[\mathrm{Cu(II)/L}]}t = k^{\mathrm{app}}t \qquad (1)$$

During the synthesis of miktoarm star polymers by using star polymer as MI, as discussed above, not all of the initiating sites in the star MI can transform into new arms due to the highly cross-linked nature of the star core and the congested environment around it, e.g. $[\mathrm{P{-}X}] < [\mathrm{R{-}X}]_0$.[36] Therefore, the IE value of the star MI ($\mathrm{IE_{star}}$), the ratio of $[\mathrm{P{-}X}]/[\mathrm{R{-}X}]_0$, was smaller than 100%. Since the apparent kinetic constant was proportional to [P−X] during the synthesis of miktoarm star polymer ($[\mathrm{P{-}X}] \sim k^{\mathrm{app}}_{\mathrm{star}}$), the $\mathrm{IE_{star}}$ of the star MI can be determined by comparing the apparent kinetic constants in the reaction of miktoarm star synthesis and a control reaction. The control reaction in Figure 2 was performed with the same reaction conditions as those in the synthesis of miktoarm star except using 1-PEBr as initiator. The moles of added 1-PEBr in the control reaction was also the same as that of the bromine initiating sites in the miktoarm star synthesis. 1-PEBr was selected as initiator for the control reaction because its chemical structure and reactivity (activation and deactivation constants) are similar to the initiating site in the (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star MI. 10% of $\mathrm{CuBr_2}$ vs total copper was added initially in all of the ATRP reactions. Therefore, the concentration of added initiator ($[\text{1-PEBr}]_0$) in the control reaction was proportional to the slope of the semilogarithmic plot ($k^{\mathrm{app}}_{\mathrm{control}}$), and the $\mathrm{IE_{star}}$ of the star MI equaled the ratio of $k^{\mathrm{app}}_{\mathrm{star}}/k^{\mathrm{app}}_{\mathrm{control}}$ (as shown in eq 2).

$$\mathrm{IE_{star}} = \frac{[\mathrm{P{-}X}]}{[\mathrm{R{-}X}]_0} = \frac{k^{\mathrm{app}}_{\mathrm{star}}}{k^{\mathrm{app}}_{\mathrm{control}}} \qquad (2)$$

Figure 3 compares the kinetic plots from the synthesis of miktoarm star polymer using the star polymer (S5 in Table 1) as MI and the control reaction using 1-PEBr as initiator. Both semilogarithmic plots were linear. It is worth noting that the straight semilogarithmic plot in the reaction for synthesis of miktoarm star indicates a constant radical concentration during the reaction. This result suggests that the reaction was not a

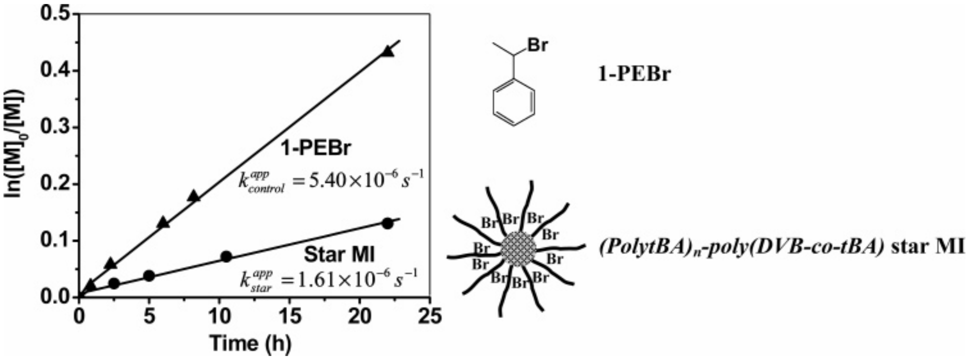


Figure 3. Semilogarithmic plots of ATRP of BA using (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymer (Table 1, entry S5) as MI and 1-PEBr as initiator for control reaction. Experimental conditions: $[BA]_0$/[initiating sites from MI or 1-PEBr]$_0$/$[CuBr]_0$/$[CuBr_2]_0$/$[PMDETA]_0$ = 300/1/1.8/0.2/2, $[BA]_0$ = 3.30 M, 60 °C in anisole.

slow initiation process, and the lower apparent kinetic constant during the miktoarm star synthesis was due to the inaccessibility of some initiating sites to the monomer and catalyst, which was ascribed to the congested structure of the cross-linked core in the star MI, as discussed above. Comparing the two apparent kinetic constants, the IE value of the (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star MI was determined as ca. 30% (IE_{star} = 1.61/5.40), meaning 30% of the initiating sites in the star MI were accessible to the monomer and catalyst complex and participated in the chain propagating process. On the basis of this kinetic method of comparing the relative rates of monomer consumption, the influence of three parameters on the IE value of star MI was studied, including the arm length of star MI, the structural compactness of star MI, and the chemical compatibility of the second generation of arms to the preformed first generation of arms.

Effect of Arm Length and Structural Compactness of the Star MI on Its IE. The influence of the star arm length and star structural compactness on the IE of star MI was systematically studied. To exclude the influence of the factor from the chemical compatibility between the two kinds of arms, *t*BA was selected as the monomer for the second arm formation. In this situation, the chemical compositions of the two types of arms were the same, and their difference was their molecular weight or arm length. Nine (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers (Table 1, S1−S9), with different arm length and structural compactness, were selected as the MIs for the ATRP of *t*BA. In all experiments, the ratios of the reagents added to the reactions were the same $[tBA]_0$/[initiating sites]$_0$/$[CuBr]_0$/$[CuBr_2]_0$/$[PMDETA]_0$ = 300/1/1.8/0.2/2 = 3.27 M. The only difference between any two polymerizations was the structure of the star MIs. The IE value of each star MI was determined by comparing its apparent kinetic constant to that of the control ATRP reaction, which empolyed 1-PEBr as initiator and kept all other experimetnal conditions the same as those in the reaction for synthesis of the miktoarm star. Table 2 lists the detailed results of each (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(poly*t*BA)$_p$ miktoarm star polymer and the IE value of its star MI.

For the (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers synthesized by the arm-first method, the preformed poly*t*BA arms radiated from the star core and covered the core surface, which directly limited the accessibility of initiating sites to the catalyst complex and monomer. Longer arms occupied a larger space and more significantly hindered access to the initiating sites when all other conditions remained the same. Thus, star MIs with longer arms should have lower IE value than star MIs with shorter arms. Higher values of star compactness (denser star structure) also had a negative effect on the IE value. Since the bromine initiating sites were distributed throughout the star core, higher star compactness, a result of higher cross-link density in the star core, decreased the free space around each initiating site. Therefore, there are fewer initiating sites in the core of star MI accessible to the monomer and catalyst complex, and the IE value of the star MI became smaller.

Table 2. Synthesis of Miktoarm Star Polymers with (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star Polymers as MIs

		star MI					
entry[a]	initiator	*l*	$M_{p,ab}/M_{p,app}$	$conv_{tBA}$	k^{app} ($\times 10^{-6}$ s^{-1})	IE[b]	$M_{p,ab}$ (g/mol)[c]
C-1[d]	1-PEBr			0.351	5.46	1.00	
M1-1	S1	20	1.24	0.208	2.95	0.54	61 100
M2-1	S2	20	1.60	0.163	2.24	0.41	174 400
M3-1	S3	20	2.19	0.083	1.09	0.20	267 000
M4-1	S4	40	1.16	0.155	2.13	0.39	53 400
M5-1	S5	40	1.56	0.133	1.80	0.33	155 600
M6-1	S6	40	2.15	0.067	0.87	0.16	239 100
M7-1	S7	90	1.20	0.051	0.66	0.12	89 000
M8-1	S8	90	1.63	0.043	0.55	0.10	129 900
M9-1	S9	90	2.17	0.021	0.27	0.05	232 500

[a] Experimental conditions: $[tBA]_0$/[initiating sites from MI or 1-PEBr]$_0$/$[CuBr]_0$/$[CuBr_2]_0$/$[PMDETA]_0$ = 300/1/1.8/0.2/2, $[tBA]_0$ = 3.27 M, in anisole at 60 °C, 22 h. [b] Calculated using eq 2. [c] Peak value of absolute molecular weight of miktoarm star polymer, GPC in THF with MALLS detector. [d] The letter "C" denotes the corresponding control reaction, and the number after the dash refers the monomer used for the second arm (1: *t*BA, 2: BA, 3: MA, 4: St).

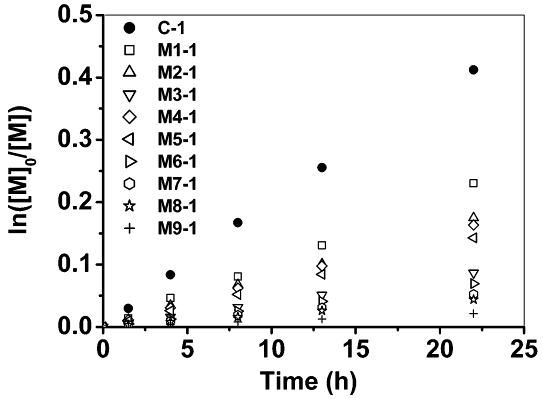


Figure 4. Comparison of the semilogarithmic plots of ATRP of *t*BA using (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers as MIs and 1-PEBr as initiator for control reaction (Table 2). Experimental conditions: $[tBA]_0$/[initiating sites]$_0$/$[CuBr]_0$/$[CuBr_2]_0$/$[PMDETA]_0$ = 300/1/1.8/0.2/2, $[tBA]_0$ = 3.27 M, 60 °C in anisole.

Figure 4 shows the semilogarithmic plots of ATRP of *t*BA during the synthesis of miktoarm star polymers using series of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers as MIs and the control reaction using 1-PEBr as initiator. It is seen that the reaction rate in the control reaction was the fastest and monomer

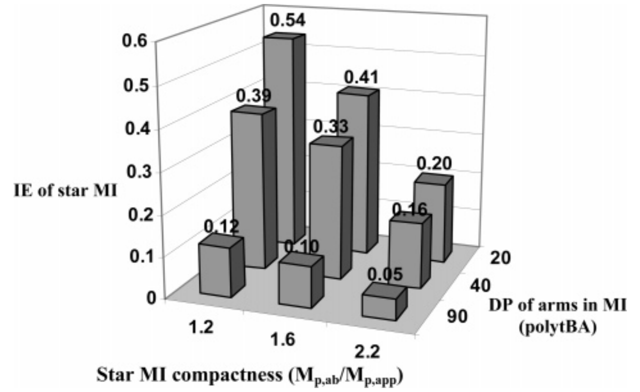


Figure 5. Influence of arm length and structural compactness of star MIs on their IE values during the synthesis of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(poly*t*BA)$_p$ miktoarm star polymers.

conversion reached 35% after 22 h. For the miktoarm star synthesis, when star polymer with different arm length and structural compactness was used as MI, the rate of *t*BA consumption was quite different. The apparent kinetic constant in each reaction was obtained via linear fitting of the kinetic plot. Under the asuumption that the IE of the control reaction was 100%, the IE of each star MI during the polymerization of *t*BA was obtained according to eq 2. The results are summarized in Table 2, and the influence of the arm length and structural compactness of each star MI on its IE value is shown in Figure 5.

It is seen in Figure 5 that the IE of star MIs decreased with increases in both star arm length (l) and star structural compactness ($M_{p,ab}/M_{p,app}$). With the same star structural compactness, star MI with longer arm length always had smaller IE values, and when the arm length was the same, star MI with higher structural compactness had smaller IE values. When the structural compactness of the star MI was 1.2, the IE decreased more significantly as a result of an increase in arm length than that when the star compactness was ca. 2.2. When the arm length was 90, the IE values of all three star MIs were less than 15%, and the difference between them was smaller than when the arm length was 20. Under a proper control of the arm length and structural compactness of the star MI, the IE of the star MI reached the highest value of 54% when the arm length was 20 and structural compactness was 1.2. On the contrary, the IE of the star MI reached the lowest value of 5% when the arm length was 90 and structural compactness was 2.2. These results mean that in the former case the number of the second generation of arms is more than half of the first generation of arms in the miktoarm star molecule, while in the latter case, the number of the second arms is only 5% of the first arms.

Effect of Chemical Compatibility between the Two Kinds of Arms on the IE of Star MI. During the synthesis of miktoarm star polymers, the generation of the second arms is also affected by the chemical compatibility between the second generation of arms and the preformed first ones. When these two types of arms are chemically compatible, the second generation of arms behave like flexible chains around the star core. Thus, all initiating sites (C−Br) in interior and at termini of the second generation of arms have a similar environment and opportunity to react with catalyst, which is essential to obtain a higher IE of star MI. On the contrary, when the two types of arms are not compatible, the second generation of arms would prefer to extend away from the first generation of arms and the star core. Therefore, the C−Br groups at termini of the second generation of arms are away from the congested star core and have more opportunity to access the monomer and catalyst complex than the noninitiated C−Br groups. The different environment for the growing and noninitiated C−Br groups would cause a lower IE of star MI.

Table 3. Influence of the Chemical Composition of the Second Arms on the IE of (Poly*t*BA)$_n$−Poly(DVB-*co*-*t*BA) Star MI during the Synthesis of Miktoarm Star Polymers

entry[a]	monomer	initiator	T (°C)	conv	k^{app} ($\times 10^{-6}$ s^{-1})	IE[b]	$M_{p,ab}$[c] (g/mol)
M5-1	*t*BA	S5	60	0.133	1.80	0.33	155 600
C-1	*t*BA	1-PEBr	60	0.351	5.46	1.00	
M5-2	BA	S5	60	0.120	1.61	0.30	148 500
C-2	BA	1-PEBr	60	0.348	5.40	1.00	
M5-3	MA	S5	60	0.109	1.46	0.23	124 400
C-3	MA	1-PEBr	60	0.395	6.35	1.00	
M5-4	St	S5	80	0.055	0.71	0.11	112 600
C-4	St	1-PEBr	80	0.398	6.41	1.00	

[a] Experimental conditions: $[\text{monomer}]_0/[\text{initiating sites from S5 or 1-PEBr}]_0/[\text{CuBr}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 300/1/1.8/0.2/2$ in anisole, 22 h. The $M_{p,ab}$ of S5 is 88 000 g/mol. [b] Calculated using eq 2. [c] Peak value of absolute molecular weight of miktoarm star polymer, GPC in THF with MALLS detector.

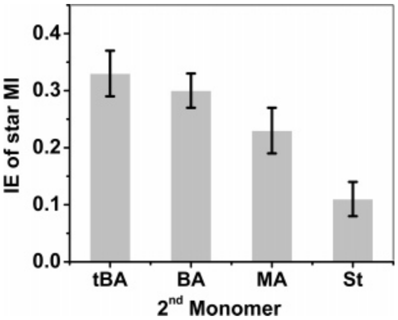


Figure 6. IE of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star MI (S5 in Table 1) during initiating the ATRP of different second monomers.

The influence of the chemical composition of the second arm on the IE of star MI was studied by using one star polymer as MI (Table 1, S5) for the ATRP of four kinds of monomers to form the second generation of arms. For each polymerization, the IE value of the star MI was determined by comparing its apparent kinetic constant to a corresponding control reaction, as discussed above. Four types of monomers, *t*BA, BA, MA, and St, were selected for chain extension from the star MI. Table 3 provides detailed information on each ATRP reaction. For the ATRP of *t*BA, BA, and MA, the reaction temperature was 60 °C, while for the ATRP of St, the reaction temperature was set at 80 °C in order to obtain a reasonable conversion within an appropriate reaction period. The kinetics of all reactions was followed via GC measurement of monomer conversions, and the reactions were stopped after 22 h.

Figure 6 shows the influence of the chemical composition of the second generation of arms on the IE of the star MI. The IE value of S5 was different when initiating the ATRP of different monomers. When the chemical composition of the second generation of arms was the same as the first generation of arms, S5 had its highest IE value: 33% (Table 3, M5-1). When the star MI was used for ATRP of BA monomer, its IE value decreased to 30%, probably due to the small difference in chemical structure between polyBA and poly*t*BA chains. With further change in the chemical composition of the second generation of arms to MA, the IE value of S5 decreased to 23% (Table 3, M5-3). These results suggested that the IE value of a star MI decreased with increasing difference between chemical composition of the second generation of arms and the first generation of arms. When both arms were composed of acrylates, such as *t*BA, BA, and MA, the values for the IE of the S5 MI were still comparable, with a small decrease from 33% for *t*BA to 23% for MA. In contrast, when S5 was used to initiate the ATRP of St, a species different from acrylates, the value for the IE of S5 decreased dramatically to 11% (Table 3, entry M5-4), indicating that fewer initiating sites in the star MI were accessible due to the greater difference in chemical composition between the poly*t*BA and polySt arms.

During the synthesis of miktoarm star polymers, the IE value of the star MI was quantitatively determined by using the kinetic method, which provided clear information about the structure of the miktoarm star polymers. For example, the star polymer (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) (S5 in Table 1) containing poly*t*BA arms and poly(DVB-*co*-*t*BA) copolymer core had a molecular weight of $M_{\mathrm{p,ab}} = 88\,000$ g/mol. On the basis of the conversions of DVB and *t*BA, the weight fraction of the cross-linked core was 18 wt % of the star polymer. The poly*t*BA arm in the star had a DP around 40, and the average arm number per star was ca. 14. During the synthesis of (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA)−(polyBA)$_p$ miktoarm star polymers by ATRP of BA using this star polymer as MI, the target DP of polyBA arms was 300 and the conversion of BA was ca. 12% (Table 3, entry M5-2). The IE value of the star MI was determined to be around 30% by the kinetic method. It meant that the average number of the second generation of arms, polyBA, in a miktoarm star polymer was around 4, and their DP was around 120. In other words, the number of the polyBA arms was 30% of the poly*t*BA arms in the miktoarm star polymer, while the polyBA arms were 3 times longer than poly*t*BA arms.

Conclusions

Miktoarm star polymers were synthesized via ATRP of various monomers using the in−out method. (Poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star polymers, synthesized by the arm-first method, were used as MIs, and their initiation efficiency (IE) for initiating ATRP of different monomers was studied by comparing the relative rates of monomer consumption in the polymerization to a control ATRP reaction conducted under the same experimental conditions as those during the synthesis of miktoarm star polymers except using 1-PEBr as initiator. Three factors were considered to have the potential to influence the IE value of the star MI. They were the arm length of star MI, the structural compactness of star MI, and the chemical compatibility of the second generation of arms to the preformed first generation of arms. It was found that the IE value of the star MI decreased with the increase of its arm length and structural compactness. When the star MI had arm length as $l = 90$ and structural compactness ($M_{\mathrm{p,ab}}/M_{\mathrm{p,app}}$) around 2.2, its IE value dropped to the lowest point of 5% within the scale of our investigation. This means that only ca. 5% of the initiating sites in the star polymers participated in the formation of the second generation of arms. In contrast, when the star MI had shorter arm as $l = 20$ and looser star structure around 1.2, it had the highest IE value as 54%, indicating more than half of the initiating sites in the star MI participated in the formation of the second generation of arms. The influence of the chemical compatibility of the two types of arms on the IE value of star MI was also studied. It was found that when the two kinds of arms had the same chemical composition, the star MI had the highest IE value. For (poly*t*BA)$_n$−poly(DVB-*co*-*t*BA) star MI, its IE value decreased when initiating the ATRP of different monomers from *t*BA, BA, MA to St. These results provide insight into the synthesis of miktoarm star polymers using multifunctional star polymers as MIs. They are valuable for indicating how to control the IE of the star MIs during the formation of the second generation of arms, which directly determines the morphology and properties of the resulting miktoarm star polymers.

Acknowledgment. The financial support from NSF (DMR-05-49353) and the CRP Consortium at Carnegie Mellon University is greatly appreciated. The authors also thank Dr. Chuanbing Tang for valuable discussion and sample analysis.

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(35) The contraction factor of branched polymer ($g = \langle R_{\mathrm{g,br}}^2\rangle/\langle R_{\mathrm{g,lin}}^2\rangle$) has a value less than 1, meaning its mean-squared radius of gyration is smaller than its linear analogue with the same molecular weight. GPC-MALLS measurement can determine the g value of a star-shaped homopolymer via comparing its $\langle R_{\mathrm{g,br}}^2\rangle$ to that of a linear analogue with the same chemical composition and molecular weight. However, for star-shaped copolymer, this method is less meaningful because it is difficult to prepare a linear analogue of the star copolymer with

precisely the same chemical composition. Therefore, the star compactness is defined as $M_{p,ab}/M_{p,app}$ here. A star polymer with a higher $M_{p,ab}/M_{p,app}$ value should have a more compact structure and correspondingly smaller g.

(36) The amount of preserved initiating site, R−X, per star MI is a theoretical value, which is equal to the average arm number per star molecule. The possible termination reaction during the star formation process is neglected although it can decrease the number of initiating sites. [P−X] equals $[R-X]_0 - [R-X]_d$, in which $[R-X]_d$ comprises the lost initiating site during the star formation due to the termination reaction and the inaccessible initiating sites in the star MI during the synthesis of the second generation of arms.

MA061702X