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Structural Control in ATRP Synthesis of Star Polymers Using the Arm-First Method

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ABSTRACT: Star polymers were synthesized via atom transfer radical polymerization (ATRP) using the "arm-first" method. First, linear poly(*tert*-butyl acrylate) (polytBA) precursors were prepared, and subsequently divinylbenzene (DVB) was added as cross-linker at certain tBA conversion. Several experimental parameters, including the polytBA arm length, the amount of cross-linker, the monomer conversion at which DVB was added, and the chemical composition of the star core (fraction of tBA units in the star core), were systematically varied. For example, the degree of polymerization of the polytBA arm was typically 40 and was varied from 20 to 90. The molar ratio of DVB to the macroinitiator was varied from 1.5 to 15, and DVB was added at 60%, 80%, and 90% tBA conversions. The influence of these factors on the structures of the star polymers was studied. Employing shorter arm lengths and using more cross-linker produced star polymers in higher yield, with higher molecular weight, with more arms per star, and with a more compact structure. The addition of DVB at lower tBA conversion caused the incorporation of more monovinyl monomer into the star core, which decreased the cross-link density of the core, facilitated incorporation of more arms into each star molecule, and increased the star size and star yield.

Introduction

Polymers with star-shaped structure containing multiple arms connecting at the central core are among the simplest form of branched topologies. Their compact structure leads to low melt and solution viscosity when compared to linear analogues with the same molecular weight.[1] Interest in the synthesis of star polymers, which began in the 1950s with living anionic polymerization, has increased in recent years due to the development of controlled/living radical polymerization (CRP).[2−5] Star polymers are synthesized via CRP using two strategies: core-first[6−16] and arm-first.[17−24] The core-first method involves the use of a multifunctional initiator, and the number of arms per star polymer is determined by the number of initiating functionalities on each initiator. The initiating sites on the star polymers can be further used for chain extension with a second monomer to form star block copolymers.[25−27] On the other hand, the arm-first method involves the synthesis of preformed linear arms and can be subdivided into two categories according to the features of the star formation procedure. The first is linear chain coupling with a multifunctional terminator or "grafting onto" a multifunctional core. The second one is chain extension of the linear arm precursor with a multivinyl cross-linking agent. In the former case, the number of arms per star is determined by the functionality of the terminator, and the resulting star polymer no longer contains any initiating sites. However, because of the slow reaction between the polymer chain end and the multifunctional terminator, this method suffers from low coupling efficiency. Often a product obtained from such a reaction is a mixture of stars with different numbers of arms.[28] In the second case, the core of the star polymer is a cross-linked microgel, and the number of arms per star macromolecule is an average value. The initiating sites in the cross-linked core are still "living" and therefore can initiate polymerization of another monomer and produce miktoarm star copolymers via the "in−out" method.[8,29−32] The latter method using a multivinyl cross-linker is much simpler for synthesis of star polymers than the former one using a multifunctional terminator. Actually, the term "arm-first method" often refers to the latter approach. Star polymers prepared using this strategy contain multiple arms per molecule, and each arm and initiating site in the star molecule are potentially available for further modification and/or functionalization.

Atom transfer radical polymerization (ATRP)[33−35] has been extensively employed for the synthesis of star polymers via the arm-first method. Star polymers produced by ATRP preserve the terminal halogen atom(s) within the core, and they can be efficiently employed as multifunctional macroinitiators (MI) for chain extension from the core by formation of a second set of arms. The synthesis of various kinds of star polymers with arms of different composition and functional groups has been reported.[18,36,37] The structure of star polymers is determined by the monomer species as well as the synthetic procedures. However, their relationship is not always straightforward.

In this paper, star polymers were synthesized via ATRP using the arm-first method. In the first step, ATRP of *tert*-butyl acrylate (tBA) was performed using ethyl 2-bromopropionate (EBrP) as initiator and CuBr/*N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA) as catalyst. At certain conversion of the tBA monomer, N_2-purged divinylbenzene (DVB) was injected into the polymerizing system as a cross-linker, which copolymerized with the remaining tBA monomer and produced the target star polymers, (polytBA)$_n$-poly(DVB-*co*-tBA), where poly(DVB-*co*-tBA) represents the core of the star polymer and *n* is the average number of polytBA arms per star molecule. In this procedure, the star polymers were formed via in-situ addition of the cross-linker DVB. This avoided the tedious purification step of the linear polytBA MI and was termed the "one-pot" process.[38] In contrast, the synthesis of star polymers using the purified linear polymers as MIs is a "two-pot" process.[17]

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Several experimental parameters, including the polytBA arm length, the monomer conversion at which DVB was added, the amount of DVB added, and hence the chemical composition of the star core (molar ratio of DVB to tBA monomers for core formation), were systematically studied during the synthesis of (polytBA)$_n$-poly(DVB-*co*-tBA) stars. The influence of all these factors on star structures, including the absolute molecular weight of the star molecule, the number-average value of the number of arms per star molecule, the star yield, and star compactness (defined as the ratio of peak values between the absolute molecular weight and apparent GPC molecular weight of the star polymers), will be discussed.

Experimental Section

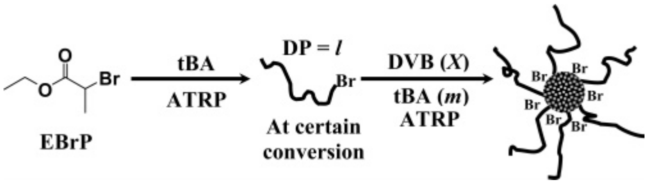
Materials. Divinylbenzene (DVB, 80%, Aldrich) and *tert*-butyl acrylate (tBA, 98%, Aldrich) were purified by passing the neat liquid through a column filled with basic alumina to remove the inhibitor. CuBr (98%, Acros) was purified using a modified literature procedure.[39] All other reagents—ethyl 2-bromopropionate (EBrP, 99%, Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), and $CuBr_2$ (99%, Aldrich)—and solvents were used as received without further purification.

General Procedures for Synthesis of (PolytBA)$_n$-poly(DVB-*co*-tBA) Star Polymer via the Arm-First Method in a One-Pot Process. A clean dry Schlenk flask was charged with tBA, PMDETA, and anisole. The flask was then degassed by five freeze−pump−thaw cycles. During the final cycle, the flask was filled with nitrogen, and CuBr was quickly added to the frozen mixture; no special care was taken to avoid moisture condensation during the addition. 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 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 determine monomer conversions and polymer molecular weights by GC and GPC measurements, respectively. At certain tBA conversions (such as 60%, 80%, and 90%), N_2-purged DVB was injected into the reaction system, and the temperature of oil bath was increased to 80 °C in order to obtain a reasonable DVB conversion within an appropriate reaction period. The reaction was stopped after 14 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 (PolytBA)$_n$-polyDVB Star Polymer via the Arm-First Method in a Two-Pot Process. The experimental procedures in each ATRP reaction were similar to those in the ATRP synthesis of (polytBA)$_n$-poly(DVB-*co*-tBA) star polymers from the one-pot process. First, ATRP was used to produce polytBA linear MIs with the ratio of reagents $[\text{tBA}]_0/[\text{EBrP}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0 = 50/1/0.5/0.5$ ($[\text{tBA}]_0 = 3.25$ M, 60 °C in anisole). At ca. 80% tBA conversion, the reaction was stopped via exposure to air and dilution with THF. The polymers were purified to remove the catalyst and unreacted monomer. The purified polytBA MI had $M_n = 5000$ g/mol and $M_w/M_n = 1.10$. Second, these linear MIs were chain extended and cross-linked with DVB to form (polytBA)$_n$-polyDVB star polymers by ATRP with the ratio of reagents $[\text{DVB}]_0/[\text{polytBA-Br}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0 = X/1/0.5/0.5$ ($[\text{polytBA-Br}]_0 = 0.065$ M, 80 °C in anisole, $X = 3$, 10, and 15). At timed intervals, samples were withdrawn for measurement of the monomer conversions and polymer molecular weights. The reaction was stopped after 14 h.

Characterization. Monomer conversions were determined from the concentration of the unreacted monomer in the samples periodically withdrawn 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 conversion. 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 were determined with a calibration based on linear polySt standards using WinGPC 6.0 software from PSS and toluene as internal standard. 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.

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



Results and Discussion

(PolytBA)$_n$-poly(DVB-*co*-tBA) star polymers were synthesized via the arm-first method in a one-pot process (Scheme 1). First, linear polytBA chains were produced with EBrP as initiator and CuBr/PMDETA as catalyst. At certain tBA conversions (average degree of polymerization of the formed polytBA chain, DP = *l*), N_2-purged DVB (*X* times the moles of the initial EBrP, $X = [\text{DVB}]_0/[\text{EBrP}]_0$) was injected into the system. The added DVB copolymerized with the remaining tBA monomer (the molar ratio between the unreacted tBA monomer to the initial EBrP is *m* when DVB was added) to form the cross-linked core of the star polymers. This procedure not only eliminated the tedious purification step of the linear precursors but also introduced monovinyl monomer (tBA) into the star core.

Figure 1 shows the results of a typical synthesis of (polytBA)$_n$-poly(DVB-*co*-tBA) star polymer. The semi-

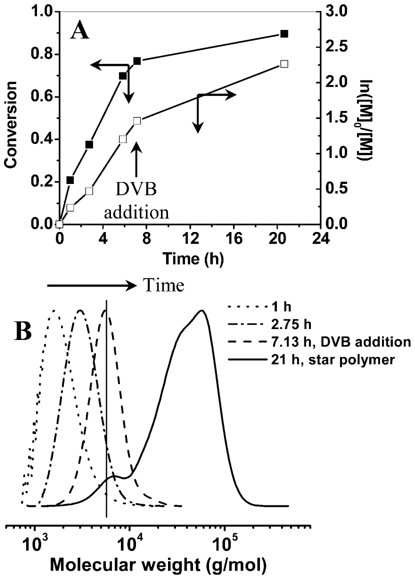


Figure 1. Dependence of tBA conversion and ln([M]$_0$/[M]) on reaction time (A) and the GPC traces (B) during the synthesis of (polytBA)$_n$-poly(DVB-*co*-tBA) star polymers via the arm-first method in a one-pot process (Table 1, entry S2). Experimental conditions: $[\text{tBA}]_0/[\text{DVB}]_0/[\text{EBrP}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0 = 50/3/1/0.5/0.5$, $[\text{tBA}]_0 = 3.25$ M, 60 °C in anisole. The temperature was elevated to 80 °C after addition of DVB at ca. 80% tBA conversion.

Table 1. Synthesis of (PolytBA)$_n$-poly(DVB-*co*-tBA) Star Polymers in a One-Pot Strategy

entry^a	$l/m/X/[\mathrm{EBrP}]_0$^{b}	$M_{\mathrm{p,app}}$^{c} (g/mol)	M_w/M_n^{c} (star)	$M_{\mathrm{p,ab}}$^{d} (g/mol)	n_{arm}^{e}	compactness ($M_{\mathrm{p,ab}}/M_{\mathrm{p,app}}$)	Y_{star}^{f} (mol %)
S1	20/10/3/1	67 700	1.84	142 900	34.1	2.11	88.2
S2	40/10/3/1	56 300	1.38	88 000	14.1	1.56	85.7
S3	90/10/3/1	58 900	1.23	70 600	5.4	1.20	73.0
S4	30/20/3/1	55 000	1.56	126 500	18.5	2.30	79.9
S5	45/5/3/1	24 500	1.24	32 100	5.1	1.31	74.6
S6	40/10/1.5/1	24 200	1.22	28 100	4.6	1.16	72.3
S7	40/10/5/1	65 400	1.71	140 600	21.6	2.15	91.4
S8	40/10/10/1	76 500	2.30	262 800	36.9	3.44	94.6
S9	40/10/15/1	128 100	3.86	676 400	87.3	5.18	94.6

[a] Experimental conditions: $[\mathrm{tBA}]_0/[\mathrm{DVB}]_0/[\mathrm{EBrP}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = (l + m)/X/1/0.5/0.5$, $[\mathrm{tBA}]_0 = 3.25$ M, 60 °C in anisole. The temperature was elevated to 80 °C after addition of DVB. [b] Definitions: l = number-average DP of polytBA arm before addition of DVB, determined from GC measurement; m = molar ratio of unreacted tBA monomer to initial EBrP when DVB was added; $X = [\mathrm{DVB}]_0/[\mathrm{EBrP}]_0$. [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 ($n_{\mathrm{arm}} = M_{\mathrm{p,ab}}(\mathrm{star}) \times \mathrm{arm}_{\mathrm{wt\%}}/M_{\mathrm{p,arm}}$). $\mathrm{Arm}_{\mathrm{wt\%}}$ is the weight fraction of polytBA arm in the star polymer, and $M_{\mathrm{p,arm}}$ was measured by GPC in THF with RI detector, calibrated with linear polySt standard. [f] Star yield: molar percentage of incorporated linear polytBA precursors, determined by multipeak splitting of the GPC-RI curves and a calculation method published elsewhere.[30]

logarithmic plot in Figure 1A was linear until the addition of DVB. The final conversion of tBA after the total 21 h reaction period was around 90%. At the same time, the unreacted DVB was nearly undetectable by GC analysis. The GPC curves at different reaction times are shown in Figure 1B. Before the addition of DVB, the GPC curves of linear polytBA shifted smoothly to higher molecular weight with increasing reaction time. After DVB addition, the fact that most of the linear chains were chain-extended with DVB and converted into star molecules was confirmed by the decreased RI signal corresponding to the unreacted linear polytBA precursors. After 14 h reaction, the area percentage of the star polymer peak in the GPC curve was around 88%, according to the multipeak splitting using Gaussian function. On the basis of the GC monomer conversions and the d*n*/d*c* values of polyDVB (0.195 mL/g, the value of linear polySt) and polytBA (0.065 mL/g) in THF at 35 °C,[40] the molar percentage of incorporated polytBA precursor (star yield, Y_{star}) was calculated, following a method published elsewhere.[30] The result indicates that finally ca. 86 mol % of the polytBA precursors were incorporated into the star molecules. For the unincorporated linear chains, part of them were still “alive” because the small peak in the GPC curve after total 21 h reaction period had a higher molecular weight than the linear chains at 7.13 h, when DVB was added (Figure 1B). This result indicates at least part of the unincorporated linear chains were further chain extended. The incomplete conversion of the linear precursors to star molecules is explained by increased steric congestion around the star core as the cross-linking reaction proceeded.

The impact of several reaction parameters on the structures of the star polymers was considered. The first parameter was the length of polytBA linear chain before the addition of DVB (l). The second was the tBA conversion when DVB was added (l/m ratio), and the third was the amount of DVB added to the reaction (X). Through changing these parameters in a systematic manner, a series of star polymers were prepared, and detailed information on the syntheses is summarized in Table 1. The structures of star polymers, including the peak value of the absolute molecular weight measured by GPC-MALLS ($M_{\mathrm{p,ab}}$), the number-average arm number per star molecule (n_{arm}), star yield (Y_{star}), and star compactness ($M_{\mathrm{p,ab}}/M_{\mathrm{p,app}}$),[41] were significantly affected by these parameters, and the influence of each factor is discussed below.

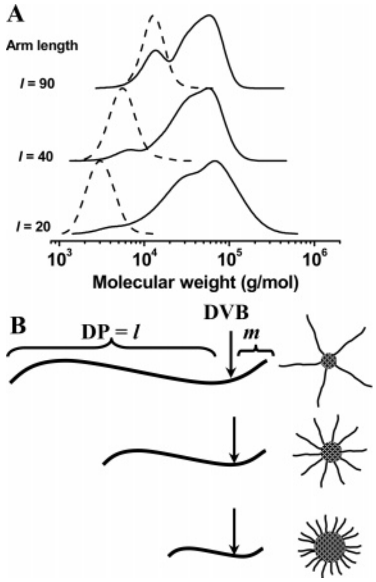


Figure 2. Influence of polytBA arm length (l) on the structures of star polymers. GPC traces of linear polytBA (dashed line) and corresponding star polymers (solid line) with RI detector (A), schematic illustrations of star polymers with different arm length (B). Experimental conditions: $[\mathrm{tBA}]_0/[\mathrm{DVB}]_0/[\mathrm{EBrP}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = (l + m)/3/1/0.5/0.5$ ($m = 10$), $[\mathrm{tBA}]_0 = 3.25$ M, 60 °C in anisole. The temperature was elevated to 80 °C after addition of DVB (Table 1, entries S1−S3).

Effect of Arm Length (*l*) on Star Structures. During the synthesis of star polymers by the arm-first method, the chain extension of the linear arm precursor by a divinyl cross-linker results in the formation of star molecules. Longer linear chains not only have smaller mobility but also sterically hinder the incorporation of more linear chains into one individual star molecule. The effect of arm length (l) on the structures of star formed was studied by fixing the amounts of unreacted tBA monomer ($m = 10$) and DVB added ($X = 3$). Figure 2A shows the GPC curves of various star polymers with different arm length l but with the same core composition (fixed m/X). The star polymers with the longest arms ($l = 90$) had the smallest overall molecular weight from GPC-RI measurement, but the molecular weight distribution was the narrowest ($M_w/M_n = 1.23$, Table 1, entry S3). In contrast, star polymers formed from the shortest arms ($l = 20$) had a much higher molecular weight and broader polydispersity (Table 1, entry S1). Figure 2B schematically illustrates the procedure and the influence of polytBA arm length on the structures of the star copolymer. With the fixed ratio of $m/X/[\mathrm{polytBA\text{-}Br}]_0 = 10/3/1$, the star molecule containing more arms is expected to have a larger star core than the star containing fewer arms, although the cross-

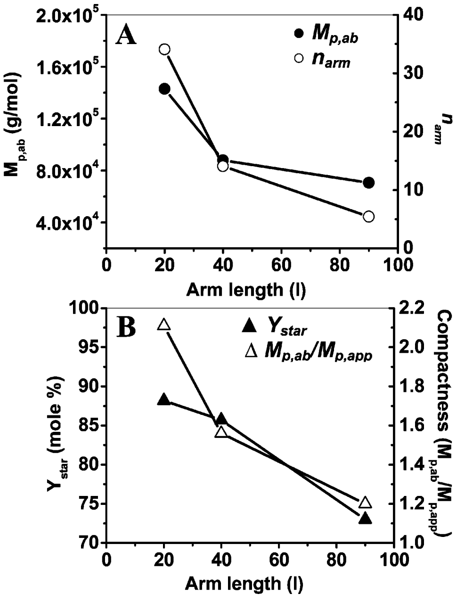


Figure 3. Effect of polytBA arm length (*l*) on the structures of (polytBA)$_n$-poly(DVB-*co*-tBA) star polymers (Table 1, entries S1−S3).

link density of the star cores should be similar. The influence of arm length on the structures of the stars is illustrated in Figure 3. Star polymers formed from the longest polytBA precursors had the lowest molecular weight ($M_{p,ab}$ = 70 600 g/mol) and the least arms per star molecule (n_{arm} = 5.4) (Figure 3A). These results confirm that longer precursor arms hindered the incorporation of more arms into one star macromolecule, so the resulting star polymer had a smaller core and looser structure ($M_{p,ab}/M_{p,app}$ = 1.20) when compared to the star polymer formed from shorter polytBA precursors (Figure 3B).

The star yield was influenced by both arm length and star compactness. Shorter arms on star molecule provided less steric hindrance and favored the incorporation of more arms into each star molecule. The results in Figure 3B indicate that Y_{star} increased dramatically when the arm length (*l*) was decreased from 90 to 40. However, further decrease in the arm length had smaller effect on the star yield, partially because the decrease of arm length also resulted in the increase of star compactness, which had a negative effect on the arm incorporation. In other words, the increase of star compactness compensated for the decrease of arm length. When the arm length was 20, the yield of star polymer only increased by 2.5% when compared to the star polymers with arm length l = 40. Thus, with the fixed values of m = 10 and X = 3, longer polytBA precursor arms lead to star polymers with lower molecular weight, fewer arms per star, looser star structure, and lower star yield. However, when the linear chain was longer, the obtained star polymer had a much narrower size distribution, and the structure resembled more of a star rather than a hairy microgel.

Effect of Monomer Conversion at Which DVB Was Added (*l/m* Ratio) on Star Structures. In the one-pot strategy, N_2-purged DVB was injected into the polymerizing system at certain conversions of tBA in order to form (polytBA)$_n$-poly(DVB-*co*-tBA) star polymers. The addition moment of DVB was an important reaction parameter because it influenced both the arm length of polytBA precursor (*l*) and the chemical composition of the core (*m*/*X* ratio). This section describes the influence of the DVB addition moment on the structures of the star polymers. The sum of *l* and *m* was fixed at 50, and the amount of DVB added (*X*) was 3. DVB was introduced to the reaction at different tBA conversions, 60%, 80%, and 90%, to vary the *l*/*m* ratio. Figure 4A shows the GPC curves of different star polymers and the corresponding linear polytBA chains when DVB was added. When DVB was added earlier (at ca. 60% tBA conversion), the final star polymer had a higher molecular weight and broader molecular weight distribution. In contrast, when DVB was added at 90% tBA conversion, the molecular weight of the star polymer was lower, and its elution peak in the GPC curve was not well separated from that of the polytBA precursor. The influence of DVB addition moment on the structures of star polymers is schematically illustrated in Figure 4B.

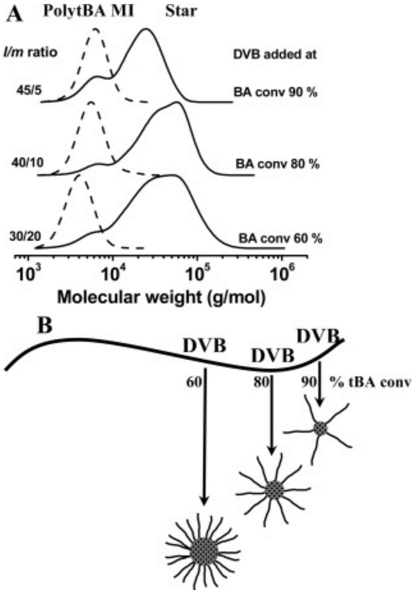


Figure 4. Influence of DVB addition moment on the structures of star polymers. GPC traces with RI detector (A) and schematic illustration of star polymers with different *l*/*m* ratios (B). Experimental conditions: $[tBA]_0/[DVB]_0/[EBrP]_0/[CuBr]_0/[PMDETA]_0 = 50/3/1/0.5/0.5$, $[tBA]_0 = 3.25$ M; 60 °C in anisole. The temperature was elevated to 80 °C after addition of DVB at 60%, 80%, and 90% conversions of tBA (Table 1, entries S4, S2, and S5).

When the total tBA amount was fixed ($l + m = 50$), early addition of DVB meant that the polytBA arm precursor was shorter, and correspondingly more unreacted tBA monomer remained in the reaction. Shorter linear chains had higher mobility and smaller size, and a larger m value decreased the cross-link density of the star core when the amount of DVB was fixed ($X = 3$). Thus, when DVB was added earlier, both factors facilitated the incorporation of linear chains into the star molecule. Figure 5 indicates that when the DVB was added at 60% tBA conversion (correspondingly, l = 30 and m = 20), the star polymers formed in the resulting copolymerization (Table 1, entry S4) had higher molecular weight ($M_{p,ab}$ = 126 500 g/mol) and contained more arms per star (n_{arm} = 18.5). A greater number of arms surrounding one cross-linked core resulted in a denser star structure ($M_{p,ab}/M_{p,app}$ = 2.30). On the contrary, the (polytBA)$_n$-poly(DVB-*co*-tBA) star polymers formed when the DVB addition occurred at 90% tBA conversion (l/n = 45/5, Table 1, entry S5) had lower molecular weight ($M_{p,ab}$ = 32 100 g/mol), fewer arms per star on average (n_{arm} = 5.1), and a looser star structure ($M_{p,ab}/M_{p,app}$ = 1.31). The star yield was influenced by the star compactness and the arm length. In Figure 5B, it is shown that the star polymers with median values of $M_{p,ab}/M_{p,app}$ and l (DVB addition at 80% tBA conversion) had the highest star yield at around 86 mol % (Table 1, entry S2). The value of Y_{star} became lower when DVB was added earlier, at 60% tBA conversion, or later, at 90% tBA conversion.

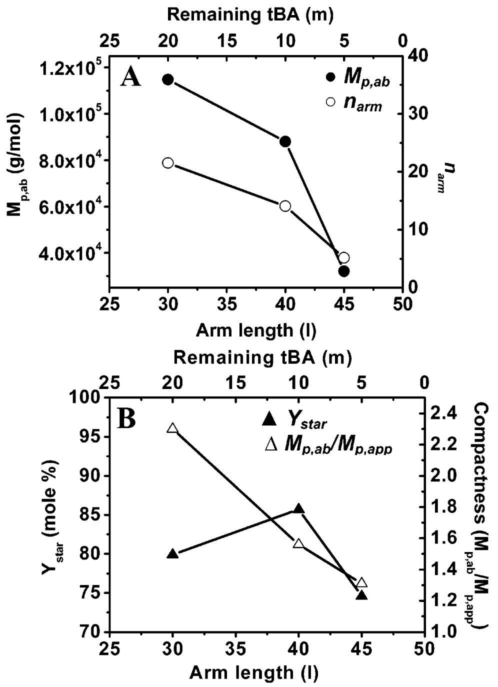


Figure 5. Effect of DVB addition moment on the structures of (polytBA)$_n$-poly(DVB-*co*-tBA) star polymers (Table 1, entries S4, S2, and S5).

Effect of the Amount of DVB Added (*X*) on Star Structures. During the synthesis of star polymers via the arm-first method, the role of the divinyl cross-linker is to bind the linear chains into the central core and form a star-shaped molecule. The amount of cross-linker added to the reaction has a very significant influence on the star molecular weight and star yield, as already reported.[18,38] In this section, the values of *l* and *m* were kept constant at 40 and 10, respectively. At ca. 80% tBA conversion, different amounts of DVB were added to the polymerizing system. The effect of DVB amount on the structures of the star copolymer formed is listed in Table 1 (entries S2 and S6−S9). Figure 6A shows the GPC traces of three star polymers, produced with different amounts of DVB ($X = 1.5$, 3, and 10). It is seen that a larger amount of DVB led to the formation of star copolymers with higher molecular weight, broader molecular weight distribution, and a larger proportion of incorporated polytBA chains. When $X = 10$, the star yield reached its peak value at 94.6 mol %, indicating that around 95% of the linear polytBA arm precursors were incorporated into star molecules during the cross-linking reaction. Further increasing the DVB amount to $X = 15$ did not result in any further raise of the star yield (Table 1, entry S9). The influence of the amount of DVB added on the star structures is schematically illustrated in Figure 6B.

It is worth noting that during star formation in a one-pot process the core of the star is composed of both DVB and tBA units. The latter increase the size of the star core but decrease the cross-link density. Thus, it is expected that the presence of tBA monomer during the cross-linking process should increase the star yield and star molecular weight. To confirm this hypothesis, a series of star polymers were synthesized using a two-pot process from DVB and the purified polytBA linear chains as MIs. The detailed data on the star polymers from this two-pot process are listed in Table 2. The average DP of the polytBA linear chains was $l = 40$. After purification and removal of the unreacted tBA monomer, these linear precursors were used as MIs. In this procedure, the core of the star contained only DVB units, i.e., $m = 0$ for the composition of the star core, leading to (polytBA)$_n$-polyDVB. Figure 7A shows that increasing the amount of DVB resulted in star polymers with higher molecular weight, broader molecular weight distribution, and higher star yield. When the amount of DVB added was 15 times the moles of linear MIs, the star yield reached the highest value (90.4 mol %). The molecular weights of the unreacted linear chains in the two-pot star polymer process were unchanged because their elution peaks in GPC curves overlapped with those of the polytBA linear MIs. The schematic structures in Figure 7B illustrate that the cores of star polymers from a two-pot process were composed of only DVB units. The difference in chemical composition of the cores between the star polymers from the one-pot and two-pot methods resulted in some differences in the structures/properties of the resulting stars, as shown in Figure 8.

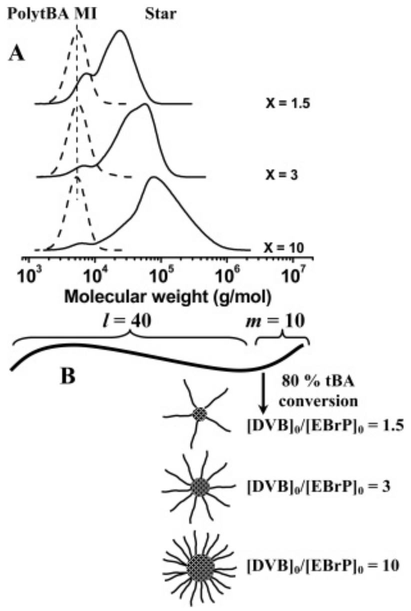


Figure 6. Influence of the amount of DVB added on the structures of star polymers. GPC traces with RI detector (A) and schematic illustration of star polymers with different DVB addition amount (B). Experimental conditions: $[tBA]_0/[DVB]_0/[EBrP]_0/[CuBr]_0/[PMDETA]_0 = 50/X/1/0.5/0.5$, $[tBA]_0 = 3.25$ M, 60 °C in anisole. The temperature was elevated to 80 °C after addition of DVB at ca. 80% tBA conversion. $X = 1.5$, 3, and 10 (Table 1, entries S6, S2, and S8).

In Figure 8, the two series of star polymers, produced by different procedures (one-pot and two-pot), had the same arm length ($l = 40$) but different chemical composition of the core. From the one-pot process, the core of the star copolymer was composed of both DVB and tBA units ($m = 10$; $X = 1.5$, 3, 5, 10, 15), while from the two-pot process, the core contained only DVB units ($X = 3$, 10, 15). The star copolymers obtained from both procedures had higher molecular weight at higher amounts of DVB added. The star copolymers with more arms had more compact structures and higher star yields. Figure 8A shows that when the same amount DVB was added to the reaction, the star polymers with a copolymer core (diluted by tBA) always had higher molecular weight and higher n_{arm} values than star polymers with cores containing only DVB units. When the amount of DVB was increased from $X = 10$ to 15, a large increase in the molecular weight of the star occurred in both cases, since star−star coupling became significant. This happened when a too large amount of DVB was used. The absolute molecular weight of star polymers ($M_{\mathrm{p,ab}}$) increased from 262 800 to 676 400 g/mol for the one-pot process when *X* increased from 10 to 15, while this value increased from 107 600 to 365 500 g/mol for the two-pot process.

Table 2. Synthesis of (PolytBA)$_n$-polyDVB Star Polymers in a Two-Pot Strategy

entry[a]	$l/m/X/[\mathrm{EBrP}]_0$	$M_{\mathrm{p,app}}$ (g/mol)	M_w/M_n (star)	$M_{\mathrm{p,ab}}$ (g/mol)	n_{arm}	compactness ($M_{\mathrm{p,ab}}/M_{\mathrm{p,app}}$)	Y_{star} (mol %)
S10	40/0/3/1	20 400	1.15	27 300	5.2	1.34	54.1
S11	40/0/10/1	44 300	1.32	107 600	17.5	2.43	71.2
S12	40/0/15/1	85 300	1.54	365 500	54.0	4.28	90.4

[a] Experimental conditions: $[\mathrm{DVB}]_0/[\mathrm{polytBA\text{-}Br}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = X/1/0.5/0.5$, $[\mathrm{polytBA\text{-}Br}]_0 = 0.065$ M, 80 °C in anisole for 14 h.

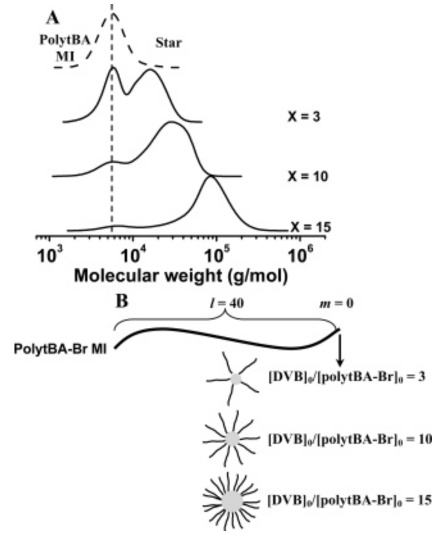


Figure 7. Influence of the amount of DVB added for core formation on the structures of star polymers synthesized in a two-pot process. GPC traces with RI detector (A) and schematic illustration of star polymers resulting from addition of different DVB amounts (B). Experimental conditions: $[\mathrm{DVB}]_0/[\mathrm{polytBA\text{-}Br}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = X/1/0.5/0.5$, $[\mathrm{polytBA\text{-}Br}]_0 = 0.065$ M, 80 °C in anisole for 14 h. $X = 3$, 10, and 15 (Table 2, entries S10−S12).

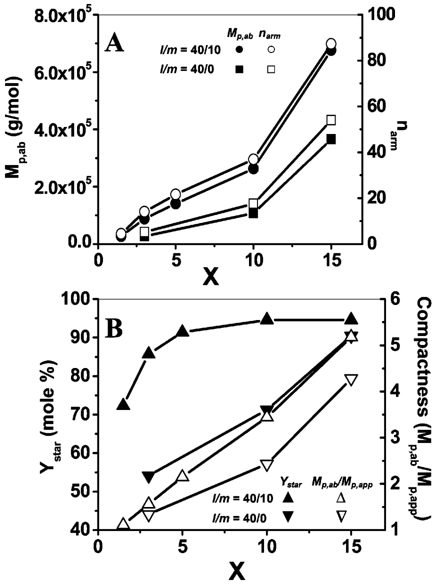


Figure 8. Effect of the chemical composition of star cores on the structures of star polymers synthesized via ATRP from the one-pot process or two-pot process (Table 1, entries S2, S6−S9 and Table 2, entries S10−S12).

Figure 8B shows that with the same amount of DVB the star with a copolymer core had a surprisingly denser structure because more linear chains were incorporated into each star molecule. Star yield was also significantly influenced by the star core composition. For stars with a core containing only DVB units, the star yield increased steadily with the amount of DVB added. In contrast, the yield of star polymers with a copolymer core composition initially increased very quickly as the amount of DVB increased and then increased much slower to a maximum value of 94.6 mol %. This was the highest star yield obtained.

When the amount of DVB added was $X = 3$, the star polymers from the one-pot and two-pot processes had the largest difference in their star yields: 86% vs 54%. Such a large difference indicates that changing the chemical composition of the star core via introduction of a monovinyl monomer during the core formation process significantly increased the star yield with the same amount of cross-linker and for the same length of arm precursor.

Conclusions

(PolytBA)$_n$-poly(DVB-*co*-tBA) star polymers were synthesized via ATRP using the "arm-first" method. First, polytBA linear MI chains were prepared using EBrP as initiator and CuBr/PMDETA as catalyst. At certain tBA conversions, instead of stopping the reaction and removing the unreacted tBA monomer, N_2-purged DVB was injected into the polymerization. The copolymerization of DVB and residual tBA monomers produced cross-linked microgel cores and formed star copolymers (one-pot process). The effect of the initial polytBA arm length (DP varied from 20 to 90), the time of DVB addition ($m = 0−20$), the amount DVB added to the core-forming copolymerization ($X = [\mathrm{DVB}]_0/[\mathrm{EBrP}]_0 = 1.5−15$), and the chemical composition of the star core (molar ratio of DVB to tBA for core formation) were systematically studied. The influence of these parameters on the molecular weight and molecular weight distribution of the star polymer, the average number of arms per star, the star yield, and star compactness was determined. The absolute molecular weight of the star polymers varied from 30 000 to 700 000 g/mol, and the average number of arms per star was varied from 5 to around 100. Up to 95% of the linear chains could be incorporated into star molecules, and the star structure could be varied from very loose to very dense ($M_{\mathrm{p,ab}}/M_{\mathrm{p,app}} = 1.2−5.2$). The star copolymer with a core containing both DVB and tBA units, from the one-pot process, had a higher star yield and higher star molecular weight when compared to the star copolymer with core containing the same amount of pure DVB units from the two-pot process. This confirmed that the introduction of monovinyl monomer units during the star core formation decreased the steric congestion of the core and facilitated the incorporation of more arms into each star molecule. All these results serve as valuable guidelines for the synthesis of other kinds of star polymers and ultimately in designing star polymers with more precise microstructure and composition.

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(41) The contraction factor of branched polymer ($g = \langle R_{g,br}^2 \rangle / \langle R_{g,lin}^2 \rangle$) 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 $\langle R_{g,br}^2 \rangle$ 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.

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