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Synthesis of Star Polymers by A New “Core-First” Method: Sequential Polymerization of Cross-Linker and Monomer

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ABSTRACT: Star polymers containing a highly cross-linked core and many arms were synthesized by sequential polymerization of cross-linker and monomer. This novel method, termed as “star from in situ generated core”, belongs to the category of “core-first” method and presents an alternative strategy for star synthesis when compared to the traditional “arm-first” method, in which monomer is polymerized first before cross-linker. To illustrate this new concept for the synthesis of star polymers by using controlled radical polymerization techniques, atom transfer radical polymerization was applied for homopolymerization of ethylene glycol diacrylate (EGDA) to generate a multifunctional cross-linked core (nanogel). At high cross-linker conversion, monovinyl monomers were added into the system and polymerized from the polyEGDA nanogel macroinitiator (MI) to form the star arms. By use of different acrylate monomers, including methyl acrylate, *n*-butyl acrylate, and *tert*-butyl acrylate, star polymers with different arm chemical compositions were successfully synthesized. Several parameters affected the star structures, such as the initial concentration of cross-linker, the molar ratio of cross-linker to initiator, and the addition moment of monovinyl monomer. The star polymers preserved the initiating sites at the chain ends, and they were further used as star MIs for arm extension by polymerization of a second monovinyl monomer to form a star block copolymer.

Introduction

Star polymers, containing multiple linear arms connected at a central branched core, represent one of the simplest nonlinear polymers.[1,2] As one of the most popular controlled radical polymerization (CRP)[3−6] techniques, atom transfer radical polymerization (ATRP)[7−10] has been widely used for synthesis of star polymers with controlled architecture, predetermined chemical composition, and multiple functionalities via one of three strategies: “core-first”,[11−15] “coupling-onto”,[16−19] and “arm-first”,[20−24] which differentiate from each other based on the formation sequence of core and arms.

The core-first method involves the use of a multifunctional initiator (core). The polymerization of monomer from the initiating sites on the preformed core generates a star molecule with preserved initiating site at the chain end of each arm, which can be further used for chain extension with a second monomer to form star block copolymers.[25−28] In the second coupling-onto method, a star polymer is synthesized by the coupling reactions between linear polymeric chains (arms) containing a reactive chain end group and a multifunctional coupling agent (core). Due to the slow reaction between the polymer chain end and the multifunctional core, an organic reaction with high coupling efficiency and benign experimental conditions is highly recommended. For example, the recently developed Cu(I)-catalyzed 2 + 3 cycloaddition reactions between an azide and an alkyne, i.e., “click reactions”,[29] have been used for synthesis of various kinds of star and miktoarm star polymers with predetermined structure and high star yield.[16−19,30]

In the third arm-first method, the linear arms of the star polymers are synthesized first followed by binding of the arms to form the core, usually by using a divinyl cross-linker. The resulting star polymers have a statistical distribution of the number of arms and a highly cross-linked core.[20−22,31] The preformed arms can be either linear macroinitiator (MI)[24] or macromonomer (MM).[32,33] The preserved initiating sites in the star cores can be further employed to initiate the polymerization of another monomer to form miktoarm star copolymers by the “in-out” method.[34−36] Recently, we further developed a simple and general arm-first method for synthesis of miktoarm star copolymers, i.e., one-pot cross-linking of a mixture of different linear MIs.[37] By use of this method, miktoarm star copolymers containing various molar ratios of arms and as many as five arm species with different chemical compositions were successfully synthesized.

It is worth noting that in the third arm-first method, monomer and cross-linker are sequentially polymerized and star polymers with various structures are synthesized by adjusting the addition moment of cross-linker and the molar ratios of monomer, cross-linker, and initiator.[24,31] In contrast, one-pot copolymerization of monomer and cross-linker under the same reagent ratios produces highly branched polymers or gels.[38−41] Such a result indicates that the polymerization sequence of monomer and cross-linker should have a significant influence on the polymer architectures. Polymerization of monomer before cross-linker results in starlike polymers with a cross-linked core, while copolymerization of monomer and cross-linker together generates branched polymers or gels. Following this logic, it is easy to imagine that the polymerization of cross-linker before monomer should also produce a starlike molecule.[42,43,47,48] Since a highly cross-linked core by homopolymerization of cross-linker is formed before the growth of arms, this synthetic strategy belongs to the category of core-first method. However, it is different from the traditional core-first method, in which the core containing multiple initiating sites is usually synthesized by separate organic reactions before polymerization. Therefore, we term this new method as “star from in situ generated core”.

The highly cross-linked cores (nanogels) containing multiple initiating sites in a statistical distribution are generated in situ

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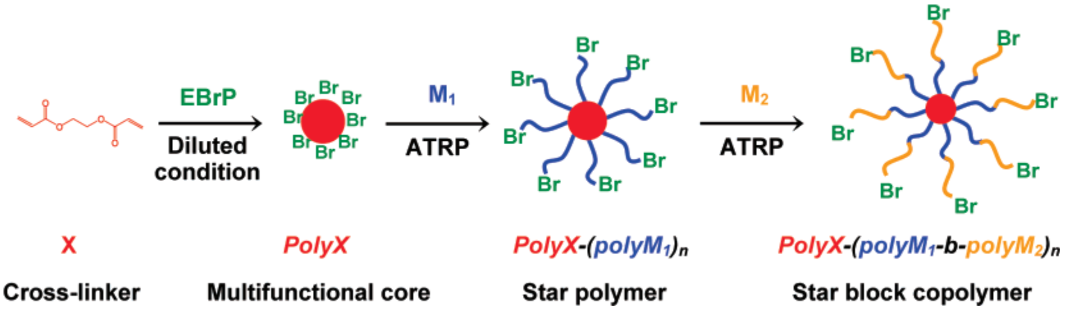
Scheme 1. Illustration for Synthesis of Star and Star Block Copolymers by the Star from in Situ Generated Core Method



by homopolymerization of divinyl cross-linker. On the basis of Flory−Stockmayer's theory,[44] when the molar concentration of reacted cross-linking units (cross-linker with both vinyl groups reacted) is larger than that of the primary chains in a system, the critical gel point of the system is reached and gelation should occur.[41] In order to prevent the macroscopic gelation, it is essential to enhance the intramolecular cyclization reactions rather than intermolecular cross-linking reactions by performing the polymerization in a diluted solution.[45] In such a way, highly cross-linked individual nanogels containing many initiating sites, such as alkyl halide, are generated in a homogeneous polymerization system (Scheme 1). At high cross-linker conversion, certain amount of monovinyl monomer (M_1) is added into the system. Polymerization of the monomer from the in situ generated core forms the linear arms and the star polymers, polyX−(polyM$_1$)$_n$, where polyX represents the in situ generated cross-linked core and n is the average number of polyM$_1$ arms per star molecule. The initiating sites preserved at the chain end of each arm can be further used for chain extension by polymerization of a second monomer (M_2) to form star block copolymers (Scheme 1). Compared to the star polymers synthesized from the traditional core-first method, this new strategy skips the tedious synthesis of the multifunctional initiator before polymerization. The structure of the formed star polymer is similar to the star synthesized by the traditional arm-first method because both of them contain a highly cross-linked core with statistically distributed arms. However, the arm-first method employs the polymerization of monomer before cross-linker, while the star from in situ generated core method applies the polymerization of cross-linker before monomer. It is worth noting that an alternative way to form a cross-linked multifunctional nanogel is copolymerization of monomer and cross-linker in a diluted solution,[46] although the incorporation of monovinyl monomer unit into the core decreases the core cross-link density and makes it more like a multifunctional branched polymer.

In this paper, we report the first synthesis of star polymers by using the star from in situ generated core method via CRP techniques. ATRP was applied for homopolymerization of a commercially available cross-linker, ethylene glycol diacrylate (EGDA), to generate the cross-linked core before the formation of arms. The multifunctional polyacrylate nanogels (polyEGDA) were used as MIs for polymerization of different acrylate monomers, including methyl acrylate (MA), *n*-butyl acrylate (BA), and *tert*-butyl acrylate (*t*BA), to form the star polymers with different arm chemical compositions. The star polymers with the preserved initiating sites at the chain ends were further used as star MIs for arm extension by polymerization of a second monomer to form star block copolymers.

Experimental Section

Materials. All monomers and cross-linker, including methyl acrylate (MA, 99%), *n*-butyl acrylate (BA, 99%), *tert*-butyl acrylate (*t*BA, 98%), and ethylene glycol diacrylate (EGDA, 90%), were purchased from Aldrich and purified twice by passing through a column filled with basic alumina to remove the inhibitor. CuBr (98%, Acros) was purified using a modified literature procedure.[35] All other reagents: ethyl 2-bromopropionate (EBrP), *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 PolyEGDA−(PolyM)$_n$ Star Polymers with Various Structures and Arm Compositions via ATRP Using the Star from in Situ Generated Core Method. A typical procedure for synthesis of polyEGDA-(polyMA)$_n$ star polymers is briefly described as follows starting with the ratio of reagents [MA]$_0$/[EGDA]$_0$/[EBrP]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 50/1.5/1.0/0.45/0.05/0.5. A clean and dry Schlenk flask was charged with EGDA (0.202 mL, 1.17 mmol of cross-linker given the purity of EGDA as 90%), PMDETA (0.081 mL, 0.39 mmol), and 2.7 mL DMF. The flask was degassed by five freeze−pump−thaw cycles. During the final cycle, the flask was filled with nitrogen before CuBr (50.2 mg, 0.35 mmol) and CuBr$_2$ (8.7 mg, 0.039 mmol) were quickly added to the frozen mixture. The flask was sealed with a glass stopper and then evacuated and back-filled with nitrogen five times before it was immersed in an oil bath at 60 °C. The N$_2$-bubbled initiator EBrP (0.101 mL, 0.78 mmol) was injected into the reaction system, via a purged syringe, through the side arm of the Schlenk flask. At 1 h, N$_2$-purged MA (3.5 mL, 38.9 mmol) was injected into the reaction system. At timed intervals, samples were withdrawn via a syringe for measurements of monomer conversions and polymer molecular weights by gas chromatograph (GC) and gel permeation chromatography (GPC), respectively. The reaction was stopped after 46 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 (PolyMA)$_n$−PolyEGDA Star Polymers by Using the Arm-First Method. PolyMA−Br linear chains ($M_{n,theor}$ = 3620 g/mol, degree of polymerization (DP) = 40, M_w/M_n = 1.07) were synthesized by ATRP at 60 °C with the ratio of reagents as [MA]$_0$/[EBrP]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 50/1.0/0.45/0.05/0.5. At ca. 80% MA conversion, the reaction was stopped and the purified linear chains were used as MIs for formation of (polyMA)$_n$−polyEGDA star polymers by using the previously published procedures.[21] The molar ratio of the reagents during star synthesis was [polyMA- Br]$_0$/[EGDA]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 1.0/1.5/0.45/0.05/0.5, and the reaction was conducted at 60 °C for 46 h.

Synthesis of PolyEGDA−(PolyBA-*b*-Poly*t*BA)$_n$ Star Block Copolymers by Using PolyEGDA−(PolyBA−Br)$_n$ Stars as MIs. After precipitation into cold methanol to remove the unincorporated linear polyBA chains, the purified polyEGDA-(polyBA−Br)$_n$ star polymers, with preserved bromine chain end functionalities, were used as MIs for the ATRP of another monomer, *t*BA, to synthesize star block copolymers. The theoretical number of initiating sites per star MI was equal to the average number of arms per star. The experimental procedures for polymerization of *t*BA was similar to those for synthesis of polyEGDA−(polyMA)$_n$ star polymers. The composition of reaction mixture for synthesis of polyEGDA−(polyBA-*b*-poly*t*BA)$_n$ star block polymers is: purified polyEGDA−

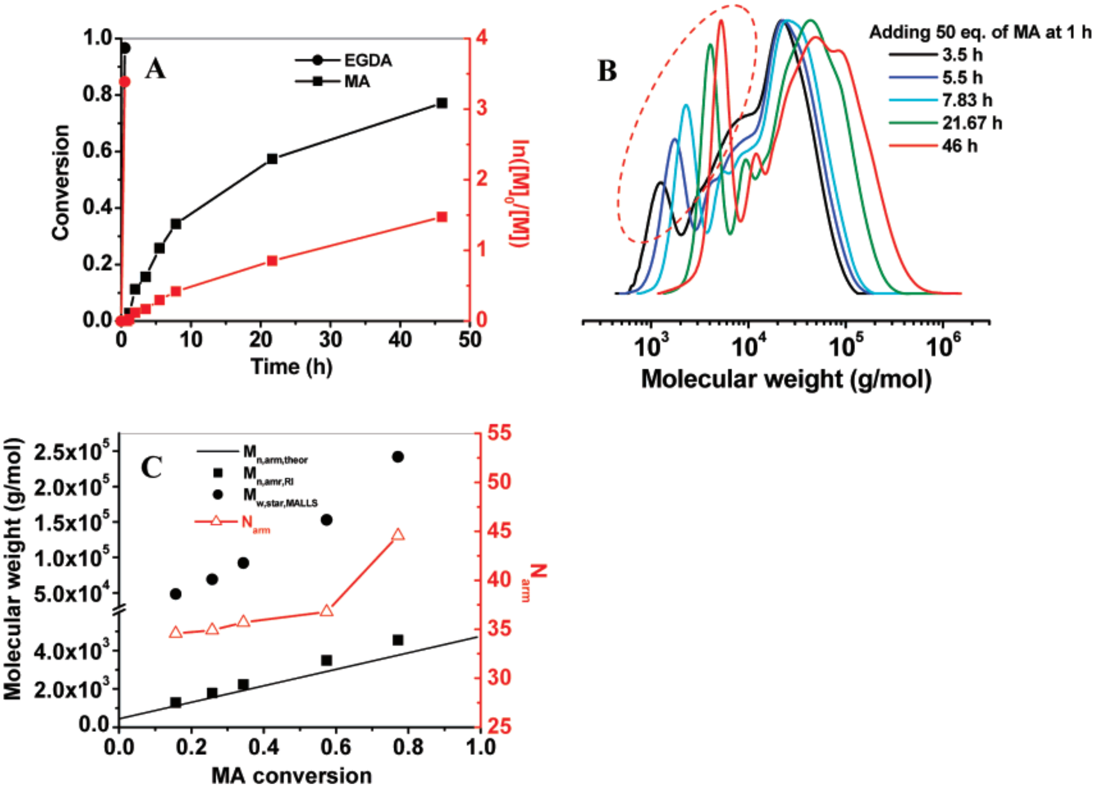


Figure 1. (A) Dependence of conversion and ln([M]$_0$/[M]) of EGDA and MA on reaction time, (B) evolution of GPC traces, and (C) molecular weights and averaged arm numbers per star molecule (N_{arm}) during synthesis of polyEGDA−(polyMA)$_n$ star polymers by sequential polymerization of EGDA and MA via ATRP. Experimental conditions: [MA]$_0$/[EGDA]$_0$/[EBrP]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[PMDETA]$_0$ = 50/1.5/1.0/0.45/0.05/0.5 in DMF at 60 °C, [EGDA]$_0$ = 0.39 M, and N$_2$-deoxygenated MA was added at 1 h. Linear polyMMA standards were used for GPC calibration in THF (Table 1).

(polyBA−Br)$_n$ star MI (0.3 g, 72.1 μmol of alkyl bromide initiating sites given $M_{n,arm,RI}$ = 4160 g/mol, M_w/M_n (arm, RI) = 1.18), *t*BA (3.17 mL, 21.6 mmol), PMDETA (22.6 μL, 108.2 μmol), anisole (1.1 mL), CuBr (14.0 mg, 97.4 μmol), and CuBr$_2$ (2.4 mg, 10.8 μmol). The reaction was conducted at 65 °C for 21 h. Samples were withdrawn periodically for GC and GPC measurements to determine monomer conversions and polymer molecular weights, respectively.

Characterization. Monomer conversions were determined from the concentration of the unreacted monomer in the samples periodically removed from the reactions and determined 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). DMF or anisole was used as the 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 as eluent at 35 °C, flow rate = 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410)). The apparent molecular weights ($M_{n,RI}$ and $M_{w,RI}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) (polyMMA) or 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. The values of refractive index increment (*dn/dc*) of star polymers were measured in THF at 35 °C by using a refractometer. Absolute molecular weights were determined using ASTRA software from Wyatt Technology.

Results and Discussion

For a successful synthesis of star polymers by using the star from in situ generated core method, a prerequisite is that no macroscopic gelation should occur during the homopolymerization of cross-linker. Then, a large amount of monovinyl monomer can be added when most of the cross-linkers and pendant vinyl groups are consumed (e.g., high cross-linker conversion). In the first screening experiment, a commercially available divinyl cross-linker, EGDA, was homopolymerized under a diluted condition to form a highly cross-linked multifunctional nanogel core without macroscopic gelation. At high EGDA conversion, MA was added into the system to grow polyMA arms from the in situ generated multifunctional core (Scheme 1).

Synthesis of PolyEGDA−(PolyMA)$_n$ Star Polymers via ATRP Using the Star from in Situ Generated Core Method. Figure 1A−C and Table 1 summarize the results during the synthesis of polyEGDA−(polyMA)$_n$ star polymers with [MA]$_0$/[EGDA]$_0$/[EBrP]$_0$/[CuBr]/[CuBr$_2$]/[PMDETA] = 50/1.5/1.0/0.45/0.05/0.5. At first, 1.5 equiv of EGDA (0.2 mL) was homopolymerized by ATRP in 2.7 mL DMF ([EGDA]$_0$ = 0.39 M). Although the molar ratio of cross-linker to initiator was larger than 1, no macroscopic gelation occurred at high EGDA conversion due to the significant intramolecular cyclization reactions under diluted condition. The conversion of EGDA reached 97% at 30 min, determined by GC analysis of the unreacted EGDA (Figure 1A). Incorporation of EGDA to a growing polymer chain consumes one vinyl group and generates one pendant vinyl group. The latter can react with a propagating radical by either intramolecular cyclization reaction or intermolecular cross-linking reaction. To ensure that most of the pendant vinyl groups were consumed before the addition of the

Table 1. Synthesis of PolyEGDA−(PolyMA)$_n$ Star Polymers by Using the Star from in Situ Generated Core Method[a]

time (h)	conversion$_{\mathrm{MA}}$[b]	$M_{\mathrm{n,arm,theor}}$ (g/mol)[c]	$M_{\mathrm{n,arm,RI}}$ (g/mol)[d]	$M_{\mathrm{w,arm,RI}}$ (g/mol)[d]	$M_{\mathrm{n,arm,RI}}$/ $M_{\mathrm{n,arm,theor}}$	$M_{\mathrm{w,star,RI}}$ (g/mol)[d]	$M_{\mathrm{w,star,MALLS}}$ (g/mol)[e]	$M_{\mathrm{w}}/M_{\mathrm{n}}$ (star)[d]	A_{star}[f]	N_{arm}[g]
2.0	0.11	920								
3.5	0.16	1110	1280	1400	1.15	18 500	48 400	2.07	0.84	34.6
5.5	0.26	1550	1780	1980	1.15	22 100	69 100	1.98	0.80	34.9
7.8	0.34	1920	2230	2580	1.16	29 900	92 100	1.96	0.78	35.7
21.7	0.57	2910	3480	4160	1.20	49 700	153 000	1.97	0.77	36.8
46.0	0.77	3760	4540	5430	1.21	74 900	242 000	2.45	0.76	44.6

[a] Experimental conditions: $[\mathrm{MA}]_0/[\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr}_2]_0/[\mathrm{PMDETA}]_0 = 50/1.5/1.0/0.45/0.05/0.5$ in DMF at 60 °C, initial $[\mathrm{EGDA}]_0 = 0.39$ M, addition of MA (3.5 mL) at 1.0 h with $[\mathrm{MA}]_0 = 6.0$ M. Linear polyMMA standards were used for GPC calibration in THF. [b] Monomer conversion determined by GC analyses. [c] Theoretical molecular weight of linear polyMA chains (arms): $M_{\mathrm{n,arm,theor}} = [\mathrm{MA}]_0/[\mathrm{EBrP}]_0 \times \mathrm{Conversion}_{\mathrm{MA}} \times \mathrm{MW}_{\mathrm{MA}} + \mathrm{MW}_{\mathrm{EBrP}} + 1.5 \times \mathrm{MW}_{\mathrm{EGDA}}$. [d] Apparent number-average and weight-average molecular weights and polydispersity of linear and star polymers measured by GPC in THF with RI detector (calibration with linear polyMMA as standard). [e] Weight-average molecular weight of star polymers measured by GPC in THF with MALLS detector. [f] Area fraction of star polymers determined by the multi-peak splitting of the GPC curve using Gaussian function. [g] Number-average value of the number of arms per star $N_{\mathrm{arm}} = M_{\mathrm{w,star,MALLS}}/M_{\mathrm{w,arm,RI}}$.

monovinyl monomer, the reaction was left for an additional 30 min before 50 equiv of N_2-deoxygenated MA (3.5 mL) was injected into the system to start the star formation.

Figure 1A shows that the conversion of MA increased with reaction time and reached 77% after 46 h. The semilogarithmic plot is slightly curved, suggesting a slight decrease of radical concentration in the system with the reaction time. Figure 1B shows the GPC traces of the polymer product, in which two or more peaks were observed and were shifted to higher molecular weight with increasing reaction time. The broad high-molecular-weight GPC peak represents the star polymers growing from the multifunctional nanogel MIs. The apparent polydispersity of the star polymers was around $M_{\mathrm{w}}/M_{\mathrm{n}} = 2.0$, which reflected the broad size distribution of the nanogel cores. The narrowly distributed low-molecular-weight GPC peak represents linear polyMA chains, originating from the free single initiating sites (red circle in Figure 1B). The molecular weight distribution of the linear polyMA was symmetric and the polydispersity was low, indicating a good control of the linear polymers in the system. The apparent molecular weights of the linear polyMA polymers ($M_{\mathrm{n,arm,RI}}$), determined by GPC in THF with RI detector and linear polyMMA as standards, were higher than the theoretical molecular weights of the linear chains (arms) ($M_{\mathrm{n,arm,theor}}$), calculated from MA conversions (Figure 1C and Table 1). The ratio of $M_{\mathrm{n,arm,RI}}/M_{\mathrm{n,arm,theor}}$ was around 1.21 at 46 h, indicating that 83% (1/1.21) of the added EBrP started linear polyMA chains and/or arms. The area fraction of the star polymers (A_{star}) slightly decreased with reaction time, according to the multipeak splitting of the GPC curves using Gaussian function.[16]

As discussed above, the slightly curved semilogarithmic plot of MA (Figure 1A) was plausibly due to the occurrence of radical coupling reactions. Since star polymers contain more initiating sites than their linear counterparts, the possibility of star−star radical coupling is higher than that of star−linear radical coupling and linear−linear radical coupling. The star−star radical coupling reactions decreased the average number of initiating sites per star molecule and resulted in a slight decrease of A_{star} with reaction time from $A_{\mathrm{star}} = 0.84$ at 3.5 h to $A_{\mathrm{star}} = 0.76$ at 46 h (Table 1).

An important parameter determining the structure of star polymers is the number-average value of the number of arms per star molecule (N_{arm}). Since the cross-linked polyEGDA star core was formed in situ by random coupling of various numbers of primary chains, the accessible number of initiating sites per star core is unknown. In order to determine the value of N_{arm} for star polymers at different times, a linear polyMA standard is needed, which should exist in the system from the beginning and grow at the same pace as the star arms. Fortunately, the coexisting linear polyMA chains, originated from the free monofunctional initiating site, served as such a standard and helped us calculate the averaged arm number per star molecule based on the ratio of $N_{\mathrm{arm}} = M_{\mathrm{w,star,MALLS}}/M_{\mathrm{w,arm,RI}}$, where $M_{\mathrm{w,star,MALLS}}$ and $M_{\mathrm{w,arm,RI}}$ are the weight-average molecular weights of the star polymer determined by GPC in THF with MALLS detector and the linear polymer determined by GPC in THF with RI detector, respectively.

In Figure 1C, the absolute molecular weights of star molecules increased with MA conversions, indicating the growth of the star polymers. Due to the compact structure of the star polymers, the value of $M_{\mathrm{w,star,MALLS}}$ was larger than the apparent molecular weight of star polymers ($M_{\mathrm{w,star,RI}}$). The averaged arm number per star molecule (N_{arm}) was almost unchanged when MA conversion was below 57% at 22 h and increased significantly when MA conversion reached 77% (Table 1). The change of N_{arm} values with MA conversions was mainly ascribed to the star−star coupling reactions although the possibility of star−linear coupling reactions cannot be completely excluded. The star−star coupling reactions include intrastar coupling and interstar coupling reactions, in which only the latter one has contribution to the increase of N_{arm} value. The evolution of N_{arm} values in Figure 1C indicates that intrastar coupling reactions should be more significant than interstar coupling reactions at low MA conversions because the value of N_{arm} was almost unchanged when MA conversion was below 57%. In contrast, interstar coupling became more dominant at high conversions, resulting in a sharp increase of N_{arm} value. This hypothesis is further supported by the change of the apparent polydispersity of star polymers ($M_{\mathrm{w}}/M_{\mathrm{n}}$) with MA conversions. The polydispersity of the star molecule was around $M_{\mathrm{w}}/M_{\mathrm{n}} = 2$ when MA conversion was below 57% but reached $M_{\mathrm{w}}/M_{\mathrm{n}} = 2.45$ at $\mathrm{conversion}_{\mathrm{MA}} = 77\%$ (Table 1), indicating the occurrence of more interstar coupling reactions at high MA conversion.

Figure 2 compares the structural compactness of the two polyMA-based star polymers synthesized using different methods: polyEGDA−(polyMA)$_n$ star polymers synthesized by the star from in situ generated core method (polymerization of cross-linker before monomer) and (polyMA)$_n$−polyEGDA star polymers synthesized by the traditional arm-first method (polymerization of monomer before cross-linker). Without further fractionation for removal of linear chains, the two star polymers were analyzed by GPC with MALLS detector. The star polymers were separated based on hydrodynamic volume, and each eluate slice was analyzed by MALLS detector to determine the absolute molecular weight ($M_{\mathrm{w,MALLS}}$). Since the light scattering detector is more sensitive to high molecular weight polymers, the unincorporated linear polymers with low molecular weight became less visible in the GPC curves when compared to the

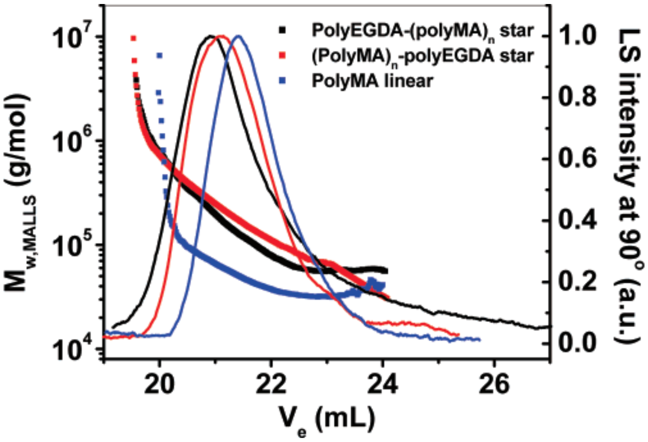


Figure 2. Absolute molecular weights (squares, $M_{w,MALLS}$) and 90° light scattering intensity (lines) as function of elution volume (V_e) for various polyMA-based polymers with different structures: polyEGDA−(polyMA)$_n$ star polymers (Table 1, 46.0 h) synthesized by the star from in situ generated core method (black), (polyMA)$_n$−polyEGDA star polymers synthesized by the arm-first method (red), and polyMA linear polymers ($M_{n,theor}$ = 32 400 g/mol) synthesized by normal ATRP of MA (blue). Both star polymers contained polyMA arms with DP ca. 40 and a polyEGDA core with $[EGDA]_0/[EBrP]_0 = 1.5$ (detailed conditions were described in the Experimental Section).

GPC results in Figure 1, where RI detector was used. At a given elution volume V_e (same hydrodynamic volume), polymers with higher molecular weight have a more compact structure. It is seen in Figure 2 that both star polymers had similar structural compactness because, at a given V_e value, both of them had similar molecular weight, which is larger than the value of the polyMA linear counterpart. These results indicate that starting from the same molar ratio of $[MA]_0/[EGDA]_0/[EBrP]_0 = 50/1.5/1$ the polymerization of either the cross-linker before monomer or the cross-linker after monomer produced starlike polymers with similar structural compactness. Both star polymers had a highly cross-linked core and many radiating arms.

Synthesis of PolyEGDA−(PolyM)$_n$ Star Polymers with Various Structures and Arm Compositions by Using the Star from in Situ Generated Core Method. Several parameters can be adjusted during the synthesis of polyEGDA−(polyM)$_n$ star polymers, including the initial concentration of EGDA, the molar ratio of EGDA to EBrP, and the addition moment of the monovinyl monomer. PolyEGDA−(PolyM)$_n$ star polymers with different structures were synthesized by changing these parameters, and the results are summarized in Table 2.

As discussed above, before the addition of monomer, the conversion of EGDA should be high and no macroscopic gelation should occur. A proper selection of the initial concentration of EGDA and the molar ratio of EGDA to EBrP is necessary to prevent the macroscopic gelation during EGDA homopolymerization. Low molar ratio of $[EGDA]_0/[EBrP]_0$ decreases the number of pendant vinyl groups per primary chain and effectively prevents the gelation based on Flory−Stockmayer theory. Diluted conditions enhance the intramolecular cyclization and suppress the intermolecular coupling during the reaction of pendant vinyl groups with radicals. It is shown in Table 2 that when the initial concentration of EGDA was $[EGDA]_0$ = 0.78 M with $[EGDA]_0/[EBrP]_0 = 3/1$ gelation occurred at 25 min with 78% EGDA conversion (entry 1). When either the value of $[EGDA]_0$ or the ratio of $[EGDA]_0/[EBrP]_0$ was decreased, such as $[EGDA]_0$ = 0.39 M and/or $[EGDA]_0/[EBrP]_0 = 1.5/1$ (entries 2−4 in Table 2), no macroscopic gelation occurred with essentially 100% EGDA conversion, which satisfied the prerequisite for the subsequent addition of MA into the system for synthesis of polyEGDA−(polyMA)$_n$ star polymers.

When the initial molar ratio of EGDA and EBrP was fixed at $[EGDA]_0/[EBrP]_0 = 1.5/1$, a higher concentration of EGDA ($[EGDA]_0$ = 0.78 M, entry 2 in Table 2) resulted in star polymers with higher molecular weight, broader molecular weight distribution, and more arms per star molecule when compared to the reaction with $[EGDA]_0$ = 0.39 M (entry 4, Table 2). Additionally, the effect of molar ratio of $[EGDA]_0/[EBrP]_0$ on the structures of the star polymers was studied when the initial concentration of EGDA was kept unchanged at $[EGDA]_0$ = 0.39 M. The results indicate that decreasing the molar ratio of $[EGDA]_0/[EBrP]_0$ from 3.0 to 1.5 (by doubling the $[EBrP]_0$ value) increased the polymerization rate of MA in entry 4 because more initiator EBrP was used. However at similar MA conversions, the polyEGDA−(polyMA)$_n$ star polymers under the condition of $[EGDA]_0/[EBrP]_0 = 1.5$ (entry 4) had a lower molecular weight and less arms per star molecule than the stars obtained under $[EGDA]_0/[EBrP]_0 = 3.0$ (entry 3). Thus, homopolymerization of EGDA with higher amount of EBrP produced polyEGDA nanogels containing less initiating sites in each nanogel MI. In other words, at a constant amount of EGDA cross-linker, increasing the EBrP amount generated more polyEGDA nanogel cores but decreased the size of the nanogels. As a result, the star polymers growing from the nanogel MI with smaller size contained fewer arms.

The addition moment of MA also had an influence on the structures of the obtained polyEGDA−(polyMA)$_n$ star polymers. Compared to the star polymers in entry 4, addition of the same amount of MA at a later stage (3 h) slowed down the MA polymerization and produced star polymers with lower molecular weight and fewer arms per star molecule (entry 5, Table 2), which is probably due to more intracore radical coupling reactions and less accessible initiating sites in the system when MA was added later in the reaction. It is worth noting that during the synthesis of star polymers by using the star from in situ generated core method a small fraction of linear polymers was always detected in the star product. As discussed above, the existence of the linear counterpart was crucial for us to calculate the averaged arm number per star molecule.

To expand the chemical compositions of the star polymers synthesized by this new method, other monomers, in addition to MA, were used for the growth of arms from the in situ generated multifunctional polyEGDA core. Since the polyEGDA nanogels contained polyacrylate chain end initiating sites, two kinds of acrylate monomers, BA and *t*BA, were employed. The results in Table 2, entries 6 and 7, show that by using a molar ratio of $[M]_0/[EGDA]_0/[EBrP]_0 = 50/2.0/1$, polyEGDA−(poly-*t*BA)$_n$ and polyEGDA−(polyBA)$_n$ star polymers were successfully produced. On the addition of *t*BA monomer at 1 h, the conversion of *t*BA reached 59% at 77 h. The absolute molecular weight of the obtained polyEGDA−(poly*t*BA)$_n$ star polymers is $M_{w,star,MALLS}$ = 286 000 g/mol and the averaged arm number per star is N_{arm} = 45.8 (entry 6, Table 2). Similar results were obtained during the synthesis of polyEGDA−(polyBA)$_n$ star polymers. After addition of BA monomer at 1 h, the conversion of BA increased with reaction times and reached 48% at 47 h (Figure 3A). The reaction was purposely stopped at low BA conversion in order to minimize the star−star coupling reactions. The GPC curves of the star polymers steadily shifted in the higher molecular weight direction with the increase of BA conversions (Figure 3B). The GPC molecular weight values of the linear polyBA arms are close to the theoretical values, indicating that 85% of the initially added EBrP initiator were

Table 2. Summary of PolyEGDA-(PolyM)$_n$ Star Polymers Synthesized by Using the Star from in Situ Generated Core Method[a]

entry	$[EGDA]_0$ (mol/L)[b]	X/Br	M	M addition moment (h)[c]	$conversion_M$ (time)[d]	$M_{w,arm,RI}$ (g/mol)[e]	$M_{w,star,MALLS}$ (g/mol)[f]	A_{star}[g]	M_w/M_n[e] (star)	N_{arm}[h]
1	0.78	3.0/1	MA	*i*						
2	0.78	1.5/1	MA	1	0.69 (41 h)	4550	389 000	0.75	2.77	85.5
3	0.39	1.5/0.5	MA	1	0.71 (68 h)	9130	607 000	0.81	2.47	66.5
4	0.39	1.5/1	MA	1	0.77 (46 h)	5430	242 000	0.76	2.45	44.6
5	0.39	1.5/1	MA	3	0.45 (68 h)	3440	119 000	0.82	2.01	34.6
6	0.39	2.0/1	*t*BA	1	0.59 (77 h)	6250	286 000	0.81	1.98	45.8
7	0.39	2.0/1	BA	1	0.48 (47 h)	4780	205 000	0.80	1.86	42.9

[a] Experimental conditions: $[M]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/Br/0.45/0.05/0.5$, in DMF at 60 °C. [b] Initial concentration of EGDA in the system. [c] Addition moment of M, when the conversion of EGDA was higher than 97%. [d] The final conversion of M and reaction time. [e] Apparent weight-average molecular weight of linear chains and apparent polydispersity of star polymers, measured by THF GPC with RI detector, calibration with linear polyMMA as standard for polyEGDA−(polyMA)$_n$ star polymers and linear polySt standards for others. [f] Weight-average molecular weight of star polymers, measured by THF GPC with MALLS detector. [g] Area fraction of star polymers, determined by the multi-peak splitting of the GPC curve using Gaussian function. [h] Number-average value of the number of arms per star $N_{arm} = M_{w,star,MALLS}/M_{w,arm,RI}$. [i] Gelation occured at 25 min with 78% EGDA conversion.

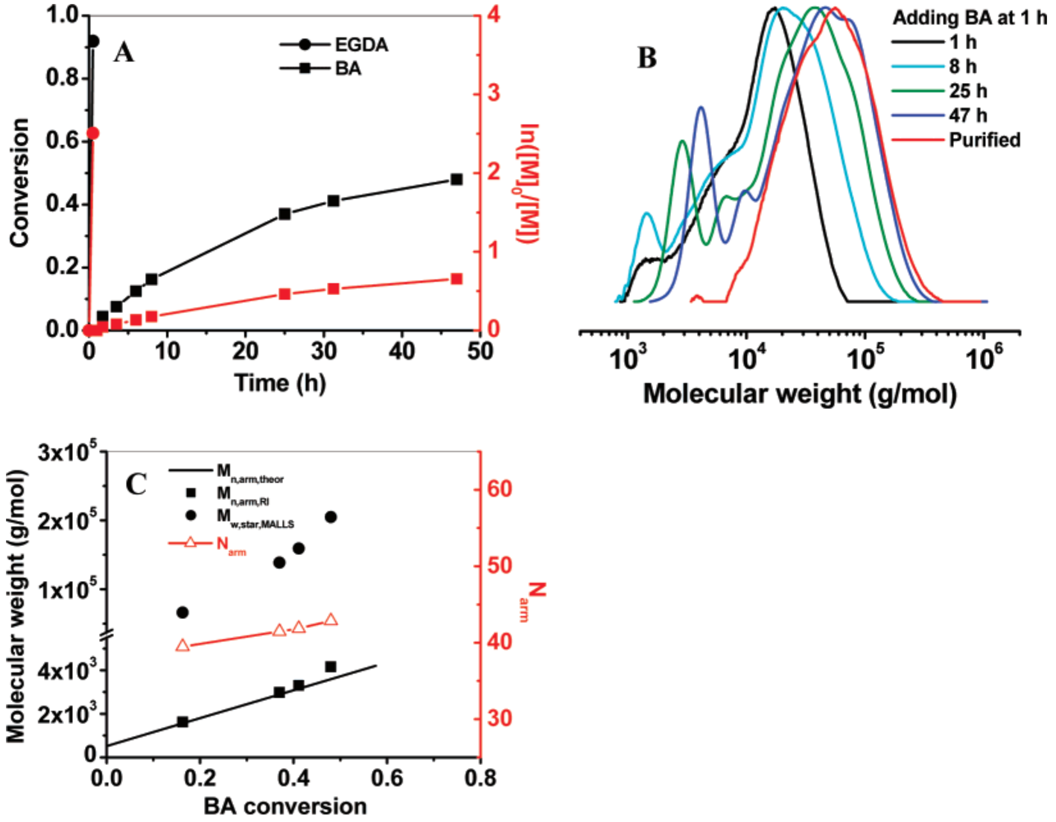


Figure 3. (A) Dependence of conversion and $\ln([M]_0/[M])$ of EGDA and BA on reaction time, (B) evolution of GPC traces, and (C) molecular weights and averaged arm numbers per star molecule (N_{arm}) during synthesis of polyEGDA-(polyBA)$_n$ star polymers by sequential polymerization of EGDA and BA via ATRP (entry 7, Table 2). Experimental conditions: $[BA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/2.0/1/0.45/0.05/0.5$ in DMF at 60 °C, $[EGDA]_0 = 0.39$ M, and N_2-deoxygenated BA was added at 1 h. Linear polySt standards were used for GPC calibration in THF.

grown into arms and/or linear chains (Figure 3C). On the basis of the ratio of $N_{arm} = M_{w,star,MALLS}/M_{w,arm,RI}$, the star polymers at 47 h contained an averaged arm number $N_{arm} = 42.9$. After purification of the star polymers by precipitation into cold methanol to remove the free polyBA linear chains (Figure 3B), the polyEGDA−(polyBA)$_n$ star polymers were used as star MIs for polymerization of a second monomer to synthesize star block copolymers.

Synthesis of PolyEGDA−(PolyBA-*b*-Poly*t*BA)$_n$ Star Block Copolymers. The star polymers synthesized by using the star from in situ generated core method should contain bromine functionality at the end of each radiating arm. Polymerization of a second monomer from the bromine initiating sites should produce star polymers with segmented arm compositions. As an example, the purified polyEGDA−(polyBA)$_n$ star polymers were used as MIs for the polymerization of *t*BA. The number-average molecular weight of the polyBA arms in the star MI was $M_{n,polyBA} = 4160$ g/mol, and the average number of bromine functionalities per star MI was assumed to be the same as the number of arms. Figure 4 shows the results obtained during the synthesis of polyEGDA−(polyBA-*b*-poly*t*BA)$_n$ star block copolymers by ATRP of *t*BA from polyEGDA−(polyBA)$_n$ star MIs.

With the target DP of poly*t*BA block as $DP_{0,tBA} = [tBA]_0/[\text{initiating sites}]_0 = 300/1$, the conversion of *t*BA increased with reaction time and reached 38% when the reaction was stopped at 21 h (Figure 4A). The GPC curves of the polymer product shifted in the higher molecular weight direction, indicating the formation of star block copolymers (Figure 4B). The weight-averaged molecular weights of the star block copolymers, determined by GPC with RI detector ($M_{w,star,RI}$) and MALLS detector ($M_{w,star,MALLS}$), increased with *t*BA conversions, and

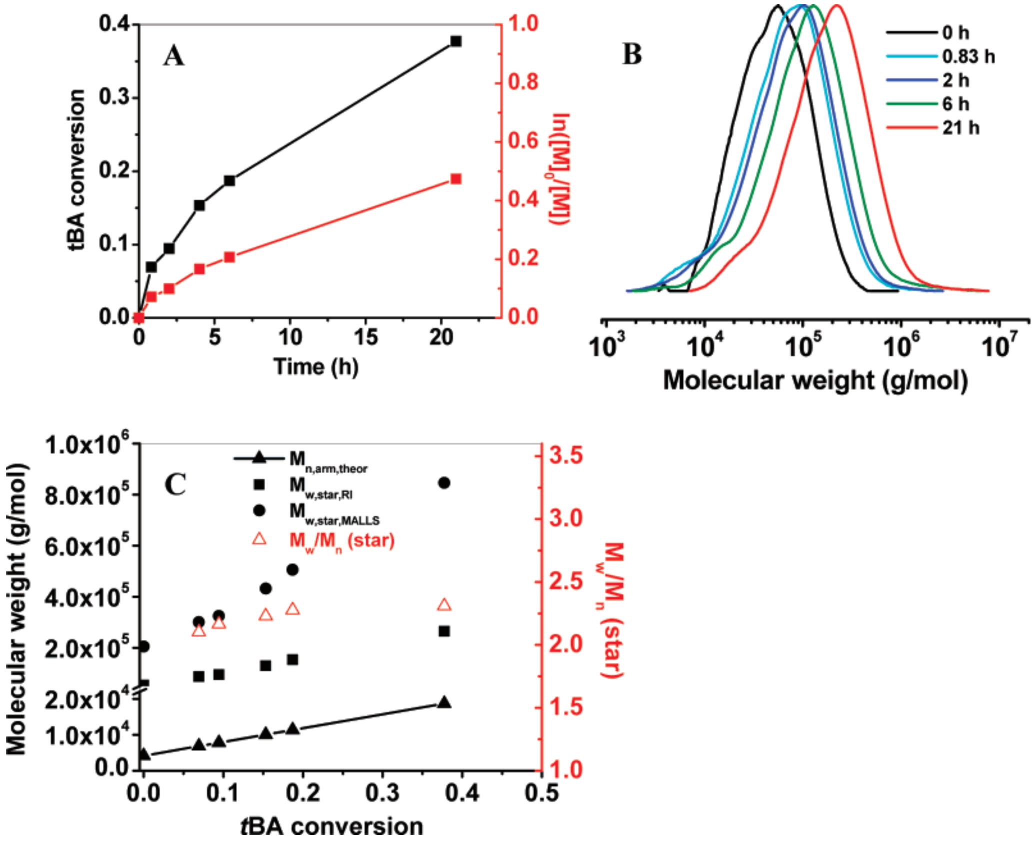


Figure 4. (A) Dependence of *t*BA conversion and $\ln([M]_0/[M])$ on reaction time, (B) evolution of GPC traces, and (C) molecular weights and molecular weight distribution during synthesis of polyEGDA−(polyBA-*b*-poly*t*BA)$_n$ star block copolymers by ATRP of *t*BA from polyEGDA−(polyBA)$_n$ star MIs. Experimental conditions: $[t\text{BA}]_0/[\text{initiating sites}]_0/[\text{CuBr}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 300/1.0/1.35/0.15/1.5$ in anisole at 65 °C, $[t\text{BA}]_0 = 4.73$ M. Linear polySt standards were used for GPC calibration in THF.

the apparent polydispersity of star polymers was $M_w/M_n = 2.31$ after 21 h (Figure 4C). The absolute molecular weight of the star block copolymer at 21 h was $M_{w,\text{star,MALLS}} = 846\,000$ g/mol, which is higher than the apparent weight-average molecular weight $M_{w,\text{star,RI}} = 264\,000$ g/mol due to the compact structure of the star block copolymers. The theoretical molecular weight of an arm in the star block copolymer was calculated as $M_{n,\text{arm,theor}} = M_{n,\text{polyBA}} + \text{DP}_{0,t\text{BA}} \times \text{conversion}_{t\text{BA}} \times \text{MW}_{t\text{BA}}$, where $\text{DP}_{0,t\text{BA}} = 300$ and $\text{MW}_{t\text{BA}} = 128.17$ (the molecular weight of *t*BA monomer). Thus, the averaged arm number per star block copolymer is $N_{\text{arm}} = M_{w,\text{star,MALLS}}/M_{n,\text{arm,theor}} = 45.3$, which is in agreement with the averaged arm number in polyEGDA−(polyBA)$_n$ star MI ($N_{\text{arm}} = 42.9$).

Conclusions

In this paper, a new method, termed as star from in situ generated core, was presented for the synthesis of star polymers containing a highly cross-linked core and many radiating arms by using ATRP technique. Compared to the traditional arm-first method, in which monomer is polymerized before cross-linker, the new strategy employed the initial polymerization of cross-linker. To illustrate the concept, ATRP was used for homopolymerization of ethylene glycol diacrylate (EGDA) under diluted conditions to form a multifunctional cross-linked polyEGDA core before the formation of star arms. At high conversion of the cross-linker, large amount of monomers was injected into the reaction system, and the multifunctional nanogels were used as MIs for polymerization of different acrylate monomers to form the star polymers with various arm chemical compositions. The star polymers synthesized by the star from in situ generated core method had a similar compactness to those from the traditional arm-first method. However, in contrast to the star polymers formed by the arm-first method, which contain dormant initiating sites at the star core, the star polymers produced by the new method preserved the initiating sites at the chain ends in the star periphery and were used as star MIs for arm extension to form star block copolymers. These results expanded the range of methodology for star synthesis and illustrated that polymerization of either the cross-linker first or monomer first can produce starlike polymers.

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