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Synthesis of Novel Star Polymers with Vinyl-Functionalized Hyperbranched Core via "Arm-First" Strategy

Zhong-min Dong,[†,‡] Xiao-hui Liu,*[,§] He-wen Liu,[⊥] and Yue-sheng Li*[,†]

[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China, [‡]Graduate School of the Chinese Academy of Sciences, Changchun Branch, [§]School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300160, China, and [⊥]Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

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ABSTRACT: Star polymers bearing vinyl-functionalized hyperbranched cores were successfully prepared at moderate-to-high monomer conversions (*ca.* 80%) via a modified "arm-first" strategy. This was achieved by reversible addition−fragmentation chain transfer polymerization of a methacrylate type asymmetrical divinyl monomer with thiobenzoate-capped polystyrenes as macro-chain-transfer agents (Macro-CTAs). Neither intermolecular nor intramolecular cross-linking occurred up to high levels of monomer conversion. The molecular weights (MWs) of Macro-CTAs significantly influence the structures of the resultant star polymers. A lower-MW Macro-CTA favors the formation of a star copolymer bearing big core and multiple short arms, whereas a higher-MW one is confined to the architecture bearing small core with only a few long arms. Moreover, the ca. 70% pendant vinyl groups remained in the hyperbranched core can be directly modified using reactions such as epoxidation and UV initiated thiol−ene addition reactions, resulting in star polymers with various functional groups in the core.

Introduction

A star polymer possessing multiple arms connecting at a central core is one of the simplest forms of branched topologies. Owing to their special globular shape, core−shell microstructure and multiple chain-end functionalities, star polymers have been applied in a variety of fields, from engine oils, coatings, contact lenses to catalysis and drug delivery systems.[1−4] Basically, the methods toward producing star polymers can be divided into three classes:[1,5,6] (i) the "core-first" approach by grafting arms from a multifunctional initiator; (ii) the "coupling-onto" approach by attaching the linear arm precursors onto a multifunctional core; and (iii) the "arm-first" approach by copolymerizing a macroinitiator or a macromonomer with a divinyl comonomer. Among them, the "arm-first" approach are the most promising, as evidenced by generating multiarm star polymers with numerous arms and a statistic distribution of arm number (n_{arm}) per star molecule. Moreover, concerning its facile route as well as better control of arm length, this approach has been attracting considerable attention for years.

The "arm-first" strategy was first developed in the context of living anionic polymerization early in 1968,[7] followed by the preparation of core cross-linked star polymers by group transfer polymerization.[8−15] With the blossom of controlled/living radical polymerization since 1990s, the "arm-first" methodology has been successfully extended to atom transfer radical polymerization,[16−29] reversible addition−fragmentation chain transfer (RAFT) polymerization[30−34] and nitroxide-mediated polymerization.[35,36] Accordingly, a wide range of star polymers with various compositions and functionalities were prepared. However, the reported polymers are usually limited to polymers bearing a cross-linked core. Despite the wide application fields of core cross-linked star polymers, the inner cross-linked core also brings some disadvantages.[5,6] For example, the cross-linked core has difficulty in performing core-functionalization reactions. Such cross-linked core may also influence the solubility of star polymers possessing multiple short arms connecting to a big core. This issue can be resolved by introducing a hyperbranched inner core instead of the cross-linked core. Unfortunately, there is no report related to the synthesis of star polymers bearing hyperbranched core via "arm-first" approach to date.

Recently, we detailed a novel strategy to synthesize hyperbranched polymers by RAFT-mediated living radical polymerization of an asymmetrical divinyl monomer.[37−39] Homopolymerization of such monomers can be equivalently viewed as a copolymerization system of two different vinyl monomers.[37,40] Therefore, the reactivity difference between the two vinyl groups toward the polymerization can be quantatively adjusted by varying their reactivity ratio values (r_1/r_2). Mediated by a rapid RAFT equilibrium and polymerized under suitable reaction conditions, the concentration of polymeric chain radicals was decreased, and thus the gelation did not occur until a hyperbranched polymer was generated.

The present paper reports the synthesis of the star polymers with vinyl-functionalized hyperbranched core via the "arm-first" strategy. As shown in Scheme 1, a thiobenzoate-capped linear polymer was used as a macro-chain-transfer agent (Macro-CTA) to mediate the radical polymerization of an asymmetrical divinyl monomer. The fast reversible chain transfer reactions during the polymerization would keep the concentration of propagation chain at a low degree and thus suppress potential cross-linking reactions. Therefore, the star polymers bearing vinyl-functionalized hyperbranched cores rather than core cross-linked star polymers can be obtained via this "arm-first" route. Importantly, the abundant vinyl functionalities in the core are potential for the further functionalization.

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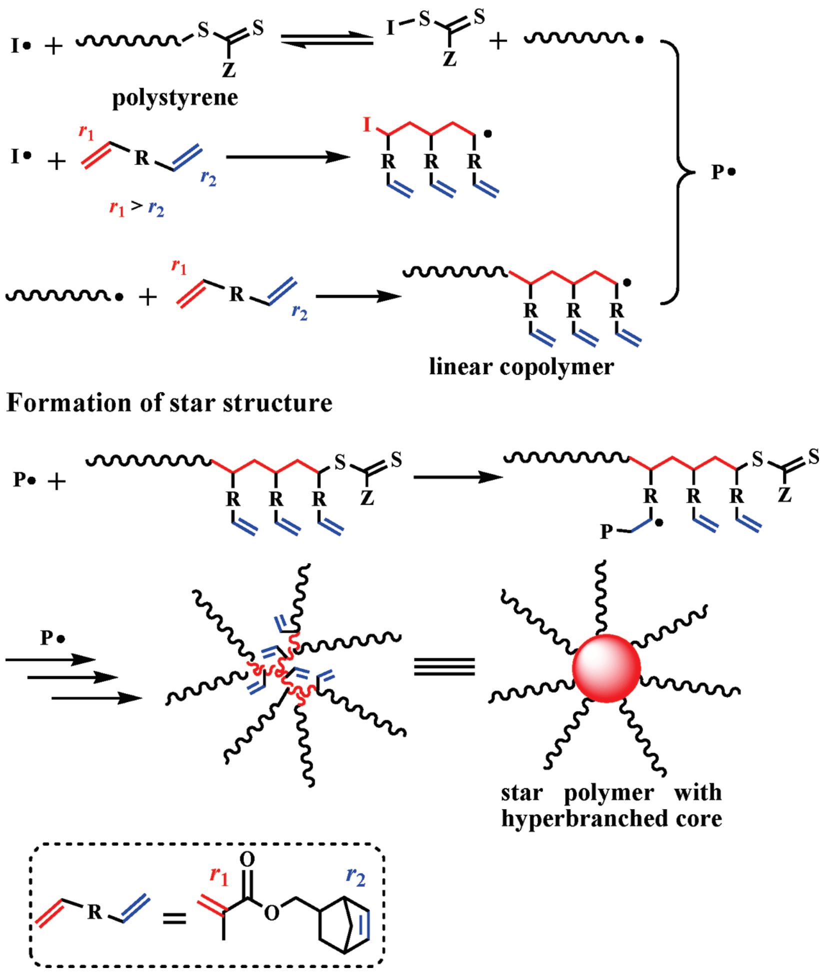
*Corresponding authors. Fax: +86-431-85262039. E-mail: (Y.S.) ysli@ciac.jl.cn.

Scheme 1. Synthetic Approach for the Preparation of the Star Polymer with Hyperbranched Core via an "Arm-First" Strategy



Experimental Section

General Data. Styrene (99%) was distilled before use. 5-Norbornene-2-methanol (97%, mixture of exo- and endo- isomers, with [exo]/[endo] = 18:82) was purchased from Aldrich and purified by distillation. Toluene (99.95%) was purified by Mbraun solvent purification system (M. Braun Co. Ltd. Germany). 2,2-Azodiisobutyronitrile (AIBN, 99%) was purified by recrystallization from hexane. 2,2-Dimethoxy-2-phenyl acetophenone (DMPA, 99%) was purchased from J&K Chemical LTD and used as received. 2-(2-Cyanopropyl) dithiobenzoate (CPDB) was synthesized according to a literature procedure.[41] 2-(5-Norbornene)methyl methacrylate (NBMMA), a methacrylate-type asymmetrical divinyl monomer, was prepared according to our earlier report.[37] All other materials without specially mentioned were used as received.

Synthesis of Linear Polystyrene (PS) as Arm Precursor. Linear PS with dithiobenzoate end functionality was synthesized via solution polymerization of styrene with CPDB as chain transfer agent. For a typical polymerization procedure, styrene (10 g, 96 mmol), CPDB (0.2122 g, 0.96 mmol) and toluene (10 mL) were mixed in a 100 mL round-bottom flask. After degassing by three freeze−pump−thaw cycles, the system was sealed and polymerized at 110 °C. The polymerization was ceased by liquid nitrogen after 8 h. The produced viscous mixture was diluted by ethyl acetate, and methanol was employed to sedimentate the product. The resultant polymer was dried *in vacuo* at 60 °C. The molecular weights of produced arm precursors were determined by size exclusion chromatography (SEC). Yield = 85.7%, $M_{w,ab} = 9.55$ kDa, and PDI = 1.03.

Synthesis of Multiarm Star Polymer. The following procedure is typical. 1.0 g of NBMMA (5.2 mmol), 0.3120 g of PS ($M_w = 3.0$ kDa, PDI = 1.02, 0.104 mmol), and 8.5 mg of AIBN (0.052 mmol) and 1 mL of toluene were mixed in a Schlenk polymerization tube. The mixture was degassed by three freeze−pump−thaw cycles to remove residual oxygen and charged with nitrogen before sealed. The system was then placed in a thermostatic oil bath at 80 °C for 8 h. The polymerization was ceased by liquid nitrogen. The produced viscous mixture was diluted by ethyl acetate, and methanol was employed to sedimentate the product. The resultant polymer was dried *in vacuo* at room temperature. The polymer yield was determined gravimetrically. Yield = 81.1%, $M_w = 150$ kDa, and PDI = 10.6. ^{1}H NMR ($CDCl_3$, δ): 0.45−0.72 (br, endo-H of $-CH_2-$ in the ring), 0.87 (s, $-CH_3$ and $-CH_2-$ backbone of NBMMA units), 1.03 (s, $-CH-$ in the ring) 1.2−2.1(br, $-CH_2-$ in bridge head, exo-H of $-CH_2-$ in the ring, and the backbone of PS units), 2.81, 2.88 (d, $-CH-$ in norbornene ring), 5.7−6.2 (2*n*H, protons of residual norbornenyl groups in the core, with *n* being the degree of polymerization of NBMMA units); 3.3−4.2 (2*n*H, $-CH_2-OCO-$ protons in NBMMA units); 6.2−7.2 (2*m*H, phenyl groups in PS arms, with *m* being the degree of polymerization of PS arms). ^{13}C NMR ($CDCl_3$): δ 16.9, 18.7 ($-CH_3$ in the backbone), 29.5 ($-CH_2-$ in the ring), 30.2 ($-CH-$ in norbornene ring), 37.8 ($-CHCH_2OCO-$), 40.0−42.0 (*C*H in the backbone of PS and NBMMA units, $-CH_2-$ in the backbone of PS units), 42.6 ($-CH-$ in norbornene ring), 44.9−45.2 (quaternary C in the backbone of NBMMA units), 49.9 (bridgehead $-CH_2-$), 54.7 ($-CH_2-$in the backbone of NBMMA units), 68.7−69.6 ($-CH_2-OCO-$), 132, 138 (carbons of residual norbornenyl groups in the core), 126, 127, 145 (phenyl groups in PS arms), 177.1 and 178.1 ($-COO-$). FTIR (cm^{-1}, CH_2Cl_2 solution): 3057 ($\nu_{=CH}$ of norbornenyl groups), 2967 (ν_{CH_3}), 2869

Table 1. Results of Arm Precursors Prepared via Reversible Addition−Fragmentation Chain Transfer Polymerization of Styrene[a]

Macro-CTA[b]	[St]:[CPDB]	yield (%)	$M_{n,th}$[c] (kDa)	$M_{n,NMR}$[d] (kDa)	$M_{w,SEC}$[e] (kDa)	PDI[e]
PS1	100:4	36.8	1.18	1.25	1.21	1.03
PS2	100:3	74.3	2.80	3.12	2.96	1.02
PS3	100:3	88.1	3.28	3.88	3.48	1.04
PS4	100:1	85.7	9.15	10.0	9.55	1.03

[a] Reaction conditions: solvent, toluene. [St] = 9.6 mol/L, polymerization at 110 °C. [b] Polystyrene (PS) used as the arm precursors. [c] Theoretical molecular weight ($M_{n,th}$) of PS arm precursor. $M_{n,th}$ = yield × ([St]/[CPDB]) × 104 + 221. [d] Number-average molecular weight ($M_{n,NMR}$) calculated from ^{1}H NMR spectra. [e] Weight-average molecular weight ($M_{w,SEC}$) and polydispersity index (PDI) detected by SEC.

Table 2. Star Copolymers Bearing Hyperbranched Core Synthesized via Radical Polymerization of NBMMA Mediated by Thiobenzoate-Ended PS as Macro-CTA[a]

entry	Macro-CTA	[M]:[PS]	t (h)	yield (%)	NB %[b]	core %[b]	$M_{w,ab}$[c] (kDa)	PDI[c]	$M_{w,core}$[d] (kDa)	n_{arm}[e]
1	PS1	100:2	8	71.6	68	87	446	10.6	401	29
2	PS1	100:3	11	80.1	62	88	230	9.20	194	29
3	PS2	100:2	8	81.1	65	62	150	10.6	93.0	19
4	PS3	100:2	10	69.7	65	61	115	8.10	69.6	13
5	PS3	100:3	17	59.5	65	47	32.3	6.08	15.2	4.9
6	PS4	100:2	12	74.8	64	34	64.8	3.82	21.8	4.5
7	PS4	100:3	13	81.9	60	23	42.4	2.71	9.75	3.4

[a] Reaction conditions: solvent, toluene. [NBMMA]:[AIBN] = 100:1. For entries 1−5, [NBMMA] = 5.2 mol/L; for entries 6−7, [NBMMA] = 2.6 mol/L, polymerization at 80 °C. [b] The content of residual norbornenyl groups in hyperbranched core (NB %) and the content of hyperbranched core in the star copolymer (core %) determined from ^{1}H NMR spectra. [c] Absolute molecular weight and polydispersity index of star copolymer detected by Tri-SEC. [d] M_w of the hyperbranched core. $M_{w,core}$ = core % × $M_{w,ab}$/100. [e] Average arm number of the star copolymer. n_{arm} = (100 − core %) × $M_{w,ab}$ / 100M_w(PS).

(ν_{CH_2}), 1731 ($\nu_{OC=O}$), 1600 and 1570 ($\nu_{C=C}$ of phenyl groups), 1265 and 1240 (ν_{C-O-C}), 989 ($\delta_{=CH}$), 700 ($\delta_{=CH}$ of phenyl groups).

Epoxidation of the Vinyl Pendants in the Star Polymer. The pendent norbornenyl groups in the hyperbranched core of the star polymer can be directly epoxidized by the following steps: 0.2 g of star polymer (entry 3 in Table 2, NB % = 65, core % = 62, $M_{w,ab}$ = 150 kDa, PDI = 10.6, and content of NB group = 0.55 mmol), 0.3 g of *m*-chloropreoxybenzoic acid (CPBA, 2.2 mmol), and 5 mL of toluene were mixed in a flask. The system was sealed and heated at 70 °C for 24 h. Toluene was then removed under reduced pressure, and methanol was used to wash out the residual CPBA. Vacuum drying gave a white epoxidized product. The conversion of NB group to epoxy group [convn % $(NB)_{epo}$] was evaluated by NMR analysis. Yield = 98.8%. Convn % $(NB)_{epo}$ = 100%. ^{1}H NMR ($CDCl_3$, δ): 3.1 (2nH, −CH−O−CH−). FTIR (cm^{-1}, CH_2Cl_2 solution): 850 (ν_{COC}).

Synthesis of Star Polymer with Hydroxy-Functionalized Hyperbranched Core.[42] OH-functionalization of the vinyl pendants in the star polymer can be achieved by UV initiated thiol−ene addition reaction. Here, 0.2 g of star polymer (entry 1 in Table 2, NB % = 68, core % = 87, $M_{w,ab}$ = 446 kDa, PDI = 10.6, and content of NB group = 0.51 mmol), 0.9 g of 2-mercaptoethanol (11.5 mmol), 1.3 mg of DMPA (5.1 × 10^{-6} mol), and 2 mL of CH_2Cl_2 were mixed in a vial. The system was sealed and placed under a UV bench lamp (365 nm, 6 W) for 4 h. Ethanol was then use to sedimentate the OH-functionalized star polymer. The light pink product was dried *in vacuo* at room temperature. The conversion of addition reaction of NB group with mercaptoethanol [convn % $(NB)_{thiol-ene}$] was evaluated by NMR analysis. Yield = 94.8%. Convn % $(NB)_{thiol-ene}$ = 71%. ^{1}H NMR ($CDCl_3$, δ): 2.7 (2nH, −S−CH_2CH$_2$OH), 3.6 (2nH, SCH$_2$−CH_2−OH). FTIR (cm^{-1}, CH_2Cl_2 solution): 3540 (ν_{OH}), 1060 (ν_{C-OH}).

Characterization. ^{1}H NMR spectra were recorded on a Bruker 300-MH$_Z$ spectrometer. ^{13}C NMR spectra were recorded with a Varin Unity 400 spectrometer operating at 100.0 MH$_Z$. In all spectra, $CDCl_3$ was used as the solvent and tetramethylsilance (TMS) was used as the internal standard. FTIR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer with CH_2Cl_2 as solvent. Absolute molecular weights ($M_{w,ab}$s), polydispersity indices (PDIs) and Mark−Houwink exponent α values of the star polymers were measured by triple detection size exclusion chromatography (TRI-SEC) containing a Waters 1525 separation module (Waters Corp) connected with M302 triple detector array (Viscotek Corp., Houston, TX), a combination of light scattering [LS angle, 7° (LALS) and 90° (RALS), laser wavelength, λ = 670 nm), refractive index (RI, λ = 670 nm), and viscosity detector (IV-DP). Two mixed bed SEC columns (GMH$_{HR}$-M with molecular weight range < 1.0 × 10^6 Da, and GMH$_{HR}$-H with molecular weight range < 1.0 × 10^5 Da, Viscotek Corp.) were employed. Additional measurements of apparent molecular weights ($M_{w,app}$) were determined by SEC with RI detector (Sin-SEC), which performed with a Waters 1525 fitted with two columns (Styragel HT3 and HT4 THF 7.8 × 300 mm column). For all SEC analyses, HPLC grade tetrahydrofuran (THF) was used as the mobile phase at 25 °C (flow rate: 1 mL/min). The analyses were based on narrow polystyrene (PS) standards.

Results and Discussion

For producing multiarm star polymers with the hyperbranched inner cores via "arm-first" route, the selected asymmetrical divinyl monomer should have a proper r_1/r_2 value. In our previous report, the novel monomer bearing a higher reactivity methacrylate group and a lower reactivity norbornene group, i.e., 2-(5-norbornene)methyl methacrylate (NBMMA, r_1/r_2 = 159), has been demonstrated to be able to produce hyperbranched polymers with higher DBs, higher monomer conversions and higher molecular weights (MWs), as a result of its proper r_1/r_2 value and optimal molecular structure.[37] Therefore, NBMMA is a suitable monomer to form the hyperbranched inner core of star polymers. Moreover, the well-defined polystyrenes (PSs) produced by RAFT polymerization were chosen as arm precursors (Table 1). MWs of the arm precursors, i.e. the arm lengths, can be simply controlled by varying the molar ratios of monomer to CTA. Four arm precursors with different arm lengths ranging from 1.2 kDa to 9.6 kDa were employed as the outside linear arms.

Synthesis of Star Polymers with Hyperbranched Cores via RAFT Polymerization of an Asymmetrical Divinyl Monomer Mediated by Linear Macro-CTA. In this strategy, PS arm precursors were employed as Macro-CTA to control the polymerization of the monomer (NBMMA), with the purpose to produce star polymer with vinyl-functionalized

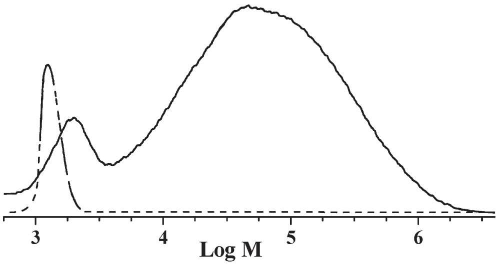


Figure 1. SEC curves of resultant star polymer (—) and original PS arm precursor (- - -). Reaction conditions: [NBMMA] = 5.2 mol/L, [NBMMA]:[AIBN]:[PS] = 100:1:2, solvent = toluene, polymerization at 80 °C for 8 h, M_w (PS) = 1.21 kDa, and PDI (PS) = 1.02.

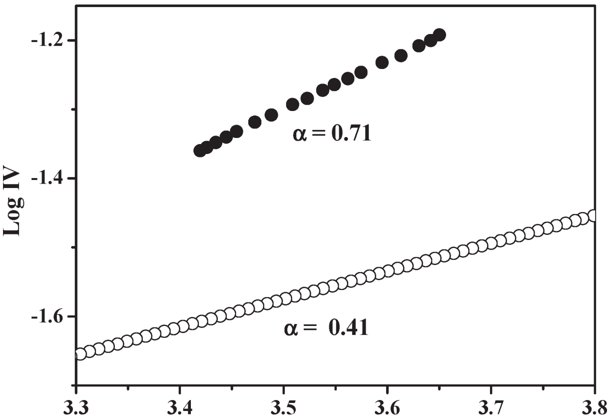


Figure 2. Mark−Houwink plot of star copolymer (○) and the original polystyrene arm precursor (●). Reaction conditions: [NBMMA] = 5.2 mol/L; [NBMMA]:[AIBN]:[PS] = 100:1:2; solvent = toluene, polymerization at 80 °C for 8 h, M_w (PS) = 2.96 kDa, PDI (PS) = 1.02.

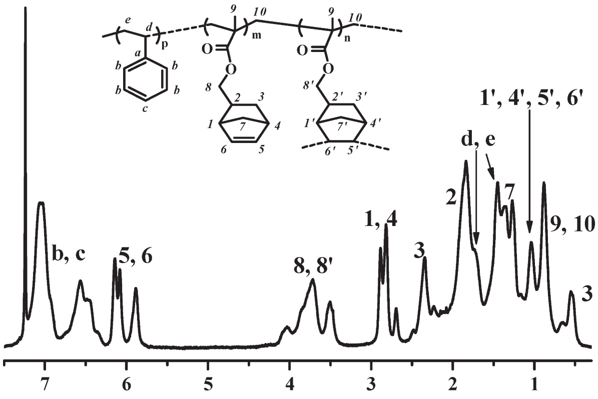


Figure 3. ^{1}H NMR spectrum of a typical star polymer. Reaction conditions: [NBMMA] = 5.2 mol/L, [NBMMA]:[AIBN]:[PS] = 100:1:2, solvent = toluene, polymerization at 80 °C for 8 h, M_w (PS) = 2.96 kDa, and PDI (PS) = 1.02. The content of residual norbornenyl groups in hyperbranched core (NB %) and the content of hyperbranched core in the star copolymer (core %) are determined by comparing the integrals of corresponding peaks: core % = 62; NB % = 65.

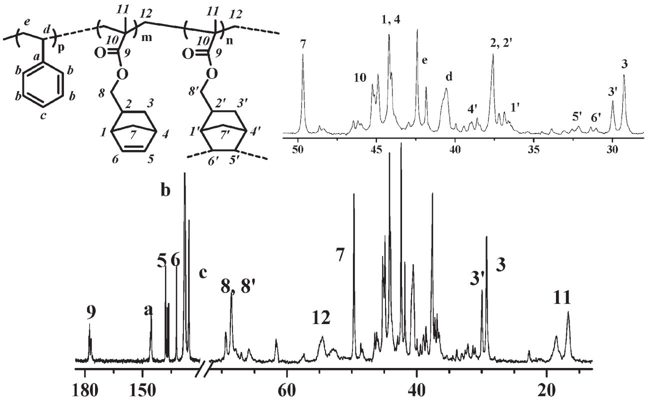


Figure 4. ^{13}C NMR spectrum of a typical star polymer. Reaction conditions: [NBMMA] = 5.2 mol/L, [NBMMA]:[AIBN]:[PS] = 100:1:2, solvent = toluene, polymerization at 80 °C for 8 h, M_w (PS) = 2.96 kDa, and PDI (PS) = 1.02. The content of residual norbornenyl groups in hyperbranched core (NB %) and the content of hyperbranched core in the star copolymer (core %) are determined via ^{13}C NMR correspondingly: core % = 62; NB % = 65.

hyperbranched inner core. The typical polymerization results were listed in Table 2. The yields of star polymers can reach as high as 80%. The resultant polymers possessed high solubility in organic solvents, such as toluene, chloroform, tetrahydrofuran, dimethylformamide, etc. Figure 1 displayed the SEC traces of star polymer and its original arm precursor. The broad peak at high MW region possibly indicates that the produced polymers possess star structures, whereas the small peak at lower MW region refers to the linear copolymer byproduct, as shown in Scheme 1. Clearly, MW of linear byproduct is higher than that of arm precursor, which means the Macro-CTA was totally consumed during the polymerization. Furthermore, a lower slope obtained from the plot of log IV versus log *M*, i.e., Mark−Houwink exponent α (Figure 2), is observed for the star polymer compared with the linear reference. For example, α value of the obtained star polymer is 0.41, much lower than that of the linear counterpart (α = 0.71). The intrinsic viscosity of the product is also lower than that of the linear counterpart at any given MW. These results powerfully support the formation of star architecture. Moreover, the core structure of these obtained star polymer can be confirmed by evaluating their composition.

The compositions of star polymers were calculated from ^{1}H NMR analyses (Figure 3). Peaks b and c at 6.2−7.2 ppm ascribed to the phenyl groups in PS stand for the linear arms. Peaks 8 and 8′ at 3.3−4.2 ppm corresponding to $-CH_2-$ protons in NBMMA units represent the inner core, whereas peaks 5 and 6 at 5.7−6.2 ppm represent the unreacted norbornenyl groups in the core. By comparing the integral ratios of the corresponding peaks, the content of the hyperbranched core in the star polymer (core %) and the residual norbornenyl functional groups in the hyperbranched core (NB %) can be evaluated by the following equations.

$$\text{core }\% = \frac{I_{8,8'}}{I_{8,8'} + 2 \times I_c} \times 100; \quad \text{NB }\% = \frac{I_{5,6}}{I_{8,8'}} \times 100$$

^{13}C NMR analyses of typical star polymers were also performed for comparison. As shown in Figure 4, core % and NB % values of the resultant polymers can also be calculated from according ^{13}C NMR data. Importantly, the results obtained from either ^{1}H NMR or ^{13}C NMR spectra matched perfectly. Table 2 listed core % and NB % values from ^{1}H NMR analyses. Obviously, NB % values were determined to be ca. 70%. In consistent with our earlier report on hyperbranched PNBMMA,[37] the approximately 30% reacted low-reactivity norbornenyl group served as branching agent rather than cross-linker during the RAFT copolymerization. That is, the resultant star polymers have a vinyl-functionalized hyperbranched core rather than a cross-linked one. Therefore, star polymers with hyperbranched inner cores were successfully produced via the modified “arm first” strategy.

As shown in Table 2, the average arm number (n_{arm}s) is significantly influenced by the initial ratio of [NBMMA] to [PS]. Usually, a higher [NBMMA]:[PS] value would enhance n_{arm}, MW, and core size of the resultant star polymer.[6,26] Contrarily, the increase of PS concentration led to the decrease of MW of star polymer ($M_{\mathrm{w,ab}}$) and MW of the hyperbranched core ($M_{\mathrm{w,core}}$). This trend is more obvious when the copolymerization was mediated by a higher MW of the arm precursor. At higher PS concentrations, n_{arm}s of the produced polymers also reduced, especially when MWs of PSs are above 3.0 kDa. Furthermore, MW of Macro-CTA, i.e. the arm length of an arm precursor (PS), significantly affects the structures of resultant star polymers. Obviously, the average arm numbers (n_{arm}s) decreased with the MW increase of arm precursors (Figure 5). PS1 with a lower M_{w} of 1.2 kDa generated star polymers containing as high as 29 arms. In contrast, a higher-MW arm precursor (PS4, M_{w} = 9.6 kDa) produced star polymers with only 4−5 arms. The phenomena, in accord with earlier reports involving the synthesis of core cross-linked star polymers via "arm-first" approach, are usually ascribed to the space hinder of a long arm precursor.[23,29] Moreover, in our system, employing a longer arm had no significant influence on the compactness of star structure.

The compactness value is defined as the ratio of absolute molecular weight ($M_{\mathrm{w,ab}}$) to apparent molecular weight ($M_{\mathrm{w,\ app}}$). Generally, a star polymer of higher compactness possesses a more compact structure. That is, n_{arm} of a high-compactness star polymer is higher than that of a low-compactness star polymer with a similar-size core. Despite the difference between the four arm precursors, the compactness values of the resultant star polymers are usually limited to a low range from 2.0 to 3.0. However, the arm lengths considerably affect the $M_{\mathrm{w,core}}$ values. For example, the polymers for entries 1, 3, 4, and 6 in Table 2 are prepared at the same [M]:[PS] ratio (100:2). Clearly, star polymers obtained from lower-MW PS arm precursors possessed higher $M_{\mathrm{w,core}}$, that is, $M_{\mathrm{w,core}}$ values decreased from 401 kDa to 21.8 kDa, corresponding to an increase in the MWs of the arm precursors from 1.2 kDa to 9.6 kDa. Likewise, MW values of the star polymer also decreased from 446 kDa to 64.8 kDa. The same trend can also be observed in entries 2, 5, and 7 of Table 2. Therefore, based on these results, we conclude that a longer arm would restrict the RAFT polymerization of NBMMA and thus a much smaller PNBMMA core was formed, together with the decrease of n_{arm}. That is, a lower-MW arm precursor favors the formation of a star copolymer bearing big core and multiple short arms, whereas a higher-MW one is confined to the architecture bearing small core with only a few long arms.

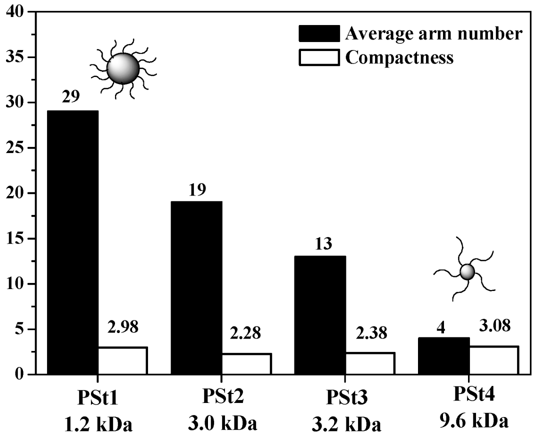


Figure 5. Dependence of average arm number (n_{arm}) and compactness ($M_{\mathrm{w,ab}}/M_{\mathrm{w,\ app}}$) of star polymer on the molecular weight of arm precursor. Reaction conditions: [NBMMA] = 5.2 mol/L, [NBMMA]:[AIBN]:[PS] = 100:1:2, solvent = toluene, polymerization at 80 °C.

Evolution of Star Structures During the RAFT Copolymerization. The evolution of star architectures was investigated in detail, and the representative results are summarized in Table 3. At the early polymerization stage, NB % is around 100%, indicating that the initiation and chain propagation reactions occur only in the higher reactivity methacrylate groups. As presented in Scheme 1, these reactions lead to the formation of linear copolymers with vinyl pendants. However, the multiple pendent vinyl groups are potential branching sites to form the hyperbranched inner core. Subsequently, NB % decreased gradually with reaction proceeding. Comparatively, the compactness and MW of resultant polymers as well as the content of hyperbranched core (core %) increased correspondingly. After 8 h polymerization, NB % decreased to 65%. MW of the resultant polymer reached as high as 150 kDa, while n_{arm} increased to 19. These results suggest the gradual formation of star architecture during the polymerization process (see the star formation reactions in Scheme 1). Considering the space hinder of arms and the lower reactivity of norbornenyl groups, there are still linear copolymers with vinyl pendants in the system during this stage.

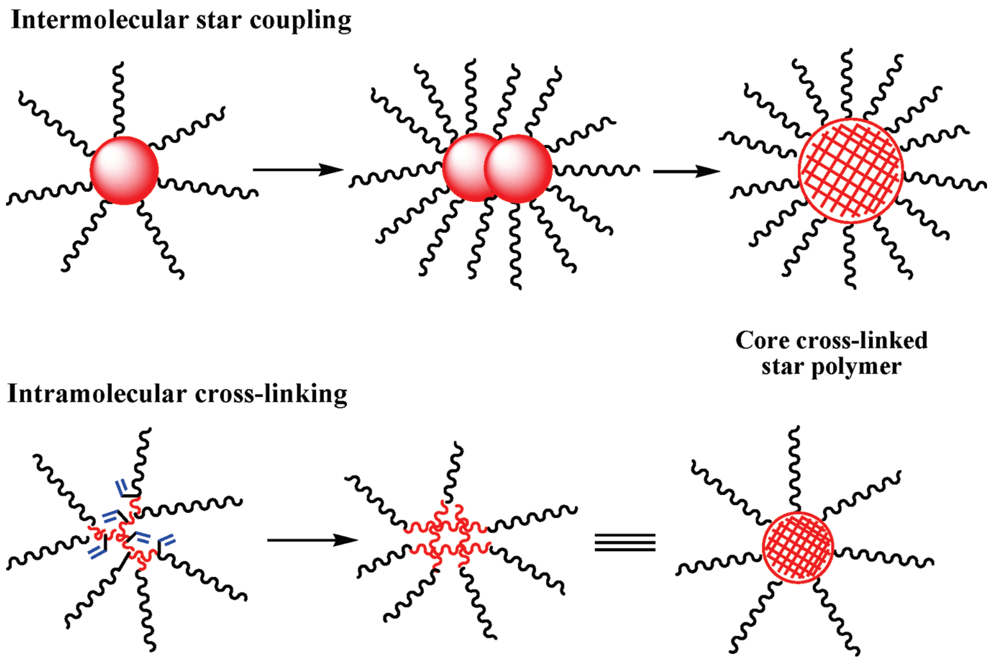
A longer reaction time would induce cross-linking reactions. Insoluble gels appeared when polymerization time was extended to 10 h. The yield of soluble part of resultant polymer decreased accordingly. Scheme 2 illustrated the possible cross-linking reactions at the late stage of the polymerization. After 10 h polymerzation, MW and n_{arm} of the produced polymer (entry 3−5 in Table 3) were twice as high as those for entry 3−4, whereas core % and NB % remained at the same level. The result indicates that intermolecular star coupling occurred during the late stage of polymerization, thus a slightly cross-linked core would be formed. On the other hand, the occurrence of intramolecular cross-linking could be evidenced by the drastic decrease of NB %. For example, the product of entry 3−6 possesses much higher MW and n_{arm} values. However, the yield of

Table 3. Star Polymers Synthesized via a Modified "Arm-First" Strategy[a]

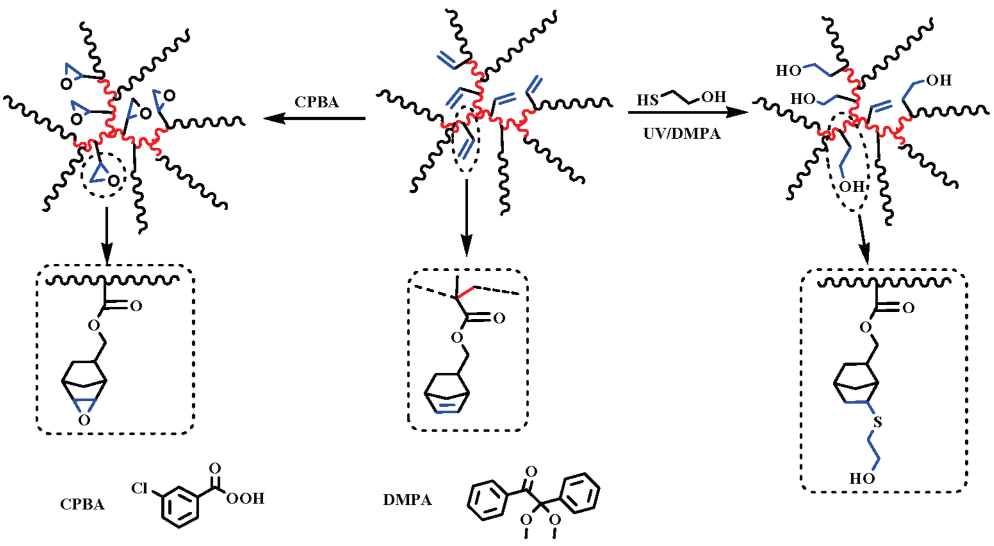
entry	t (h)	yield (%)	NB %	core %	$M_{\mathrm{w,ab}}$[b] (kDa)	PDI (T)[b]	$M_{\mathrm{w,app}}$[c] (kDa)	PDI (S)[c]	n_{arm}	$M_{\mathrm{w,ab}}/M_{\mathrm{w,\ app}}$[d]	M_{w}(core) (kDa)
3−1	1	13.7	100	21	8.90	1.68	8.90	1.59	2.3	1.00	1.87
3−2	2	40.5	92	43	14.9	2.84	14.5	2.37	2.8	1.03	6.42
3−3	4	49.4	87	40	38.4	6.40	35.6	2.70	7.6	1.08	15.5
3−4	8	81.1	65	62	151	10.6	65.9	5.48	19	2.28	93.0
3−5	10	71.2[e]	65	62	365	12.5	88.8	6.13	47	4.11	225
3−6	12	58.3[e]	31	36	661	18.2	156	7.36	83	4.25	413

[a] [NBMMA] = 5.2 mol/L, [NBMMA]:[AIBN]:[PS] = 100:1:2, solvent = toluene, polymerization at 80 °C, M_{w} (PS) = 2.96 kDa, and PDI (PS) = 1.03. [b] Absolute molecular weight ($M_{\mathrm{w,ab}}$) and polydispersity index [PDI (T)] of star copolymer detected by Tri-SEC. [c] Apparent molecular weight ($M_{\mathrm{w,\ app}}$) and polydispersity index [PDI (S)] of star copolymer detected by Sin-SEC. [d] The compactness of a star polymer is defined as the ratio of $M_{\mathrm{w,ab}}$ to $M_{\mathrm{w,\ app}}$. [e] The yield of the soluble part of the product.

Scheme 2. Possible Cross-Linking Side Reactions in the Late Stages of the Polymerization of 2-(5-Norbornene)methyl Methacrylate Mediated by Thiobenzoate-Capped PS



Scheme 3. Post-Polymerization Modifications of Star Polymer with Vinyl-Functionalized Hyperbranched Core



soluble portion of produced polymer reduced to 58.3%, together with the decrease of NB % to 36%. The further increase of reaction time would result in the intermolecular cross-linking and thus insoluble core cross-linked star polymers would be formed eventually.

Postpolymerization Functionalization of the Star Polymer. The ca. 70% norbornenyl groups in the hyperbranched core can be directly converted to various functional groups including epoxy groups and hydroxy groups (Scheme 3). NMR analyses (Figure 6) revealed that these vinyl groups have been successfully transformed to epoxy functionalities by epoxidation reactions. After epoxidation, signals ascribed to protons of norbornenyl groups (peaks 5,6) disappeared completely. Peaks representing the −CH− protons connecting to norbornenyl groups (peaks 1,4) also vanished. Accordingly, a new peak was detected at 3.1 ppm, which can be assigned to the protons of the oxirane ring. That is, the norbornenyl groups have been quantitatively converted to epoxy groups. The same result can also be concluded from FTIR analyses in Figure S1 in the Supporting Information. The absorption band at 850 cm^{-1} corresponding to epoxy groups is observed after epoxidation. The characteristic absorption band of vinyl group at 3057 cm^{-1} vanished accordingly.

These norbornenyl groups can also be performed UV initiated thiol−ene addition reaction with 2-mercaptoethanol. The success of mercaptoethanol addition was proved by FTIR analysis (Figure 7). In contrast with the spectrum of the original star polymer, the absorption bands at 3540 and 1060 cm^{-1} are observed, corresponding to the characteristic stretching vibration mode of O−H and C−OH groups, respectively. Characteristic band of norbornenyl groups at 3050 cm^{-1} can also be observed in the final product, indicating the incomplete transformation of vinyl

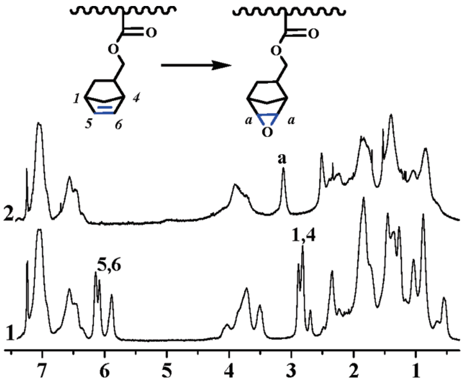


Figure 6. ^{1}H NMR spectra of star polymer with vinyl-functionalized hyperbranched core before (1) and after (2) epoxidation reaction. Sample from entry 3 in Table 2 ($M_{\mathrm{w,ab}}$ = 150 kDa, PDI = 10.6, the content of hyperbranched core in the star copolymer is 62%, and the norbornenyl content in the hyperbranched core is 65%) was used as original star polymer. 100% of residual norbornenyl groups were transformed into epoxide groups.

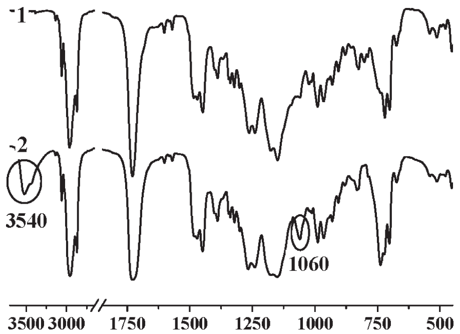


Figure 7. FTIR spectra of original star polymer (1) and hydroxylated star polymer (2). Sample from entry 1 in Table 2 ($M_{\mathrm{w,ab}}$ = 446 kDa, PDI = 10.6, the content of hyperbranched core in the star copolymer is 68%, and the norbornenyl content in the hyperbranched core is 87%) was used as original star polymer. The conversion of residual norbornenyl groups is 71%.

groups. The conversion of norbornenyl groups was ca. 70% (calculated from ^{1}H NMR spectra, see Figure S2 in the Supporting Information). The unreaction of a few pendant vinyl groups is due to that they are embedded in the hyperbranched core and thus the attacking reagents do not easily access them.

Conclusion

Star polymers with hyperbranched cores have been successfully produced by simply introducing a suitable asymmetrical divinyl comonomer (NBMMA) into "arm-first" strategy. Neither intermolecular nor intramolecular cross-linking occurred up to high levels of monomers conversion (ca. 80%) by employing RAFT technique to keep a low propagation chain concentration via a fast reversible chain transfer equilibrium. A longer reaction time may induce star coupling or intramolecular cross-linking, resulting in core cross-linked star polymers eventually. Arm length of an arm precursor would considerably influence the star structure of obtained polymers. The lower-MW arm precursor favors the formation of a star copolymer bearing big core and multiple short arms, whereas a higher-MW one is confined to the architecture bearing small core with only a few long arms. The obtained polymer had good solubility in common organic solvents despite its core size. Finally, there are ca. 70% pendant norbornenyl groups remained in the hyperbranched core, which can be directly performed chemical modifications, which endows the resultant polymer with a widen range of application fields especially as core-functionalized star copolymers. For example, the norbornenyl groups can be quantitively converted to epoxy functionalities by epoxidation reaction. Hydroxylation of these vinyl groups can also be achieved by UV initiated thiol−ene addition reaction. The conversion of vinyl pendants was calculated to be ca. 70%.

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Supporting Information Available: FTIR characterization of the epoxidated star polymer along with NMR analysis of the hydroxylated star polymer. This information is available free of charge via the Internet at http://pubs.acs.org/.

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