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Synthesis of amphiphilic star block copolymers of polystyrene with PEG core via ATRP—control of chain architecture and the formation of core–shell type globular structure

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Abstract

Amphiphilic star block copolymers made of poly(ethylene glycol) (PEG) core and branched PS arms having controlled chain lengths and numbers were synthesized by atom transfer radical copolymerization (ATRP) of styrene and chloromethylstyrene (CMS) in the presence of tetrafunctional PEG macroinitiator. The chain lengths and number of PS chains were controlled by adjusting the initial feed ratio of CMS to styrene and CMS to hydrophilic tetrafunctional macroinitiator, respectively, for a given polymerization time. The obtained polymers have well defined and controlled architectures. Use of excess amount of CMS and longer reaction time leads to the synthesis of dendrimer like amphiphilic block copolymer having four hyperbranched polymer arms, whose shape is closer to globular core–shell structure compared to general star shape polymers.

Keywords: Dendrimer; Hyperbranched; Amphiphilic

1. Introduction

Dendrimers, hyperbranched polymers, and star polymers have received much attention because these dense, highly branched polymers are expected to have different physical properties compared to their linear analogs [1,2]. Usually hyperbranched polymers have been developed as alternatives to dendrimers, as they can be prepared in a single, one pot reaction. Generally hyperbranched polymers are synthesized via condensation polymerization using AB_X $(X>1)$ type monomers. Recently the synthesis of hyperbranched polymers have been extended to functionalized vinyl monomers by a method termed self-condensing vinyl polymerization (SCVP) via atom transfer radical polymerization (ATRP) [3]. Gaynor et al. reported hyperbranched poly(chloromethylstyrene) (HPCMS) [4] and Weimer et al. reported more detailed study on polymerization conditions and structures such as degree of branch (DB), etc. [5]. Recently, Gnanou et al. reported dendrimer-like polystyrene by iterative ATRP and chain end modification from a tetrafunctional initiator [6].

Amphiphilic copolymers are important for various practical applications in which the combination of hydrophilic and hydrophobic properties of these materials may be utilized, e.g. as emulsifiers, dispersion stabilizers, and compatibilizers [7]. The general types of amphiphilic copolymers are block or graft type polymers, and these are synthesized via various living polymerization methods such as traditional living anionic polymerizations [8], and living radical polymerizations [9,10]. Among these living polymerization methods, atom transfer radical polymerization (ATRP) has been a field of intensive research in recent years. An ATRP system consists of an initiator, metal halide complexes with some ligands, and monomers. Thus far, ATRP system has been adapted successfully for polymerizations of styrene, acrylate, methacrylate, acrylonitrile, and other functional monomers. ATRP also allows the preparation of polymers with novel compositions and topologies, i.e. block copolymers [11,12], graft copolymers, random/statistical copolymers, star block copolymers [13], and hyperbranched polymers [14,15].

Star shape amphiphilic block copolymers, which are reported up to date, generally contain linear arms. The block copolymers containing arms with globular structures by the incorporation of dendrons or hyperbranched structures are, however, rarely synthesized. Fréchet et al. [16–18] reported the synthesis of amphiphilic star block copolymers containing dendrons. These block copolymers contain 2- or 4-arm PEG

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in core as a hydrophilic block and polyether dendrons in shell as hydrophobic block, and the synthesis of a dendron required many reaction steps.

A closer look of the ATRP system and the globular structures gives one an idea of making amphiphilic star block copolymers using alternative approach via hyperbranched structure, i.e. it seems possible to make a nearly symmetric core–shell structure by self condensing polymerization of AB type vinyl monomer from the initiation of tetra-functional or multifunctional initiator via ATRP. Use of hyperbranched polymers as replacement of corresponding dendrons in the synthesis of nearly symmetric amphiphilic core–shell like structures, however, has not been reported. About the possibility of the globular amphiphilic polymers through self-condensing polymerization, we reported preliminary results some years ago [19], and reported the synthesis and micellar behavior of a dumbbell shaped block copolymer [20,21].

In this study, we tried to prepare amphiphilic star block copolymers containing tetra-armed PEG core as the hydrophilic part and polystyrene having controlled number of branches and chain lengths as the hydrophobic part. The number of branches per initiator functional group was controlled via adjustment of the mole ratio of chloromethylstyrene (CMS) to macroinitiator, and the average chain length or branch length was controlled via adjustment of the mole ratio of styrene to CMS. Through this attempt, we tried to obtain highly branched star block copolymers, which do not contain HPCMS homo or copolymers. In another attempt, we tried to synthesize starburst core–shell type amphiphilic block copolymer by hyperbranched CMS polymerization from the 4-arm PEG macroinitiator. Copolymerization with styrene was employed in order to control the chain length between branching points as well as molecular weight of the hyperbranched structure, because homo polymerization of CMS makes a hyperbranched structure with low molecular weight due to steric crowding.

2. Experimental

2.1. Materials

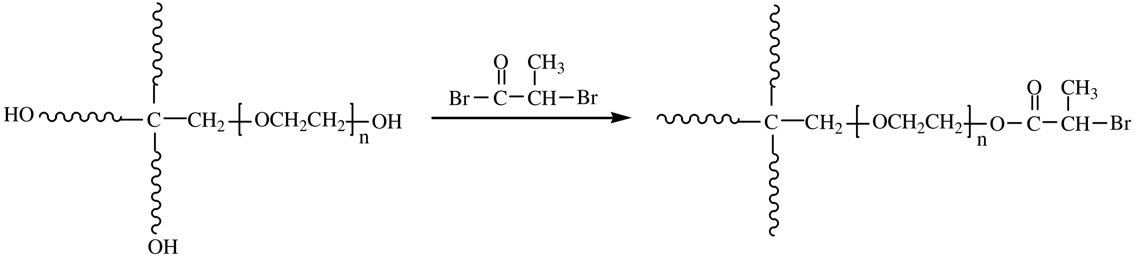
Pentaerythritol ethoxylate (15/4 EO/OH, ave. M_n 797, Aldrich) was dried by azeotropic distillation with toluene. Chloromethylstyrene (CMS) was vacuum distilled. Styrene was used after passing through alumina column to remove inhibitor. CuCl was purified according to the literature procedure [22]. Anisole was purified by distillation over CaH_2. 2,2′-Bipyridyl (bpy), CuCl, 2-bromopropionyl bromide, aluminum oxide (neutral) were used as received from Aldrich.

2.2. Synthesis of tetra-arm hydrophilic tetrafunctional macroinitiator

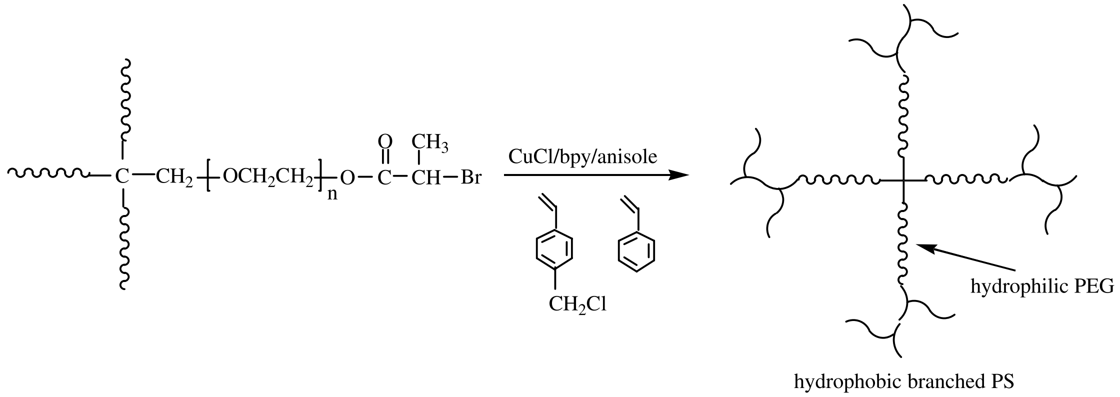
The synthesis of a hydrophilic 4-arm PEG macroinitiator was performed as shown in Scheme 1. Into a three neck round bottom flask, fitted with a dropping funnel, thermometer, and magnetic bar, was placed 5.78 g (47 mmol) of 4-dimethylaminopyridine, 2.5 mL (31 mmol) of pyridine, 15 g (19 mmol) of pentaerythritol ethoxylate, and 250 mL of dry CH_2Cl_2. After cooling to 0 °C, 8.27 mL (79 mmol) of 2-bromopropionyl bromide was slowly added with stirring. The reaction was continued for 18 h. The product was isolated from insolubles by filtration, and the resultant CH_2Cl_2 solution was washed with aqueous sodium bicarbonate solution and water. After drying, CH_2Cl_2 was evaporated and the crude product was recrystallized from cold ether.

2.3. Polymerization procedure

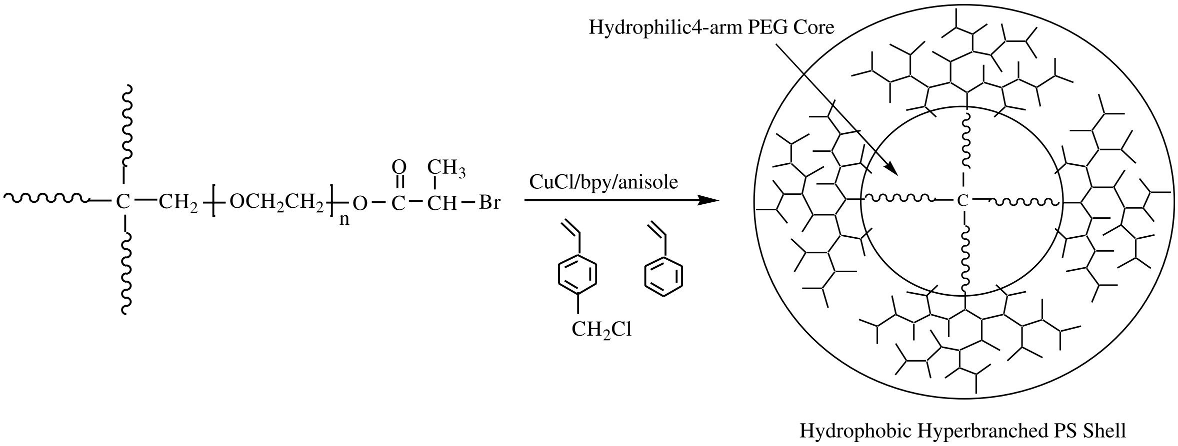
Synthesis of star block copolymer with controlled chain length is illustrated in Scheme 2, and the synthesis of core–shell like star block copolymer is illustrated in Scheme 3. One-neck round-bottom flask equipped with a stir bar was charged with 4-arm macroinitiator, styrene, chloromethylstyrene, bipyridyl (3-folds to catalyst), and anisole. The amount of anisole was adjusted to be ca. 50 vol% of the total solution. After degassing with nitrogen for 20 min, CuCl was added. The solution was degassed for an additional 10 min. The flask was immersed in an oil bath at 120 °C for polymerization. At predetermined interval small portions of the reaction solution were withdrawn via syringes, diluted with THF, and filtered with 0.45u Teflon filter to measure molecular weight by GPC. After polymerization, the green $CuCl_2$ was removed by passing through an alumina column. The polymer solutions were precipitated in methanol. The polymer was dried under vacuum at room temperature. In the synthesis of core–shell type block copolymer, the crude polymer was extracted with cyclohexane at room temperature for 1 day, for removal of homopolymerized poly(chloromethylstyrene) (HPCMS), or CMS/styrene copolymer.



Scheme 1. Synthesis of tetrafunctional macroinitiator.



Scheme 2. Synthesis of amphiphilic star block copolymer with controlled architecture.



Scheme 3. Synthesis of dendrimer like core–shell type star block copolymer.

2.4. Characterization

Molecular weight and its polydispersity index (PDI) were analyzed by gel permeation chromatography (GPC) in THF at 35 °C at a flow rate of 0.3 mL/min using a Waters 616 HPLC chromatography equipped with Waters 712 WISP autosampler and Waters 410 differential refractive index detector. Linear polystyrene standards were used for calibration. ^{1}H NMR spectrum was recorded using a Varian Gemini 300 spectrometer in $CDCl_3$ with TMS as an internal standard.

3. Results and discussion

Tetrafunctional macroinitiator was prepared by reacting pentaerythritol ethoxylate with 2-bromopropionyl bromide. Fig. 1 shows ^{1}H NMR spectra of macroinitiator and pentaerythritol ethoxylate. The hydroxyl, methylene ($C(CH_2O–)_4$), and ethylene ($–OCH_2CH_2O–$) signals of pentaerythritol ethoxylate appeared at 3.1, 3.5 and 3.7 ppm in Fig. 1 (a), respectively. After reaction of 2-bromopropionyl bromide, the hydroxyl peak of pentaerythritol ethoxylate disappeared and a new signal appeared at 1.9 ppm (a, $CH(CH_3)–Br$), 3.9 ppm (d, $–OCH_2CH_2–OOC–$), 4.2 ppm (e, $CH_2–OOCCH(CH_3)–Br$), and 4.5 ppm (f, $–OOCCH(CH_3)–Br$) due to the substituted pentaerythritol ethoxylate. The methylene

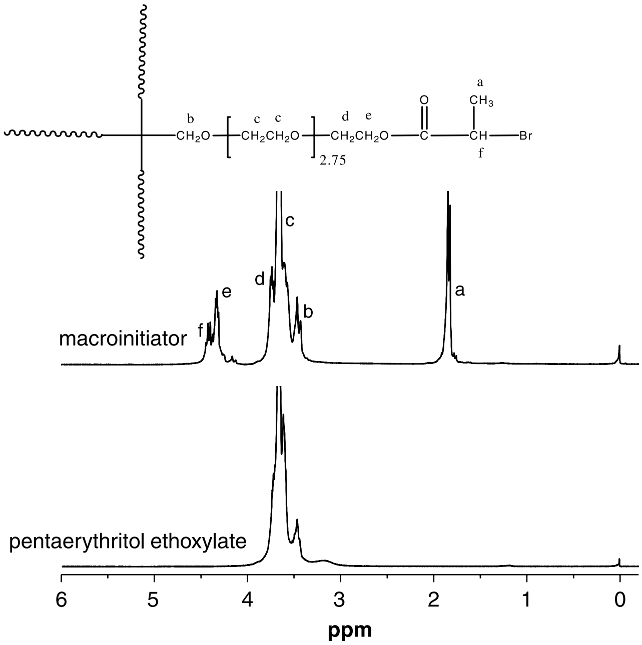


Fig. 1. ^{1}H NMR spectra of (a) tetrafunctional macroinitiator, and (b) pentaerythritol ethoxylate.

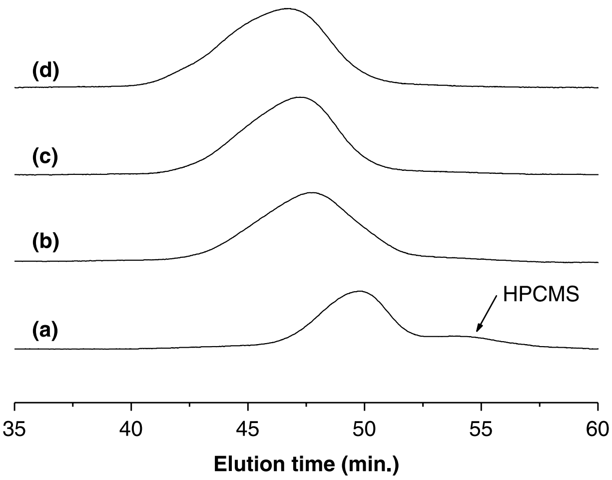


Fig. 2. GPC traces of amphiphilic star block copolymers (PEG_4-*b*-PS_8) as a polymerization time (a) 0.5 h, (b) 1 h, (c) 1.5 h, (d) 2 h.

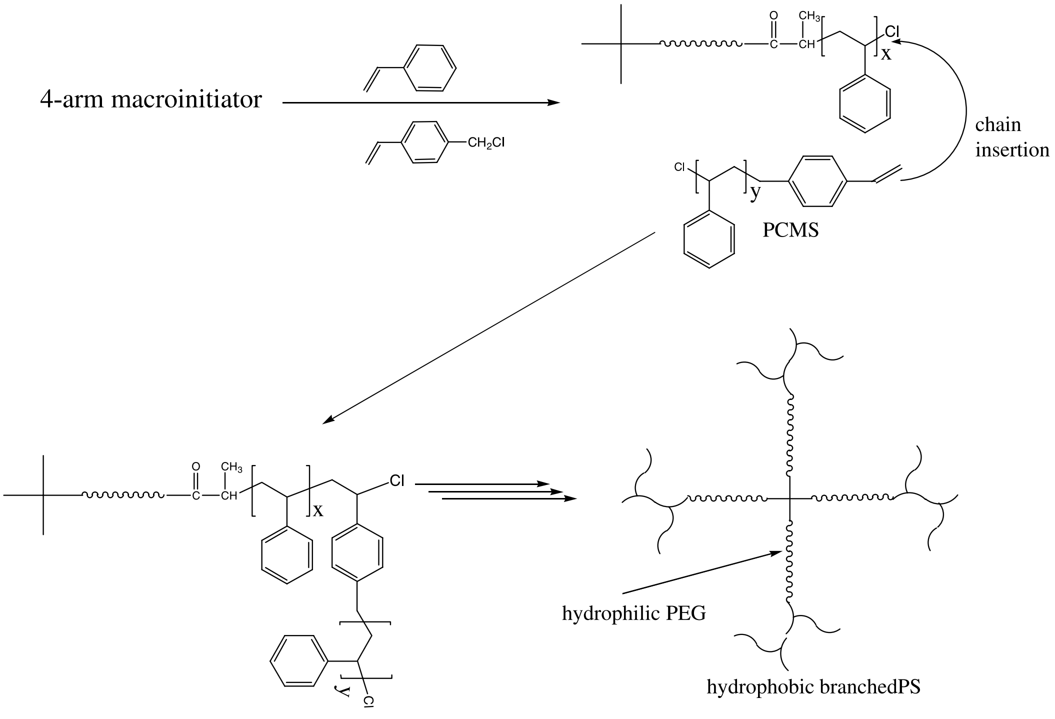
(b, $C(CH_2O–)_4$) and ethylene (c, $–OCH_2CH_2O–$) signals are shown unchanged.

3.1. Control of the number of branches and their molecular weights

In the next step, amphiphilic star block polymer was synthesized by ATRP using the macroinitiator, styrene, and CMS as a linking agents as in Scheme 2. For the synthesis and structural control of multi-branched star-block copolymers, synthetic strategies of previous workers were followed [4,5]. According to the report by Weimer et al. [5] the amount of catalyst is important to get a polymer having high degree of branch (DB). They reported that DB is quite low when the used ratio of catalyst to CMS is low such as 0.01, due to the different reactivity of primary benzyl chloride (1-BCl) from that of the secondary benzyl chloride (2-BCl). Similar observation was reported by Hawker et al. [23] in a stable free radical polymerization. And Weimer et al. observed quite extent of branching, which approached the DB of a theoretical hyperbranched structure when they used high catalyst to CMS ratio. For the control of the number of branches per initiator functional group, we adjusted the feed ratio of CMS to macroinitiator, and used large amount of the catalyst such as 2 equiv to CMS in order to ensure a facile branching reaction from 1-BCl. In the polymerization, bromopropionyl group was used as an initiating group for better initiator efficiency. The branch length was controlled via adjustment of the mole ratio of styrene to CMS.

The GPC traces of PEG_4-*b*-PS_8 in Fig. 2 show molecular weight increases as the polymerization proceeds. From GPC results, the proposed chain growing mechanism of synthesized polymer is shown in Scheme 4. In early reaction (Fig. 2 (a)), two kinds of polymers are shown at elution times of 50 and 54 min, and these are probably caused by two kinds of growing species initiated from 4-arm macroinitiator and CMS, respectively. The polymer initiated from CMS (PCMS) at elution time of 54 min has polymerizable vinyl group. Therefore, as polymerization proceeds, PCMS is inserted into growing polymer chain from 4-arm PEG macroinitiator. The polymer with inserted PCMS grows continuously as polymerization proceeds and the polymer reaches a targeted architecture, consequently.

In the scheme, active chain ends are represented as chlorine atoms because it is known that Br exchanges with Cl through CuCl catalyst after the first initiation reaction, and this fact may



Scheme 4. Proposed chain growing scheme for controlled architecture.

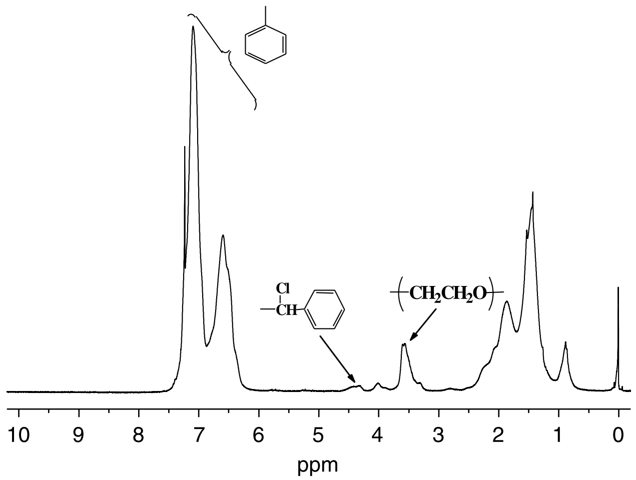


Fig. 3. ^{1}H NMR Spectrum of amphiphilic star block copolymer in $CDCl_3$.

bring equal rate of polymerization for both main chain and side chain polymerizations [24]. At 2 h (Fig. 2 (d)) some coupling reaction of polymer chains appeared as shown from the high MW tailoring at elution time of 41 min. Fig. 3 shows the NMR spectrum of PEG_4-*b*-PS_8 after polymerization for 1.5 h. At around 7 ppm, the aromatic proton peak of the styrene appeared, and this peak shows that the amphiphilic block copolymer was synthesized. The molecular weight of PS is calculated by integration ratio of phenyl ring at around 7 ppm to ethylene peak ($–OCH_2CH_2O–$) at around 3.5 ppm. The number of PS branches is calculated by the integration ratio of chain end groups (C*H*(phenyl)–Cl) at around 4.2 ppm to ethylene groups ($–OCH_2CH_2O–$) at around 3.5 ppm.

The synthetic results targeting two chains per arm (total eight chains per molecule, PEO_4-*b*-PS_8) are summarized in Table 1. In these polymers, targeted molecular weight of each PS chain is 2000 at 80% conversion. The table shows that calculated number of chains per arm as well as the M_n of each PS chain agree well with the targeted values. For the polymers with reaction times of 1.5 and 2 h, GPC M_n shows some discrepancy from the M_n by NMR. This result is caused by the some side reactions such as coupling of growing polymer chain. If any coupling reaction occurs, the molecular weight measured by GPC will increase, but molecular weight measured by NMR will stay the same, because the M_n by NMR is calculated from the ratio of PS block to PEG block. In the Table 1 the best result was obtained with the one polymerized for 1.5 h, and this result tells that the molecular architecture is possible to be controlled throughout the control of polymerization time under a given reaction condition.

On the basis of Table 1 we tried the synthesis of polymers with different number of branches and chain lengths. Table 2 summarized the characteristics of the copolymers containing various chain length and number of PS chains. Each polymerization conditions are shown in Table 2. This table also shows that GPC molecular weight values of the synthesized amphiphilic block copolymers are quite different from ^{1}H NMR results. The discrepancy in molecular weights is due to the difference in their hydrodynamic volume for a highly branched star polymer compared to linear PS structure used for GPC standard. The NMR results in Table 2 can tell that targeted architectures are attainable. In the case of PEG_4-*b*-PS_8 4k, molecular weight and number of PS branches are somewhat smaller than designed. This result may be caused by the increased difficulty of monomer and CMS diffusion to growing active polymer chain especially at high conversion because of higher viscosity of the polymerization medium, compared to the polymerization system with low molecular weighted polymers. Data also show successful synthesis of three PS branches per PEG initiating site. A more careful design of the reaction could lead controlled synthesis for more number of polystyrene branches.

3.2. Preparation of core–shell type block copolymer

Core–shell type amphiphilic block copolymers were synthesized by the hyperbranched polymerization of CMS or copolymerization of CMS with styrene, by initiating from the tetra-functional initiator as in Scheme 3. Used catalyst ratio to CMS was 0.1, which is enough for the formation of highly branched structure without gel formation, but may not be enough for the formation of perfect hyperbranched structure. After polymerization, HPCMS was produced as a side product because CMS was used quite large amount compared to the tetrafunctional PEG initiator (Fig. 4 (a)). This adduct was removed via cyclohexane extraction as shown in the GPC trace (Fig. 4 (b)). The molecular weight (MW) and its distribution were characterized after removal of homopolymerized CMS.

Table 1
Synthetic results of star block copolymers for the controlled architecture of PEG4-*b*-PS8 by ATRP

Sample	Target		GPC			NMR		
	$M_{n\ th\ PS}$ [a]	Chain number[b]/arm	Time (h)	$M_{n\ GPC}$ [c]	PDI	$M_{n\ NMR}$ [d]	No. arm	$M_{n\ arm}$
1	2000	2	0.5	7900	1.11	–	–	
2			1	10,400	1.70	–	–	
3			1.5	13,700	1.55	20,000	2.11	2200
4			2	17,300	1.60	21,000	2.08	2300

Conditions: $[\text{macroinitiator}]_0 = 1.3$ mM, $[\text{CMS}]_0 = 5.2$ mM, $[\text{St}]_0 = 168$ mM, $[\text{CuCl}]_0 = 8.4$ mM, [2,2′-bipyridine] = 25.2 mM, Temp. = 120 °C.

[a] Target molecular weight of each PS chain at 80% conv.: $([\text{St}]_0/([\text{macroinitiator}]_0+[\text{CMS}]_0))\times 104.15$.

[b] Target chain number of synthesized PS per PEG arm: $([\text{CMS}]_0/[\text{macroinitiator}]_0)/4+1$.

[c] Molecular weight of synthesized block copolymer calculated from GPC.

[d] Molecular weight of synthesized block copolymer calculated from ^{1}H NMR.

Table 2
Synthetic results of star block copolymers for controlled number of PS chains and molecular weight

Entry	Sample	Target		GPC		NMR		
		$M_{\mathrm{n\ th\ PS}}$[a]	Chain number[b]/arm	M_n[c]	PDI	M_n[d]	No. arm	$M_{\mathrm{n\ arm}}$
5	PEG$_4$-*b*-PS$_8$ 1k	1000	2	5900	1.73	10,000	1.5	700
6	PEG$_4$-*b*-PS$_8$ 2k	2000	2	12,200	1.60	21,000	2.08	2300
7	PEG$_4$-*b*-PS$_{12}$ 2k	2000	3	17,300	1.60	28,000	3.37	2000
8	PEG$_4$-*b*-PS$_8$ 4k	4000	2	22,000	1.62	43,000	3.2	3200

Conditions: $[\mathrm{macroinitiator}]_0 = 1.3$ mM, $[\mathrm{CMS}]_0 = 5.2$ mM except sample 7, and 10.4 mM for sample 7, $[\mathrm{St}]_0 = 52$ mM for sample 5, 168 mM for sample 6, 312 mM for sample 7, 312 mM for sample 8. $[\mathrm{CuCl}]_0 = 8.4$ mM, [2,2′-bipyridine] = 25.2 mM, Temp. = 120 °C; polymerization time. 2 h for all samples.

[a] Target molecular weight of each PS chain at 80% conv.: $([\mathrm{St}]_0/([\mathrm{macroinitiator}]_0+[\mathrm{CMS}]_0))\times 104.15$.

[b] Target chain number of synthesized PS per PEG arm: $([\mathrm{CMS}]_0/[\mathrm{macroinitiator}]_0)/4+1$.

[c] Molecular weight calculated from GPC.

[d] Molecular weight calculated from ^{1}H NMR.

Fig. 5 shows GPC traces versus polymerization time. In the early stage of polymerization (1 h), increase of MW is prominent from the macroinitiator. After 3 h of reaction, modest increase of MW was achieved with some high MW tailing due to the coupling reaction of growing polymer chains. At 3 h, the conversion was 68%. Above this conversion, polymer concentration becomes higher that the possibility of coupling of growing polymer chain increases.

MW was also characterized by ^{1}H NMR. Fig. 6 shows the ^{1}H NMR spectrum of synthesized polymer. From aromatic proton peak at ca. 7 ppm and oxyethylene peak at ca. 3.5 ppm, it is clear that amphiphilic polymer was synthesized. The molecular weight of polymer is calculated by the integration ratio of aromatic proton resonance peak at ca. 7 ppm to oxyethylene peak at ca. 3.5 ppm. Some double bond peaks due to elimination reaction of chain end were shown at ca. 5–6 ppm [5]. The elimination reaction can be enhanced by the presence of bipyridyl used as the ligand of the catalyst.

Table 3 shows the synthetic result of star shape copolymers. As polymerization proceeds, the increase of molecular weight of polymers levels off at around M_n of 5000 in GPC result. But M_n calculated from NMR increases from 1350 to 7000. The difference of M_n is originated from its hydrodynamic volume and also may be originated form polymer architecture. Generally hydrodynamic volume of a hyperbranched polymer system increases more slowly than their linear analogue with increase of molecular weight. In our system the synthesized polymer contains four hyperbranched polymers connected to the 4-arm macroinitiator. As a consequence, the shape of the obtained block copolymer will be very closer to a dendrimer. The difference of M_n between NMR and GPC reflects this fact. Polydispersity indices (PDI) are 1.34–1.67 except the polymer obtained after 12 h reaction. This value is narrower compared to the case where only CMS is polymerized with monofunctional initiator [4]. The reason of the broad PDI of the polymer obtained after 12 h reaction, is due to more pronounced coupling reaction of growing polymer chain as the %conversion reaches higher. Zhu [25] reported that PDI becomes narrower to close globular structure in branched polymer system. Thus PDI of synthesized polymer is narrower than pure hyperbranched PCMS because synthesized star shape polymer is closer to globular structure than pure hyperbranched PCMS.

Weimer et al. reported that degree of branch (DB) of hyperbranched PCMS could be calculated from the ratio of 2° benzylic proton at around 4.8 ppm to 1° benzylic proton at around 4.5 ppm. The DB of a perfect dendritic polymer is 0.5 and the DB of a linear polymer is 0 [5]. The DB of synthesized polymers based on NMR results is shown in Table 3. DB of the synthesized polymers is 0.22–0.25, and these values are very similar to the reported value of Weimer et al. with the catalyst to CMS ratio of 0.1. Obtained values indicate that the structure of the synthesized polymer takes a form between perfect

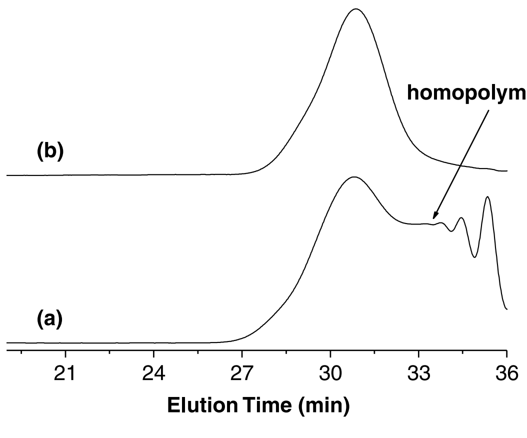


Fig. 4. GPC traces of star shape block copolymer (a) before separation (b) after separation.

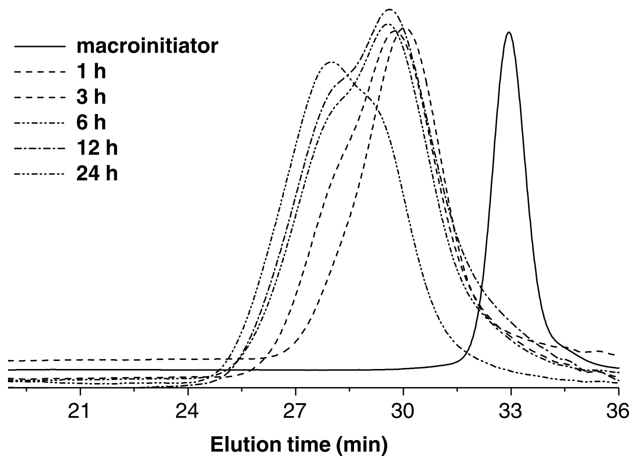


Fig. 5. GPC traces of dendrimer like star block copolymers (CMS only).

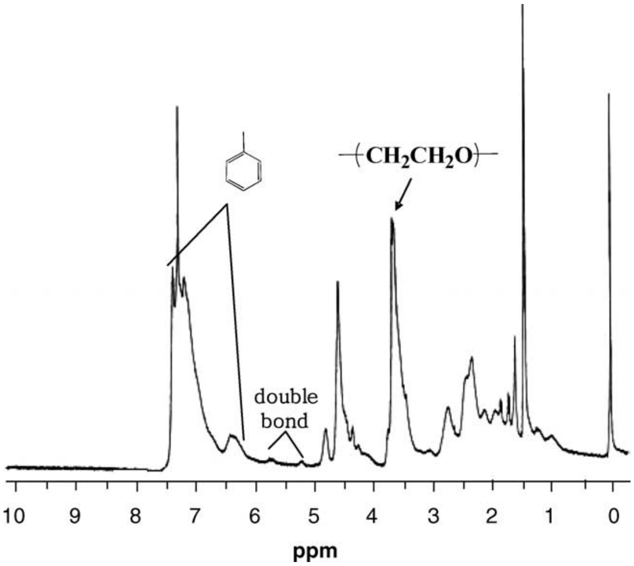


Fig. 6. ^{1}H NMR spectrum of dendrimer like star block copolymer (CMS only).

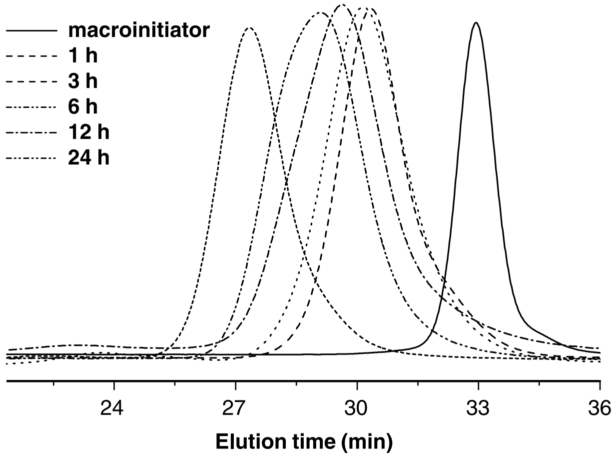


Fig. 7. GPC traces of dendrimer like star block copolymer (CMS: styrene = 1:10).

dendritic structure and linear structure. Also this medium value is originated from the different reactivity of two propagating 2 and 1° radical species during polymerization. Yan et al. [26] reported theoretically simulated DB of hyperbranched polymers obtainable via a self-condensing vinyl polymerization (SCVP) such as ATRP. They reported that the maximum theoretical DB of a hyperbranched polymer is 0.465, and that of DB for AB_2 polycondensation is 0.5 in the maximum MW. This indicates that polymer structure synthesized via SCVP shows the median structure between a dendrimer and a linear polymer, and our experimental results confirm this theoretical expectation.

In polymerization system using CMS only, the obtained polymer has high chain density and low molecular weight due to steric crowding, which prohibits a facile approach of the catalytic system and monomer to the dormant alkyl chloride bond. If CMS is copolymerized with another vinyl monomer, the obtained polymer will have a loose chain density and higher attainable molecular weight. So, CMS was copolymerized with styrene in the presence of 4-arm macroinitiator. Employed molar ratios of styrene to CMS in the feed were 10, 20, and 50. In these cases, styrene/CMS copolymers were shown and they were extracted off using cyclohexane. The GPC traces of the remaining block copolymers were shown in Figs. 7–9, for styrene/CMS ratio of 10, 20, and 50, respectively. As shown in the figures, molecular weights of obtained polymer increased as the polymerization time for a given styrene/CMS ratio. The synthetic results are summarized in Table 4. As in the table, polymers with quite narrow PDI were obtained when the styrene/CMS ratio was 10. And polymers with higher molecular weights were obtained when the styrene/CMS ratios were 20 or 50, compared to the case with the ratio of 10 for a given reaction time. The styrene/CMS ratio of 20 gave polymers with higher molecular weights than the system with the ratio of 50 for a given reaction time. The large increase of M_n after reaction time of 24 h with the monomer ratio of 20 is probably due to intermolecular coupling reaction between star block copolymers. Fig. 10 is the GPC traces of unfractionated star block copolymers when the styrene/CMS ratio was 50. It shows slight amount of intermolecular coupling reaction after 24 h. And it is evident from Fig. 9 that its purified polymer shows the similar GPC profile. Low molecular weighted HPCMS copolymers were large after short reaction times, but

Table 3
Synthetic results of dendrimer like core–shell type copolymer with CMS alone

Polymerization time	M_n[a]	M_p[b]	PDI	M_n[c]	M_n/arm[d]	DB[e]
Macroinitiator	1200	–	1.07	1350	–	–
1 h	3800	4500	1.34	4900	900	0.22
3 h	4000	5000	1.60	6500	1300	0.24
6 h	4900	5400	1.67	7400	1500	0.25
12 h	4000	5400	1.98	7000	1400	0.23
24 h	7000	–	1.58	5800	–	0.12

Polymerization conditions: $[I]_0 = 2.62$ mM, $[CMS]_0 = 131$ mM, $[CuCl]_0 = 13.3$ mM, $[bpy]_0 = 26.6$ mM, Temp. = 110 °C.

[a] From GPC.
[b] Peak molecular weight from GPC.
[c] From NMR.
[d] M_n of each HPCMS arm.
[e] Degree of branch.

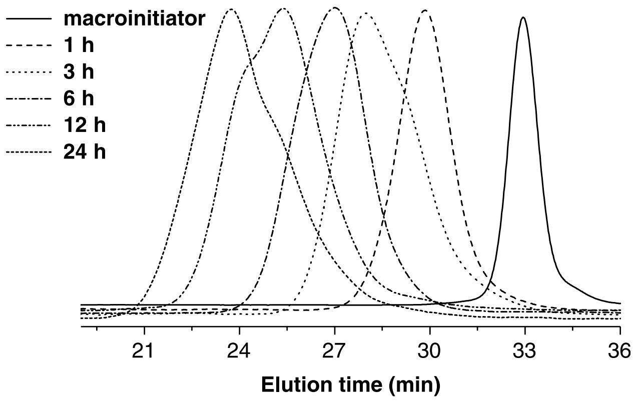


Fig. 8. GPC traces of dendrimer like star block copolymers (CMS: styrene = 1:20).

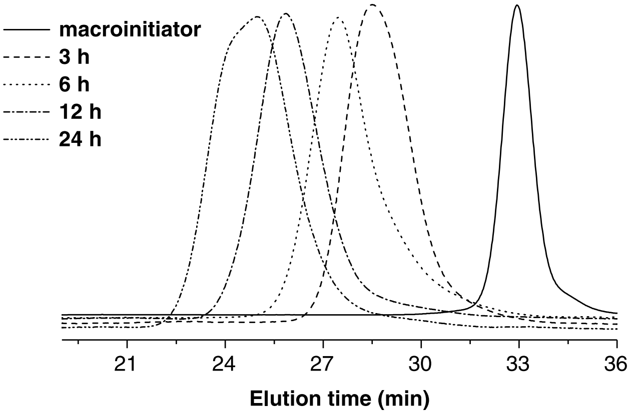


Fig. 9. GPC traces of dendrimer like star block copolymers (CMS: styrene = 1:50).

quite reduced after longer reaction times, and these were easily removed by fractionation. Therefore, from the comparison of the data in Table 4 and GPC traces in four figures, it is clear that star block copolymers with globular structure can be obtained by a proper control of the reaction parameters, probably employing the styrene/CMS ratio <20.

Slower polymerization rate was observed with the increase of styrene/CMS ratio. In ATRP system, the polymerization rate is affected by initiator concentration. Actual initiator concentration in copolymerization system becomes lower as the styrene/CMS ratio increases, because CMS acts as inimer (*ini*tiator + mono*mer*). The same phenomenon was reported by Hong et al. [27]. They prepared hyperbranched polyacrylate copolymer synthesized by copolymerization of 2-(2-bromopropionyloxy)ethyl acrylate (used as AB type monomer) and methyl acrylate. They reported that the polymerization rate became slower with increase of methyl acrylate concentration. The peak molecular weight increased as the ratio of styrene/CMS increased. PDI became narrower, probably due to reduced intermolecular coupling reaction between star polymers owing to the reduced CMS concentration, and resulting slow polymerization rate. This will also promote homogeneity of the reaction system. In high CMS concentration, active radical concentration is high and the polymerization rate is fast, and the possibility of side reaction is high. By increasing the ratio of styrene/CMS, therefore, control of polymerization is facile.

Table 4
Synthetic results of core–shell type star block copolymers

CMS: styrene[a]	Polymerization time (h)	M_n[b]	M_p[b]	PDI[b]
1: 10	1	3200	3900	1.20
	3	3500	4200	1.22
	6	4100	5200	1.38
	12	5700	6400	1.24
	24	11,300	13,600	1.20
1:20	1	4300	4700	1.17
	3	6800	10,300	1.38
	6	14,900	15,900	1.30
	12	30,700	35,300	1.68
	24	49,400	89,900	2.24
1:50	3	6600	8200	1.20
	6	9600	12,900	1.29
	12	21,500	27,600	1.34
	24	35,800	43,800	1.55

Polymerization conditions: $[I]_0 = 0.66$ mM, $[CMS]_0 = 33.6$ mM, $[CuCl]_0 = 3.43$ mM, $[bpy]_0 = 6.86$ mM, Temp. = 110 °C.

[a] Mole ratio of CMS to styrene.

[b] From GPC.

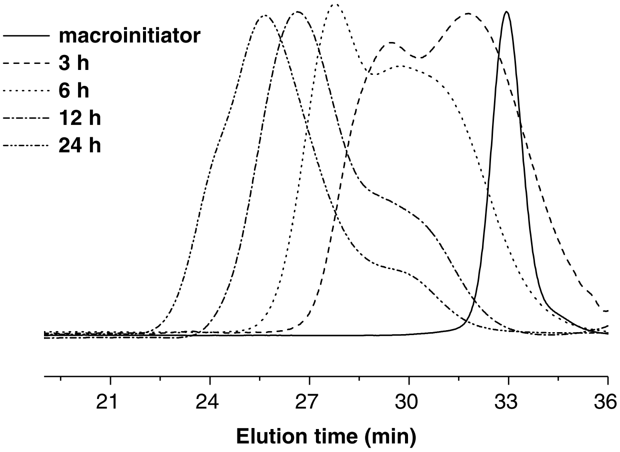


Fig. 10. GPC traces of unfractionated dendrimer like star block copolymers (CMS: styrene = 1:50).

4. Conclusions

Hydrophilic tetrafunctional macroinitiator was synthesized by the reaction of pentaerythritol ethoxylate with 2-bromopropionyl bromide, for amphiphilic star block copolymers containing PEG in core and PS in shell. The synthesized tetrafunctional macroinitiator was polymerized with styrene and chloromethylstyrene, and the latter was used as a linking agent to produce amphiphilic block copolymers by ATRP. The number of PS branches is well controllable by adjusting the initial feed ratio of CMS to hydrophilic tetrafunctional macroinitiator. Average chain length of the PS branches was also controllable by adjusting the feed ratio of styrene to CMS, and polymerization time. The resulting copolymers have controlled architecture with 2–3 branches per bromopropionyl group and with the chain length of <2300. But PDI becomes slightly broader as the polymerization proceeds due to side reactions including coupling. The novel dendrimer like star shape amphiphilic block copolymers containing PEG core and hyperbranched PS shell were synthesized via ATRP. Homopolymerized CMS was removed by cyclohexane extraction. The MW is 4900–7000 and PDI is 1.34–1.67. PDI became broader as the polymerization proceeded. The broadening may be due to some side reactions such as coupling. The DB is 0.12–0.25. This result agrees well with other reports. In the case of copolymerization with CMS and styrene, the increase of MW is pronounced compared to CMS alone and also the synthesized polymer shows more controlled molecular structures.

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