Architecture of Rod Consisting of Hyperbranched Pendant Chains-Coil Block Copolymers by ATRP Approach

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ABSTRACT: Atom transfer radical polymerization (ATRP) was applied to a novel synthesis of rod consisting of hyperbranched pendant chains-coil block copolymers. The procedure included the following steps: (1) esterification reaction of poly(ethylene glycol) methyl ether (PEO) with 2-bromoisobutyryl bromide (BIBB) yielded a PEO-Br macroinitiator, (2) ATRP method of 2-hydroxylethyl methacrylate (HEMA) using PEO-Br provided PEO-*block*-poly(2-hydroxyethyl methacrylate) (PHEMA) block copolymers, (3) esterification of PEO-*block*-PHEMA with BIBB yielded block-type polyinitiator, and (4) ATRP of HEMA-Br inimer using block-type polyinitiator provided coil-rod (consisting of hyperbranched pendant chains) block copolymers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3554–3561, 2008

Key words: rod-coil block copolymers; macroinitiator; ATRP; hyperbranched polymers

INTRODUCTION

There has been rapid growth in the number of techniques employed in the area of controlled/living radical polymerization, such as atom transfer radical polymerization (ATRP),[1,2] nitroxide-mediated radical,[3] and reversible addition-fragmentation chain-transfer (RAFT) polymerization.[4–7] Until recently, ionic polymerizations (anionic or cationic) were the only living technique available that efficiently controlled the structure and architecture of vinyl polymers. Although these techniques ensure low polydispersity materials, controlled molecular weight and defined chain ends, they are not useful for certain polymerization and copolymerization of functionalized vinyl monomers.

On the other hand, variation of molecular architecture has become an increasingly important tool in the search for materials with excellent properties. The design and synthesis of suitable block copolymers, such as those consisting of both flexible components and rigid components, as building blocks for highly ordered supramolecular architectures have attracted considerable attention in the past several decades.[8,9] The resulting supramolecular structures can potentially offer various functionalities by means of their photophysical, electrochemical, or biological properties through the rod blocks.[10–12] Because of the combined results of the orientation of the rod block and microphase separation of the two incompatible blocks, rod-coil block copolymers exhibit distinct self-assembling behaviors and morphologies compared to their coil-coil counterparts.[13–17] More recently, the cylindrical brush-coil block copolymers were prepared by ATRP approach.[18–22] In general, cylindrical brush (comb) blocks take not rod but worm-like conformation in solution.

Ishizu and Mori[23] presented a novel route to hyperbranched polystyrene (HPS) from 4-vinylbenzyl-*N,N*-diethyldithiocarbamate (VBDC) as an inimer by one-pot photopolymerization. Photolysis of VBDC leads to the initiating benzyl radical with an inactive dithiocarbamate (DC) radical. This radical mechanism is very similar to the alkoxyamine-initiated living radical polymerization system, details of which were published by Moad and Rizzardo.[24] We also made it clear from kinetic analysis that free-radical polymerization of inimer VBDC proceeded by a living radical mechanism.[25] Such hyperbranched polymers formed a single molecule due to a very high

density. In fact, hyperbranched molecules behaved as hard spheres such as dendrimers in solution.[26,27] We have also prepared hyperbranched poly(ethyl methacrylate) (HPEM) from 2-(N,N-diethyldithiocarbamate)ethyl methacrylate (DCEM)[28] as an inimer by one-pot photopolymerization.[28,29] These HPEM showed solution properties similar to HPS nanoparticles. On the other hand, Matyjaszewski's group also prepared HPS from p-chloromethylstyrene[30] and hyperbranched polyacrylates from acrylic halide inimers[31] via ATRP. Then, we can expect to construct the rod consisting of hyperbranched pendant chains-coil block copolymers by combination of block copolymer synthesis and hyperbranched polymer propagation via a living radical mechanism.

In this article, we presented a novel route to rod consisting of hyperbranched pendant chains-coil block copolymers via a living radical mechanism. The block consisting of hyperbranched pendant chains is speculated to exhibit rigid rod structure due to highly branching density. We also studied the dilute solution properties of such rod-coil block copolymers by light scattering.

EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA, Tokyo Kasei Organic Chemicals, Tokyo) was dried over calcium hydride (CaH$_2$) and distilled in vacuo. Poly(ethylene glycol) methyl ether (PEO; M_n = 5000, M_w/M_n = 1.13, Aldrich, Milwaukee), 2-bromoisobutyryl bromide (BIBB), triethyl amine (Et$_3$N), 2,2′-bipyridyl (bpy), methanol, tetrahydrofuran (THF), diethyl ether, chloroform (CHCl$_3$), N,N-dimethylformamide (DMF) (Tokyo Kasei Organic Chemicals, Tokyo), CaH$_2$, sodium metal, MgSO$_4$, copper(I) bromide, (CuBr), CuCl, CuCl$_2$ (Kanto Kagaku Reagent Division, Tokyo) and basic aluminum oxide (Merck, Frankfort) were used as received.

Synthesis of PEO-block-PHEMA diblock copolymer 2

Synthetic route for PEO-block-PHEMA diblock copolymers is shown in Scheme 1. A mixture of PEO (2.65 g, terminal OH groups = 0.53 mmol), BIBB (0.30 mL, 1.59 mmol), and Et$_3$N (0.22 mL, 1.59 mmol) as an acid acceptor was stirred in THF (dried over Na chips; 20 mL) for 3 h at 0°C, followed by stirring at room temperature for 18 h. Reaction product (PEO-Br macroinitiator 1) was poured into a large excess of diethyl ether and separated by filtration. ATRP operations were carried out in a sealed glass apparatus using high-vacuum techniques (degassed polymerization mixture). A typical polymerization condition for the synthesis of PEO-block-
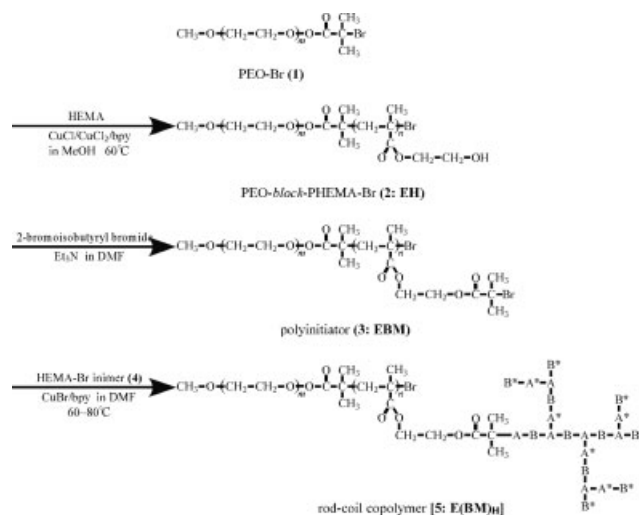
Scheme 1 Synthesis route for rod consisting of hyperbranched pendant chains-coil block copolymers: A-B* indicates HEMA-Br inimer, where A and B* are double bond and functional group, respectively.

PHEMA diblock copolymer 2 (EH; E and H indicate PEO and PHEMA blocks, respectively) is as follows. PEO-Br (0.9 g, 0.18 mmol), HEMA (1.87 g, 14.4 mmol), CuCl (22.8 mg, 0.23 mmol), CuCl$_2$ (3.1 mg, 0.023 mmol) and bpy (143 mg, 0.9 mmol) ([PEO-Br] : [HEMA] : [CuCl] : [CuCl$_2$] : [bpy] = 1 : 80 : 1.3 : 0.26 : 5, where [PEO-Br] indicates Br concentration of macroinitiator), were dissolved in methanol (25 vol % monomer solution) and the resulting mixture was stirred at room temperature for 1 h to form a copper complex, CuCl/bpy. After ATRP at 60°C for 3 h, the polymer mixture was diluted with methanol. This solution was filtered through a column filled with basic aluminum oxide to remove the catalyst, and the polymer was precipitated in an excess of diethyl ether and dried in vacuo to a constant weight.

Preparation of block-type polyinitiators 3

A mixture of 2 (EH2: 3 g, hydroxy groups = 14.7 mmol), BIBB (2.8 mL, 22 mmol), and Et$_3$N (3.2 mL, 22 mmol) as an acid acceptor was stirred in THF (dried over with CaH$_2$; 20 mL) for 3 h at 0°C, followed by stirring at room temperature for 24 h. Reaction mixture changed from cloudy to homogeneous solution during esterification. Reaction product (PEO-block-poly[2-(2-bromobutyloxy)ethyl methacrylate] (PEO-block-PBBEM) 3 (EBM) was poured into a large excess of diethyl ether and separated by filtration (degree of esterification; 100%).

Synthesis of hema-Br inimer (A-B*) 4

Under nitrogen, a solution of BIBB (40.8 mL, 330 mmol) in 50 mL of THF (dried over with Na chips)

was added dropwise to a stirring solution of HEMA (40 mL, 330 mmol) and Et$_3$N (26.7 mL, 363 mmol) in 250 mL of THF. The reaction was cooled in an ice bath. During the addition, a white precipitate formed (Et$_3$N-HBr). After complete addition of the acid bromide (1 h), the reaction was stirred at room temperature for 3 h. The precipitate was filtered. The THF was evaporated to give yellow oil. The CHCl$_3$ solution of this yellow oil was washed with water and then dried over MgSO$_4$. The CHCl$_3$ was evaporated to give a yellow oil: yield 75%. ^{1}H NMR (CDCl$_3$) δ 6.14 ppm (s, 1H); 5.60 ppm (s, 1H); 4.39 ppm (m, 4H); 1.93 ppm (s, 9H).

Preparation of rod-coil block copolymers 5

ATRP operations for the synthesis of rod-coil block copolymers were carried out under nitrogen at 60–80°C. Typical polymerization conditions for the synthesis of rod-coil copolymer 5 [E(BM)$_H$1] are as follows. Block-type polyinitiator 3 (EHB1; 0.5 g, Br groups = 1.44 mmol), CuBr (0.21 g, 1.44 mmol) and bpy (0.67 g, 4.32 mmol) ([Br] : [CuBr] : [bpy] = 1 : 1 : 3, where [Br] indicates Br concentration of block-type polyinitiator 3) were dissolved in DMF (1.6 mL), and the resulting mixture was stirred at room temperature for 1 h to form a copper complex, CuBr/bpy. HEMA-Br inimer (0.4 mL, 1.54 mmol) was dropwise slowly to polyinitiator solution (HEMA-Br concentration = 25 vol %) for 2 h at 80°C. Subsequently, the similar addition of DMF solution (1.6 mL) of HEMA-Br (0.43 g, 1.54 mmol) was repeated every 2 h three times at 80°C. The solution was filtered through a column filled with basic aluminum oxide to remove the catalyst, and the polymer was precipitated in excess of diethyl ether and dried *in vacuo*. The rod-coil copolymer was fractionated by precipitation fractionation in CHCl$_3$-hexane system.

Characterization

Polydispersities (M_w/M_n) of PEO-Br 1, block-type polyinitiator 3, and rod-coil copolymer 5 were determined by gel permeation chromatography (GPC; Tosoh high-speed liquid chromatograph HLC-8120, Tokyo) using two TSK gel columns, GMH$_{xL}$ [excluded-limit molecular weight (M_{ELM} = 4 × 10^8)] and G2000H$_{XL}$ (M_{ELM} = 1 × 10^4), in series in THF as eluent (flow rate of 1.0 mL/min) at 40°C using the calibration of polystyrene (PS) standard samples. The M_w/M_n of PEO-*block*-PHEMA was also determined by GPC (Hitachi Lachrom, Tokyo) using two TSK gel columns (GMH$_{HR}$-M) in DMF as eluent flow rate of 1.0 mL/min at 40°C. The number-average molecular weight (M_n) of PEO-*block*-PHEMA 2 was determined by the M_n of PEO-Br and composition of block copolymer determined by proton nu-

clear magnetic resonance (^{1}H NMR) in dimethyl-d_6 sulfate (DMSO-d_6). The M_n of rod-coil copolymers 5 was determined by the composition from ^{1}H NMR in CDCl$_3$. ^{1}H NMR spectra (300 MHz, Bruker GPX300 NMR spectrometer) of 1, 2, 3, 4, and 5 were performed in CDCl$_3$ or DMSO-d_6.

The diffusion coefficient (D_0) of rod-coil copolymers 5 was determined by the extrapolation to zero concentration on dynamic light scattering (DLS, Photal DLS-8000PNA: Otsuka Electronics, Tokyo, He-Ne laser: λ$_0$ = 632.8 nm, 10 mW) data with cumulant method at 25°C in 2–10 mg/mL CHCl$_3$ solution of 5. The scattering angle was in the range 30–150°. Sample solutions were filtered through membrane filters with a nominal pore of 0.2 μm just before measurement.

Morphological behavior of 5 was obtained as follows. CHCl$_3$ solution of 0.1 wt % concentration was dropped on a microscope mesh coated with carbon film for taking transmission electron microscopy (TEM). The specimen was sputtered with Pd-Pt at 20° of tilt angle. Morphological results were obtained on a Hitachi H-500 TEM at 100 kV.

RESULTS AND DISCUSSION

We have reported more recently that well-defined PEO-*block*-poly(methyl methacrylate) (PMMA) was prepared, initiated by macroinitiator PEO-Br, by means of ATRP, where esterification of the terminal hydroxyl group of PEO with BIBB yielded a macroinitiator PEO-Br.[32] That is to say, a ^{1}H NMR spectrum of PEO-Br displayed the expected resonances for the ethylene protons (δ 3.75 ppm) of PEO and the methyl protons (1.98 ppm) of the isobutyryl groups. The functionality (Br group) was calculated to be unity from the integration ratio of ethylene protons of PEO to methyl protons of isobutyryl group.

The PEO-*block*-PHEMA diblock copolymers (EH: E and H indicate PEO and PHEMA blocks, respectively) were prepared by ATRP. It is well known for the block copolymer synthesis that poly(methacrylate) macroinitiator having a bromine atom at the end group effectively initiated the ATRP of methacrylate monomers in the presence of the catalyst CuCl; that is, halide exchange should take place.[33–35] Halide exchange contributes to increase the relative rate of initiation to propagation. In the case of high reactive monomer such as HEMA, a less active catalyst must be used to reduce termination reactions.[36] We used a CuCl/CuCl$_2$/bpy catalyst system in this work. The polymerization conditions and results of PEO-*block*-PHEMA are listed in Table I. A typical GPC profile of diblock copolymer EH2 (reaction temperature; 60°C) is shown in Figure 1 using a refractive index (RI) detector. The GPC distribution of EH2 has a single and narrow molecular weight dis-

TABLE I
Polymerization Conditions and Results of PEO-*block*-PHEMA[a]

	Feed			Block copolymer			
Code	[PEO]/[HEMA]/[CuCl]/ [CuCl$_2$]/[bpy]	Temp (°C)	Conv. (%)	$10^{-4}M_n$[b]	M_w/M_n[c]	$DP_{n,PHEMA}$[d]	$(DP_{n,PHEMA})_{theo}$[e]
EH1	1/80/1.3/0/5.0	60	89	1.42	1.29	71	73
EH2	1/80/1.3/0.26/5.0	60	67	1.28	1.24	60	55
EH3	1/80/1.3/0.43/5.0	60	62	1.19	1.21	53	51
EH4	1/80/1.3/0.13/5.0	40	39	0.92	1.20	32	32
EH5	1/40/1.3/0.26/5.0	40	29	0.89	1.20	30	24

[a] Polymerized using macroinitiator PEO-Br (M_n = 5000) in methanol (monomer concentration = 25 vol %) for 3 h.
[b] Determined from M_n of PEO-Br and composition of block copolymer.
[c] Determined by GPC in DMF as eluent using the calibration of PS standard samples.
[d] Degree of polymerization of PHEMA block; determined by ^{1}HNMR in DMSO-d_6.
[e] Theoretical degree of polymerization of PHEMA block.

tribution (M_w/M_n = 1.24) and shifts completely to the high-molecular-weight side compared with that of the PEO-Br precursor (M_w/M_n = 1.13). To elucidate the M_n of diblock copolymer, we determined the composition of diblock copolymer by ^{1}H NMR spectrum in DMSO-d_6. Figure 2(a) shows a typical ^{1}H NMR spectrum of EH2 diblock copolymer. The single peak observed at δ = 3.50 ppm (a) is attributed to the ethylene protons of PEO block. The peaks at 3.58 (e) and 3.90 ppm (f) can be assigned to the methylene protons of PHEMA block. The peak observed at 4.80 ppm (g) is attributed to the hydroxy protons. Three divided peaks at 0.65–1.10 (d) can be also assigned to the α-methyl protons of PHEMA block. The degree of polymerization of the PHEMA block ($DP_{n,PHEMA}$ = 60) was determined from the signal intensity ratio of the methylene protons (f) to the ethylene protons (a). The $DP_{n,PHEMA}$ of EH2 showed somewhat large value compared with theoretical degree of polymerization [$(DP_{n,PHEMA})_{theo}$ = 55] (assuming that one molecule of the initiator generates one polymer chain and the initiator efficiency is unity). This means that the initiator efficiency is small than unity in the block synthesis.
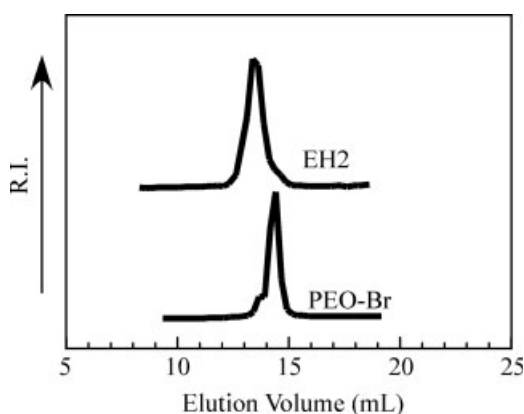
EH1 was the polymerization system in the absence of CuCl$_2$. In the same polymerization conditions, EH1 showed high conversion (89%) and somewhat
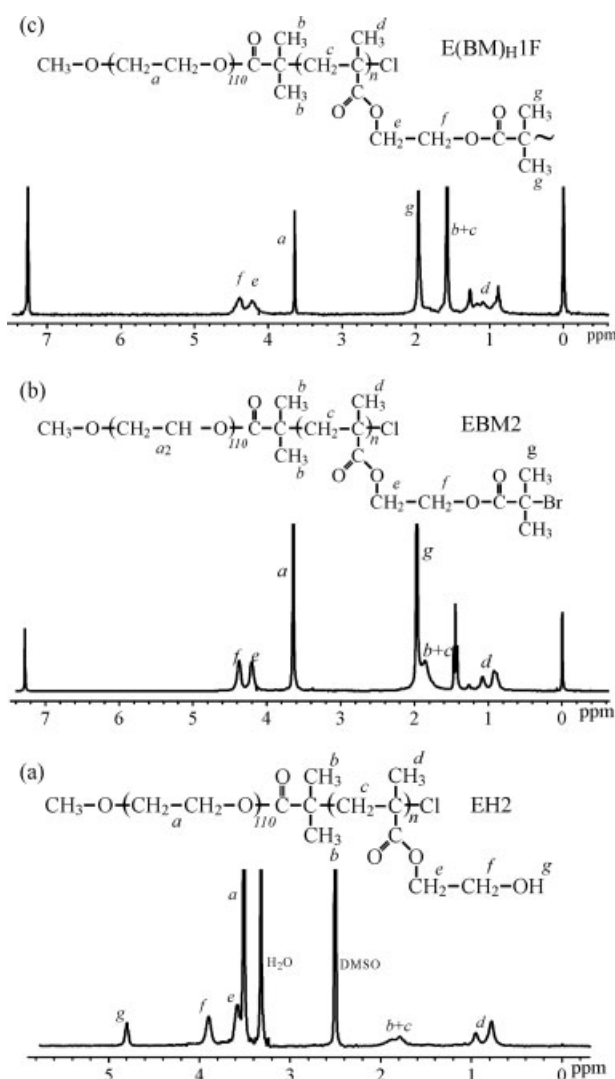

Figure 2 ^{1}H NMR spectra of (a) PEO-*block*-PHEMA 2: EH2 (in DMSO-d_6), (b) polyinitiator 3: EBM2 (in CDCl$_3$), and rod-coil copolymer 5: E(BM)$_H$1F (in CDCl$_3$).

Figure 1 GPC profiles of PEO-Br and PEO-*block*-PHEMA EH2 in DMF as eluent at 40°C.

broad polydispersity (M_w/M_n = 1.29) compared with EH2. However, The DP$_{n,PHEMA}$ (71) was closed to theoretical value [(DP$_{n,PHEMA}$)$_{theo}$ = 73]. In general, ATRP of HEMA was carried out using protected monomer of HAMA such as 2-(trimethylsilyloxy)ethyl methacrylate to improve high reactivity and solubility in solvent.[36] It should noticed to achieve narrow polydispersity for the PEO-*block*-PHEMA synthesis using direct addition of HEMA monomers. On the other hand, EH4 and EH5 was carried out at 40°C to obtain lower DP$_{n,PHEMA}$ under low conversion. As shown in Table I, not only the DP$_{n,PHEMA}$ but also polydispersity (M_w/M_n = 1.20) could be controlled under such polymerization conditions. Methanol as solvent employed in this work seems to work as good solvent for both PEO and PHEMA chains. It was concluded that the well-defined PEO-*block*-PHEMA block copolymers were synthesized by ATRP of HEMA initiated by PEO-Br using the catalyst CuCl/CuCl$_2$/bpy system.

Subsequently, the esterification of hydroxy groups (OH) in PHEMA blocks was carried out with BIBB in THF solution. The reaction mixture changed into homogeneous solution with proceeding esterification. Figure 2(b) shows the ^{1}H NMR spectrum (in CDCl$_3$) for the esterification product EBM2. The peak at 2.00 ppm (g) represents the methyl protons in bromoisobutyryl groups. The peaks observed at 4.37 (f) and 4.21 ppm (e) are assignable to the methylene protons in PBBEM block. The integration ratio of methyl protons (g) to the methylene protons (f+e) was 6 : 4. Moreover, the methylene and hydroxy protons of PHEMA block disappeared completely in this spectrum. These results indicate that the esterification for the product EBM2 (3) proceeded with quantitatively in these reaction conditions.

In preliminary experiments, we performed rod-coil copolymer synthesis by stirring a mixture of polyinitiator EBM, large excess of HEMA-Br inimer, and catalyst in DMF (inimer concentration = 40 vol %) at 100°C. As a result, the polymerization products provided a mixture of rod-coil copolymer and hyperbranched HEMA-Br homopolymer. The key to such rod-coil copolymer synthesis is effective initia-

tion of polyinitiator and subsequent rapid propagation of hyperbranched structure. Therefore, the rod-coil copolymers 5 were prepared by not only slow dropping of dilute HEMA-Br inimer solution to polyinitiator 3 solution but also repeating this procedure for several times, varying inimer concentration and polymerization temperature. Polymerization conditions for rod-coil copolymers are listed in Table II. Typical GPC profiles of E(BM)$_H$1 are shown in Figure 3 as a parameter of reaction time (after 4 and 8 h) in THF as eluent. The hyperbranched HEMA-Br homopolymer was removed in the precipitation process to recover the product (THF-diethyl ether system) due to relatively small molecular weight. The GPC distribution after 4 h shifts to high-molecular-weight side compared to polyinitiator EBM1 as a precursor, but exhibits the shoulder at the low-molecular-weight side. This means that polyinitiator was not consumed completely within 2 h of reaction time. On the other hand, the GPC distribution after 8 h has a monomodal pattern and shifts to high-
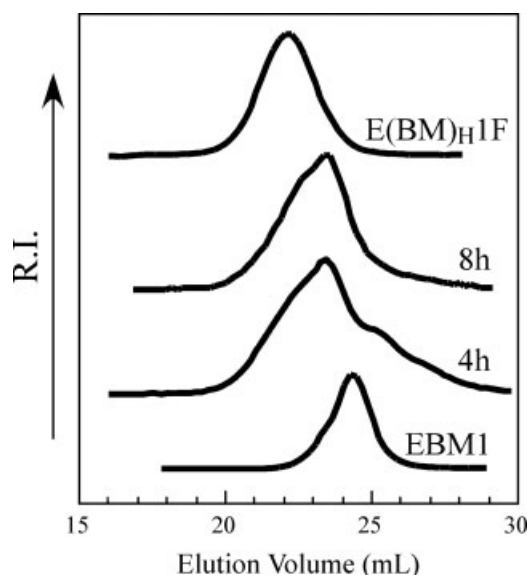

Figure 3 GPC profiles of rod-coil copolymer E(BM)$_H$1 changing reaction time (4 and 8 h) and its fraction E(BM)$_H$1F in THF as eluent at 40°C.
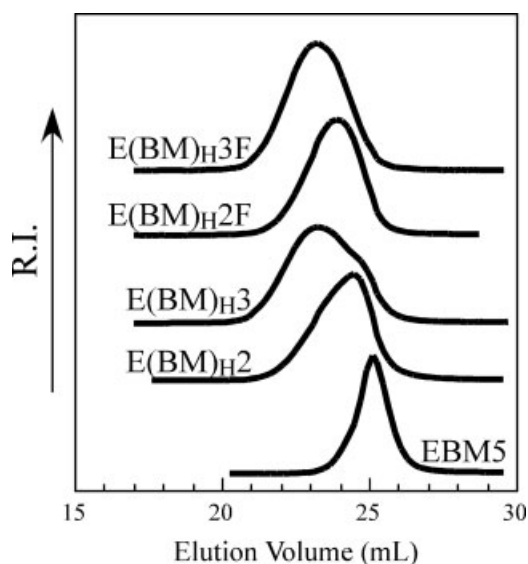
Figure 4 GPC profiles of rod-coil copolymers [E(BM)$_H$2 and E(BM)$_H$3] and their fractions [E(BM)$_H$2F and E(BM)$_H$3F] in THF as eluent at 40°C.

molecular-weight side compared with polyinitiator precursor. The molecular weight distribution is broad due to hyperbranched structure. The conversion of HEMA-Br inimer was 32% from gravimetric method. The other inimer was consumed by the homopolymer. The efficiency of the inimer for hyperbranching is low. Then, we carried out the precipitation fractionation of E(BM)$_H$1 using a CHCl$_3$-n-hexane system. The GPC profile of this fraction [E(BM)$_H$1F] is also shown in Figure 3. It was found that the rod-coil copolymer with relatively narrow polydispersity (M_w/M_n = 1.38) was obtained by this procedure. In general, irreversible biradical coupling is an inherent side reaction for all living radical polymerization systems. The GPC distribution for such biradical coupling product should showed bimodal or multimodal pattern. So, such side reactions were not observed in the experiment E(BM)$_H$1. Usually, CuBr$_2$ is added in the ATRP to prevent bimolecular coupling. In our work, CuBr$_2$ was not used for the preparation of rod consisting of hyperbranched pendant chains-coil copolymers. On the other hand, the experiment E(BM)$_H$2 was carried out under the conditions of low initial concentration of HEMA-Br and high number of times (10) for dropping of HEMA-Br with short time (0.5 h) at 70°C. The experiment E(BM)$_H$3 was also carried out under similar conditions as E(BM)$_H$2 but dropping HEMA-Br concentration increased gradually during polymerization at 60°C. GPC profiles of E(BM)$_H$2 and E(BM)$_H$3 are shown in Figure 4. Both GPC distributions shifts to high-rod-molecular-weight side compared to EBM5 precursor but exhibit relatively broad molecular weight distributions. We also carried out the

precipitation fractionation of these products using a CHCl$_3$-n-hexane system. Each GPC profile of these fractions [E(BM)$_H$2F and E(BM)$_H$3F] is also shown in Figure 4.

^{1}H NMR spectrum (in CDCl$_3$) of E(BM)$_H$1F is shown in Figure 2(c). The single peak observed at 3.65 ppm (a) is attributed to the ethylene protons of PEO block. The peak at 2.00 ppm (g) and two peaks at 4.38 (f) and 4.22 ppm (e) are assignable to the methyl and methylene protons of hyperbranched PBBEM, respectively. The degree of polymerization of hyperbranched PBBEM (DP$_{n,\text{PBBEM}}$ = 300) was estimated from the integration ratio of methyl protons (g) to ethylene protons (a). The DP$_{n,\text{PBBEM}}$ of E(BM)$_H$2Fand E(BM)$_H$3F was also estimated by ^{1}H NMR spectra. The characteristics of rod-coil copolymers are summarized in Table III. It was concluded from these results that the reaction conditions for E(BM)$_H$3 synthesis was optimum to introduce the large units of hyperbranched pendant chains.

To discuss the geometrical anisotropy and intermolecular interaction, we determined the translational diffusion coefficient (D_o) of rod-coil copolymers. In general, the mutual diffusion coefficient D(C) is defined as D(C) [equiv] $\Gamma_e q^{-2}{}_\theta \rightarrow 0$, where Γ_e, q, and θ are the first cumulant, scattering vector, and scattering angle, respectively. Angular dependence of $\Gamma_e q^{-2}$ ($qR_h < 1$, where R_h is hydrodynamic radius) for E(BM)$_H$3F is shown in Figure 5(a) (in CHCl$_3$ at 25°C). The observed data almost fitted on a flat line. This means that E(BM)$_H$3F takes spherical shape in solution. Figure 5(b) shows size distribution of E(BM)$_H$3F by means of DLS in CHCl$_3$ at 25°C. Single narrow peak is observed at D_h = 15 nm.

Figure 5(c) shows TEM photograph of E(BM)$_H$3F, sputtered with Pd-Pt at 20° of tilt angle. It is found from this texture that spherical particles are visible clearly on the carbon substrate. The average particle size (D_n) and height (H) were estimated to be 20 and 10 nm, respectively. The H is given as following equation: $H = L\tan \theta$, where L (27.5 nm) and θ (20°) indicate the shadow length and tilt angle, respectively, [see the sketch in Fig. 5(c)]. The D_n observed is somewhat large compared to hydrodynamic radius D_h in solution due to collapsed structure in the solid state. PEO coil may cling to the surface of a

TABLE III
Characteristics of Fractionated Rod-Coil Copolymers E(BM)$_H$F

Code	M_w/M_n[a]	DP$_{n,\text{PEO}}$	DP$_{n,\text{PHEMA}}$	DP$_{n,\text{PBBEM}}$
E(BM)$_H$1F	1.48	110	75	300
E(BM)$_H$2F	1.58	110	24	173
E(BM)$_H$3F	1.52	110	24	218

[a] Determined by GPC in THF as eluent using the calibration of PS standard samples.
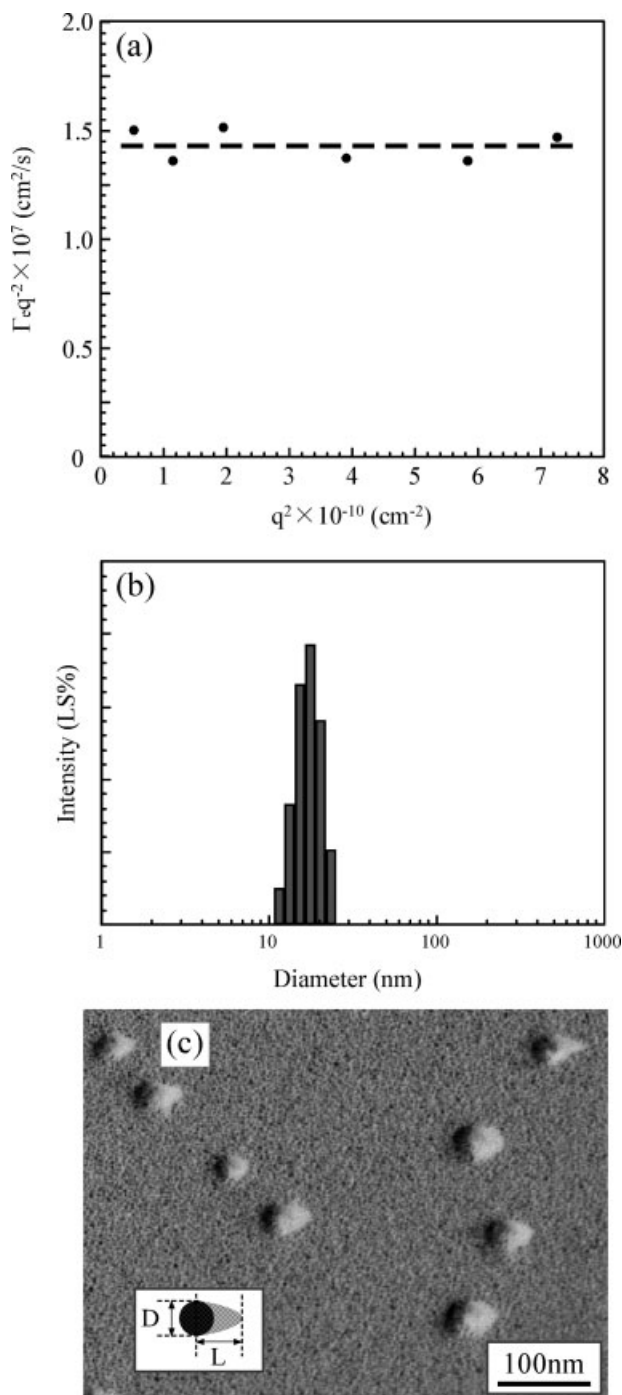
Figure 5 DLS data of rod-coil copolymer E(BM)$_H$3F: (a) angular dependence and (b) size distribution in CHCl$_3$ at 25°C, and (c) TEM photograph of E(BM)$_H$3F sputtered with Pd-Pt at 20° of tilt angle.

block consisting of hyperbranched pendant chains in the solid state. The E(BM)$_H$3F consists of short PHEMA length (DP$_n$ = 24) compared to that of PEO coil (DP$_n$ = 110). Generation number (n) of hyperbranched structure was estimated to be three, assuming that HEMA-Br hyperbranched chains are generated from all the Br groups of block-type polyinitiator [PBBEM hyperbranched units were nine

(refer the ratio DP$_{n,\text{PBBEM}}$/DP$_{n,\text{PEO}}$ in Table III)]. The total unit numbers of hyperbranched structures from one Br-initiating site are seven at the third generation, because $n_1 = 1$, $n_2 = 2$, and $n_3 = 4$, where n_i is hyperbranched unit number in the i-generation. The block consisting of hyperbranched pendant chains behaved as a rigid sphere in solution due to short PHEMA length. Therefore, the structure of E(BM)$_H$3F is very similar to the tadpole-like molecule in which the tail is coil-like molecule but attached head is a hyperbranched nanoparticle.

In this work, we present a novel synthetic strategy for the rod-coil copolymer in which a linear flexible chain is connected to rod block consisting of hyperbranched pendant chains. To obtain well-defined rod-coil copolymers, we need to control the generation of hyperbranched pendant chains It is interesting to make clear the solution and solid properties (diffusion coefficient, micelle formation, and phase behavior, etc.). The results obtained will be reported in the near future.

CONCLUSIONS

We have explored the scope of the synthetic approach to rod consisting of hyperbranched pendant chains-coil block copolymers with ATRP method. Monodisperse PEO-*block*-PHEMA could be synthesized by ATRP of HEMA initiated by PEO-Br macroinitiator using the catalyst CuCl/CuCl$_2$/bpy. Subsequent esterification of such block copolymer with BIBB yielded a block-type polyinitiator PEO-*block*-PBIEM. The grafting from ATRP approach of inimer HEMA-Br from block-type polyinitiator is a new route to construct the rod-coil copolymers.

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