

## Synthesis and Characterization of Dumbbell Type Amphiphilic Block Copolymers via ATRP

Sung Guk An, Chang Gi Cho (✉)

Centers for Advanced Functional Polymers, Department of Textile & Polymer Engineering,  
Hanyang University, Seoul, 133-791, South Korea

E-mail : [cgcho@hanyang.ac.kr](mailto:cgcho@hanyang.ac.kr)

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### Summary

Dumbbell type amphiphilic block copolymers, two polymeric globules connected with poly(ethylene glycol) 2000 or 4000 (PEG 2k, PEG 4k), were synthesized and characterized. The outer polystyrene globules are hyperbranched poly(chloromethyl styrene) synthesized via atom transfer radical polymerization. The degree of branch of the hyperbranched polymer tells that the structure is rather closer to a dendrimer than a general hyperbranched polymer. The synthesized polymers have well controlled structures. The molecular weights and its distributions were characterized by GPC and <sup>1</sup>H-NMR. The synthesized polymers were micellized in water using dialysis method and critical micelle concentration was measured using pyrene fluorescence method.

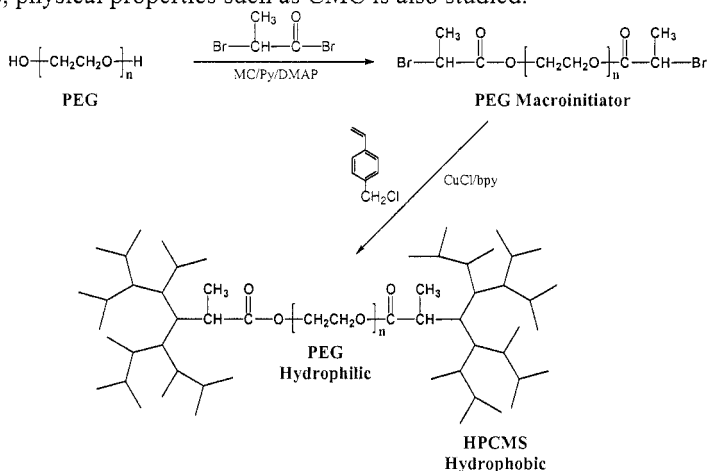
### Introduction

New polymeric materials with novel physical properties are desirable for many specific applications, and well tuned physical properties usually need well defined polymeric molecular structure in terms of molecular weights, polydispersity, the number of functional groups, and the presence or absence of precisely controlled branching [1]. These polymers are mainly prepared by precise design and careful synthesis through living polymerizations to control their molecular structures. Among various 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, graft copolymers, random/statistical copolymers, and hyperbranched polymers [2,3].

Dendrimers and hyperbranched polymers have received much attention because these dense, highly branched polymers are expected to have different physical properties

compared to their linear analogs [4]. 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 ATRP[5]. Matyjaszewski et al. reported hyperbranched poly(chloromethylstyrene) (HPCMS) [6] and Fréchet et al. reported more detailed study on polymerization conditions and structures such as degree of branch (DB), etc. [7].

Amphiphilic block copolymers are of considerable interest for various applications in which the combination of hydrophilic and hydrophobic properties of these materials may be utilized, e.g. as emulsifiers, dispersion stabilizers, and compatibilizers [8]. PEG was mostly studied as a hydrophilic block for amphiphilic block copolymers because of its biocompatibility and good water solubility, etc. General types of PEG based amphiphilic copolymers are block or graft type copolymers composed of their linear blocks. Other polymeric architectures, except linear or graft type copolymers, were rarely studied. Generally, these linear type polymers are synthesized by living anionic polymerization. Recently, controlled radical processes such as ATRP etc. were applied to amphiphilic copolymer synthesis. Batsberg et al. reported the synthesis of PS-PEG-PS triblock copolymer via ATRP [9,10]. The micell behavior of PS-PEO-PS linear block copolymer synthesized by ATRP is studied by Yuan et al [11]. Dworak et al. reported hyperbranched poly(chloromethylstyrene) (HPCMS) system containing linear PEO via Williamson synthesis [12]. However, these methods have some drawbacks such as difficulty in control of polymer architecture, broad molecular weight distribution, and the existence of unreactive compound, etc. In this paper, we report the synthesis of well-controlled dumbbell type amphiphilic block copolymers via ATRP. Two end globules are hyperbranched structures synthesized by ATRP of chloromethylstyrene (CMS) as a AB type monomers. However the physical properties such as critical micell concentration (CMC) of dumbbell type polymer is not reported in any other research. Therefore, physical properties such as CMC is also studied.



**Scheme 1.** Synthesis of dumbbell type amphiphilic block copolymer (HPCMS-b-PEG-b-HPCMS).

## Experimental

### *Materials*

2,2'-Bipyridyl (bpy), CuCl, 2-bromopropionyl bromide, aluminum oxide (neutral) were used as received from Aldrich. PEG was dried by azeotropic distillation with benzene. Chloromethylstyrene (CMS) was purified by vacuum distillation or alumina fresh column to remove inhibitor.

### *Synthesis of PEG macroinitiator*

Macroinitiator was synthesized according to reported process [9]. In a 3-neck round bottomed flask equipped with a thermometer, gas inlet, gas outlet, and dropping funnel, was placed a solution of 50 g of PEG 4k (or PEG 2k), 4.58 g of N,N'-dimethylaminopyridine (DMAP), and 2.53 g of triethylamine in 200 mL of methylene chloride. The solution was cooled to  $-15\text{ }^{\circ}\text{C}$  by stirring in an ice/acetone bath in a nitrogen atmosphere. 50 mL of 13.49 g of 2-bromopropionyl chloride solution was slowly added for 1 h. The solution was stirred for 18 h at room temperature. The solution was concentrated in a evaporator to 100 ml and filtered. The filtrate was precipitated into anhydrous ether. The obtained precipitate was recrystallized from anhydrous ethanol, twice.

### *Polymerizations*

CMS and macroinitiator were added to a flask containing CuCl (1 mol% to CMS) and dipyrindyl (bpy) (2 mol% to CMS). Nitrogen was bubbled for 20 minutes. Polymerization was conducted for 3 hours at  $110\text{ }^{\circ}\text{C}$  in an oil bath. After polymerization, the green CuCl<sub>2</sub> was removed by passing through an alumina column. The polymer solution was concentrated, then precipitated in hexane. The crude polymer was extracted with cyclohexane at  $40\text{ }^{\circ}\text{C}$  for 1 day in order to remove any self polymerized CMS. The polymer was dried in a vacuum at room temperature.

### *Micelle formation*

Micelles of HPCMS-b-PEG-b-HPCMS were prepared according to reported dialysis method as follows [14]. Polymer solution was prepared by dissolving 0.1 g of polymer in 10 mL of DMF. To form micelle and remove DMF, the polymer solution was dialyzed in a cellulose membrane (nominal molecular weight cut off : 4000 – 6000) for 24 h against 18 L of water which was exchanged at intervals of 3-6 h. The micellar solution was centrifuged to remove aggregates and then characterized.

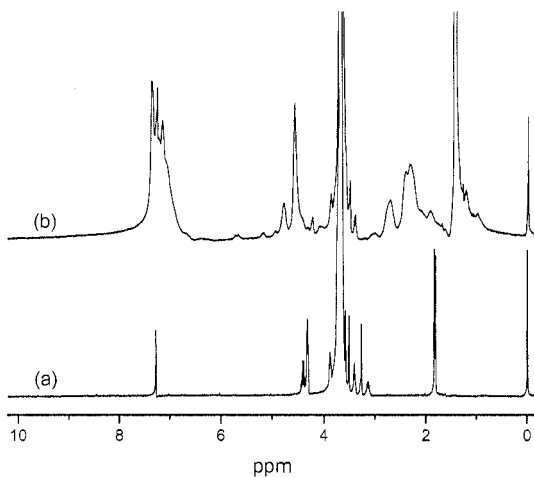
### *Characterization.*

Molecular weight and its distributions were analyzed by GPC in THF at  $25\text{ }^{\circ}\text{C}$  using Waters 616 HPLC chromatography equipped with Waters 2410 refractive index detector. Polystyrene standards were used for calibration. <sup>1</sup>H-NMR spectra were recorded with a Varian VXR/Unity 300 in CDCl<sub>3</sub> with TMS as an internal standard.

DSC analysis was carried out with Perkin Elmer DSC 7 under nitrogen. The heating rate was 10 °C/min. Fluorescence spectra were recorded on Shimadzu RF-5301PC Spectro fluorophotometer. Micelle size and its distribution were characterized with Brookhaven Laser Light Scattering System with BI 9000AT detector (incident laser: 514 nm). Micell shape was characterized with Transmission Electron Microscope (TEM, JEOL 2010).

## Results and Discussion

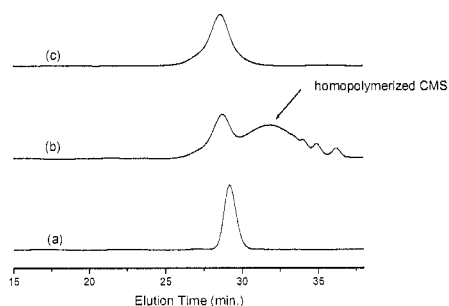
Scheme 1 shows the synthetic routes of macroinitiators and polymers. In the first step hydrophilic telechelic macroinitiators, PEG macroinitiators, were prepared by reaction of PEG 4k or PEG 2k with 2-bromopropionyl bromide. Figure 1 (a) shows  $^1\text{H}$  NMR spectrum of macroinitiator 2k. After reaction, a new signal appeared at 4.2 ppm, due to the substitution of 2-bromopropionyl groups. In the second step the amphiphilic dumbbell type block copolymers, hyperbranched poly(chloromethylstyrene)-b-PEG-b-hyperbranched poly(chloromethylstyrene) (HPCMS-b-PEG-b-HPCMS), were synthesized by ATRP using hydrophilic PEG macroinitiator and CMS.



**Figure 1.**  $^1\text{H}$ -NMR spectra of (a) macroinitiator (PEG 4k macroinitiator) and (b) HPCMS-b-PEG 4k-b-HPCMS.

For the synthesis and structural control of HPCMS, synthetic strategies of previous workers were followed [6,7]. According to the report by Fréchet et al. polymerization temperature and the amount of catalyst, etc. are important variables to get a polymer having high DB, and molecular weight of HPCMS can be controlled mainly by polymerization temperature. Used polymerization temperature in this research was 110 °C and the catalyst ratio to CMS was 0.1 mol%. After polymerization, homopolymerized HPCMS was produced as a side product because CMS itself contains the initiating groups for ATRP (Figure 2 (b)). The product purification was

carried out by extraction with cyclohexane to remove homopolymerized HPCMS. In the synthesis of PS-*b*-PEG-PS via ATRP, Batsberg et al.[8] reported some unreacted PEG macroinitiators. However, in our system unreacted PEG macroinitiators were not shown in the GPC chromatograms (Figure 2). GPC curve of purified block copolymer was shown in Figure 2(c). In this curve, self-polymerized PCMS, which is shown in (b), disappeared after cyclohexane extractions. Although bpy was used 2-fold excess to CuCl to suppress elimination reaction of chloromethine end functional groups by bpy, some elimination reaction occurred as evidenced by NMR peaks around 5.8 ppm in Figure 1 (b), which could be attributed to the existence of a double bond.



**Figure 2.** GPC traces of (a) PEG 4k macroinitiator, and HPCMS-*b*-PEG 4k-*b*-HPCMS ((b) : before separation, (c) : after separation).

According to the report by Frechet et al., the degree of branch (DB) of hyperbranched poly(CMS) can be calculated by the NMR ratio of 2° proton peak (4.8 ppm) relative to 1° proton (4.5 ppm) peak in the chain end of HPCMS block. DB is 0.5 for a perfect dendritic structure and 0 for a perfect linear structure. In our system obtained DB is 0.4 and it tells that the structure of synthesized HPCMS block rather closer to a perfect dendritic structure than a random hyperbranched structure.

Table 1 shows the synthetic results of dumbbell type amphiphilic block copolymers. These tables show that the synthesized copolymer has well defined structures. The disagreement of molecular weights of the synthesized dendritic amphiphilic block copolymers between GPC and <sup>1</sup>H-NMR is due to the difference in their hydrodynamic volumes and solution properties. The block ratio of HPCMS was adjusted ca. 50 wt% compared to PEG block to give adequate water solubility to the synthesized block copolymers.

Table 1. Synthetic Results of Dumbbell Type Amphiphilic Block Copolymers

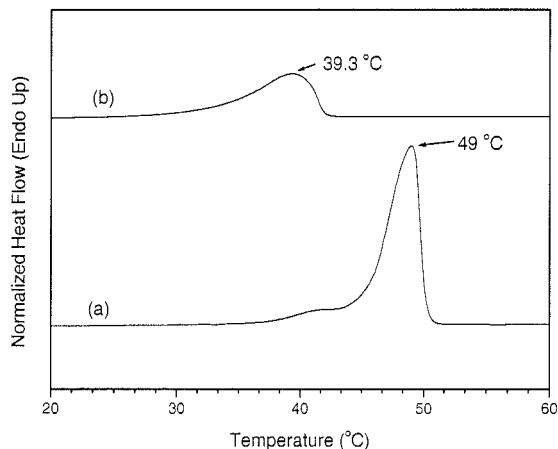
	Macroinitiator			HPCMS- <i>b</i> -PEG- <i>b</i> -HPCMS				Block ratio <sup>3</sup>
	Mn <sup>1</sup>	PDI <sup>1</sup>	Mn <sup>2</sup>	Mn <sup>1</sup>	PDI <sup>1</sup>	Mn <sup>2</sup>	Mn <sup>2</sup> <sub>HPCMS</sub>	
PEG 2k	3200	1.03	2200	8800	1.5	4700	2300	1.15/1
PEG 4k	4800	1.05	4400	6100	1.2	7700	3700	0.92/1

<sup>1</sup> measured by GPC

<sup>2</sup> measured by NMR

<sup>3</sup> molecular weight of HPCMS

<sup>4</sup> weight ratio of HPCMS / PEG

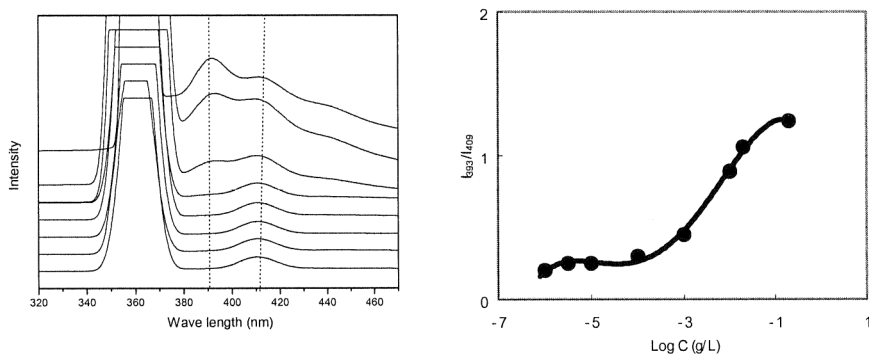


**Figure 3.** DSC thermograms of (a) PEG 4k and (b) HPCMS-b-PEG 4k-b-HPCMS.

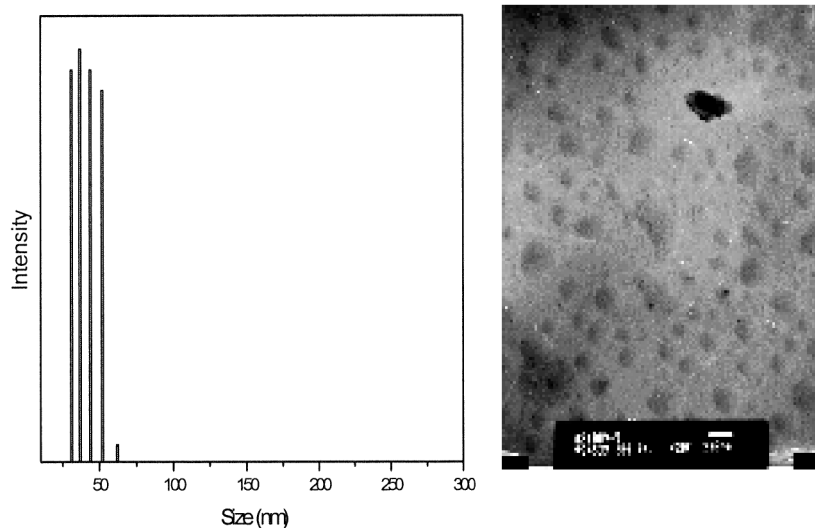
Figure 3 shows DSC traces (second run) of synthesized polymers. The observed melting point of the PEG 4k macroinitiator is 49 °C and that of HPCMS-b-PEG 4k-b-HPCMS (Figure 3 (b)) was 39 °C. The temperature range of melting of the dumbbell was somewhat broader compared to PEG 4k macroinitiator. The melting peak in the copolymer is originated due to the presence of PEG segment. This result shows that chain mobility and intermolecular chain stacking of the middle PEG segments of the copolymer molecules are retarded in highly branched polymers such as hyperbranched polymers due to bulky polymer segment. The HPCMS block has a hyperbranched structure. So, the crystallization of the PEG block in core is retarded and, also, the formed crystal of PEG block is imperfect and small. Solution properties of amphiphilic polymers in water are very important because many amphiphilic polymers are applied as micelles. For the copolymers synthesized in this research, unimolecular micelles can be obtained in diluted W/O type micellar solution. However, due to the simplicity of the study, O/W type micelle was studied with a pyrene probe in this research. Micelle was formed by dialysis method. The synthetic copolymer was solubilized in DMF, and dialysis was proceeded in deionized water bath for 24 h. During dialysis, the DMF is displaced with water, and polymers in membrane formed micelles. There are several methods to measuring critical micelle concentration (CMC). In this study fluorescence measurements were carried out by fluorescence spectrophotometer using pyrene as a fluorescent probe to determine CMC of HPCMS-b-PEG 4k-b-HPCMS.

Figure 4 shows the fluorescence spectra and a plot of the intensity ratio of  $I_{393}/I_{409}$  from pyrene fluorescence spectra vs.  $\log C$  for HPCMS-b-PEG 4k-b-HPCMS. From Figure 4 (b), the CMC value of HPCMS-b-PEG 4k-b-HPCMS was calculated to be  $5.79 \times 10^{-4}$  g/L. In the case of HPCMS-b-PEG 2k-b-HPCMS, the CMC is  $3.2 \times 10^{-5}$  g/L. The size of micelle was determined using dynamic light scattering (DLS). DLS measurements were carried out using a dynamic light scattering spectrometer at wave length of 514 nm at 25 °C. The measured micelle sizes, size distribution, and shape

were shown in Figure 5. The average diameter was 44.7 nm and its distribution was 1.47. The image on copper grid shows the deposited micelle size ranging 20-200 nm, confirming the result from DLS. If it is assumed that HPCMS behaves as a rigid sphere of size ca. 0.7 nm [14] then one can estimate that 20-30 molecules are associated in a micelle. Generally, the higher content of hydrophilic block and the lower total molar mass led to the higher CMC value in PS-*b*-PEO diblock copolymers system and the range of CMC value is 0.001 ~ 0.005 g/L. But Yuan et al. reported that CMC of PS<sub>4</sub>-*b*-PEO<sub>227</sub>-*b*-PS<sub>4</sub> is 0.01 g/L and the value is very different, from normal expectation, probably due to the unusual hydrophilic-lipophilic value of the material compared with that of our material [11].



**Figure 4.** (a) Fluorescence spectra and (b) plot of the intensity ratio  $I_{393}/I_{409}$  (from pyrene fluorescence spectra) vs.  $\log C$  for HPCMS-*b*-PEG 4k-*b*-HPCMS



**Figure 5.** Micellar size distribution and image of HPCMS-*b*-PEG 4k-*b*-HPCMS measured by dynamic light scattering and TEM, respectively.

## Conclusions

Dumbbell type amphiphilic block copolymers containing PEG and HPCMS were synthesized. The synthesized block copolymer had well defined structures. The molecular weights of HPCMS-b-PEG-b-HPCMS were 4700 (for PEG 2k), 7700 (for PEG 4k) and its distributions were 1.5 (for PEG 2k), 1.2 (for PEG 4k), respectively. The DBs were 0.4. The micelle formation was studied using DLS and TEM. The micelle size of HPCMS-b-PEG 4k-b-HPCMS was 54 nm and its distribution was 1.4. The CMCs were  $3.2 \times 10^{-5}$  g/L (for PEG 2k) and  $5.79 \times 10^{-4}$  g/L (for PEG 4k), respectively.

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