

# 원자이동 라디칼 중합을 이용한 분자구조가 제어된 양친매성 고분자의 합성

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## Synthesis of Amphiphilic Block Copolymers having controlled structures via ATRP

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### Introduction

The design and synthesis of new polymers is desirable to obtain materials with novel physical properties. Generally, these new polymers have their well-defined nature with the number of functional groups, molecular weight, polydispersity, and the presence or absence of branching being precisely controlled<sup>1</sup>. These polymers are mainly synthesized by living polymerizations to control of their structures. Among of various living polymerization Atom transfer radical polymerization (ATRP) has been a field of intensive research in recent years<sup>1</sup>. The copper-based ATRP system has been adapted successfully for polymerization of styrene, acrylate, methacrylate, acrylonitrile, and other monomers. ATRP also allow the preparation of polymers with novel compositions and topologies, i.e., block copolymers, graft copolymers, random/statistical copolymers, and hyperbranched polymers<sup>2</sup>.

Hyperbranched polymers have received much attention because these dense, highly branched polymers are expected to have different physical properties compared to their linear analogs. Hyperbranched polymers have been developed as an alternative to dendrimers, as they can be prepared in a single, one pot reaction. Generally hyperbranched polymers are synthesized via condensation polymerization using ABX ( $X > 1$ ) type monomers. The recently, the synthesis of hyperbranched polymers have been extended to functionalized vinyl monomers by a method termed self-condensing vinyl polymerization (SCVP) such as ATRP<sup>3</sup>.

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 stabilizer, and compatibilizer. Block copolymers based poly(ethylene glycol) (PEG)/poly(ethylene oxide) (PEO) have been extensively studied and the micellar phase structures investigated because PEG donate the good water solubility and biocompatibility etc. General types of these copolymer are block or graft copolymers and other copolymers except block or graft type are rarely studied. In this study we report the synthesis of dumbbell type amphiphilic block copolymers containing PEG unit and hyperbranched poly(chloromethyl styrene) (HPCMS). The hyperbranched structures are introduced via ATRP using chloromethyl styrene as a AB type inimer

(initiator and monomer)<sup>4,5</sup>. The solution properties of synthesized copolymer in water will be studied

## Experimental

### Synthesis of PEG 4k macroinitiator

PEG 4k macroinitiator was prepared according to a literature method <sup>7</sup>.

### Polymerizations (Synthesis of HPCMS-b-PEG 4k-b-HPCMS)

CMS and PEG 4k macroinitiator was polymerized in the presence of CuCl (1 mol% relative to CMS) and dipyriddy (bpy) (2 mol%), at 110 C, under nitrogen atmosphere. CMS and macroinitiator was added to a flask containing CuCl/bpy. N<sub>2</sub> gas bubbled for 20 minute. The polymerization goes 3 hours. The green CuCl<sub>2</sub> was removed by passing through a column of alumina. The polymer solution was concentrated and precipitated in hexane. The crude polymer was extracted with cyclohexane at room temperature for 1 day, for removal of self polymerized CMS. The polymer was dried in vacuum at room temperature.

### Characterization

Molecular weight and structures of synthesized macroinitiator and copolymer. were characterized by GPC using polystyrene standards, and also by <sup>1</sup>H-NMR. Critical micell concentration (CMC) is determined by fluorescence method using pyrene<sup>6</sup>. Micell size and shape are characterized by light scattering (LS) and TEM, respectively.

## Result and Discussion

**Scheme 1** shows the synthetic routes of macroinitiators and polymers. In the first step of the synthesis of amphiphilic hyperbranched polymers containing ethylene glycol core and hyperbranched PS arm, hydrophilic telechelic and 4-arm macroinitiator were prepared by reacting PEG 4000 (PEG 4k) with 2-bromopropionyl bromide, respectively. **Figure 1 (a)** shows <sup>1</sup>H NMR spectrum of macroinitiator. After modification of PEG, a new signal appeared at 4.2 ppm, due to the substitution of 2-bromopropionyl group. The amphiphilic dumbbell type block copolymer was synthesized by ATRP using hydrophilic PEG 4k macroinitiator and CMS. The product purification was carried out by extraction with cyclohexane (for self polymerized PCMS) and water (for unreactive macroinitiator). GPC trace of separated block copolymer was shown in **Figure 2 (b)**. In this **Figure 2 (c)**, self-polymerized PCMS (b) was disappeared after cyclohexane extractions and unreacted PEG macroinitiator is not appeared. Although bpy was used 2-fold excess compare to CuCl for reduction of elimination of chloromethin end functional groups by bpy, some elimination reaction is occurred (double bond peak around 5.8 ppm. in **Figure 1 (b)**). Frechet<sup>5</sup> et al reported the characterization of degree of branch (DB) of hyperbranched Poly(CMS) (HPCMS). They reported the ratio of 2<sup>o</sup> proton peak (4.8 ppm.) relative to 1<sup>o</sup> proton (4.5 ppm.) in chain end of HPCMS block are 0.5 for perfect dendritic structure and 0 for perfect linear structures. In our system DB is 0.4 and it shows the structure of synthesized HPCMS block is closed to perfect dendritic 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 difference 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 volume and solution properties. The block ratio of HPCMS is adjusted below 50wt% compare to PEG block to donate water solubility of synthesized block copolymers. The crystallinity is important factor in many amphiphilic polymer systems. In order to determine critical micell concentration (CMC) of HPCMS-b-PEG 4k-b-HPCMS, fluorescence measurements were carried out by fluorescence spectrophotometer using pyrene as a fluorescent probe. **Figure 3** plots the intensity ratio of I<sub>393</sub>/I<sub>409</sub> from pyrene fluorescence spectra vs. log C for HPCMS-b-PEG 4k-b-HPCMS. From **Figure 3**, CMC value was calculated to be 5.79 \*10<sup>-4</sup>. The synthesized block copolymer was micellized in water. The synthetic copolymer was solubilized in DMF, and dialysis proceeded in water bath for 24h. During dialysis, the DMF is displaced with water, and polymers in membrane formatted micell. The size of micell is determined using dynamic light scattering (DLS). DLS measurement were carried out using a dynamic light scattering spectrometer at wave length of 514 nm at 25 oC. Micell sizes and size distribution were shown in **Figure 4**. The average diameter is 44.7 nm and its distribution is 1.47. In **Figure 5** TEM image of micell is shown.

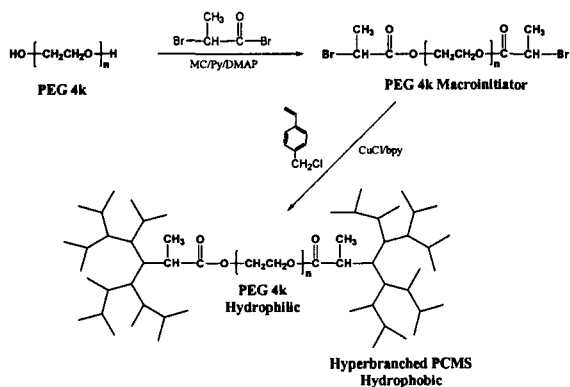
## Summary

We synthesized dumbbell type amphiphilic block copolymers containing PEG and HPCMS. The synthesized block copolymer has well defined structures. The micell formation is studied using DLS and TEM. The physical properties of dumbbell type amphiphilic block copolymers having various molecular weight is will be discussed in the meeting.

## References

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Table 1. Synthetic results of HPCMS-b-PEG 4k-b-HPCMS



Scheme 1. Synthesis of dumbbell type amphiphilic block copolymers (HPCMS-b-PEG 4k-b-HPCMS).

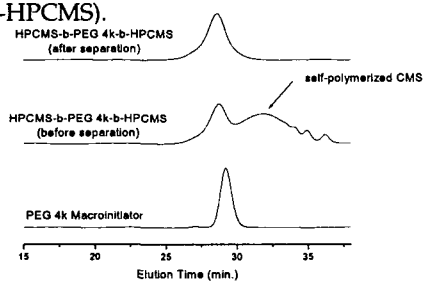


Figure 2. GPC traces of macroinitiator and HPCMS-b-PEG 4k-b-HPCMS.

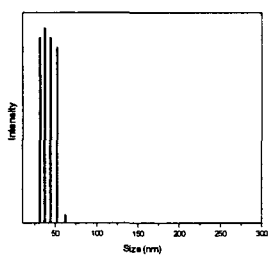


Figure 4. Micell size and its distribution of HPCMS-b-PEG 4k-b-HPCMS.

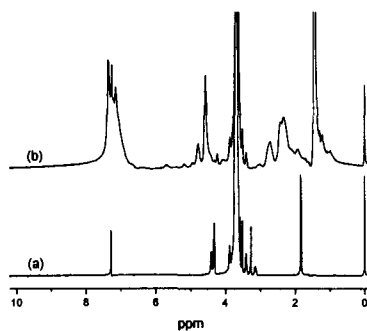


Figure 1.  $^1\text{H-NMR}$  spectra of PEG 4k macroinitiator (a) and HPCMS-b-PEG 4k-b-HPCMS (b).

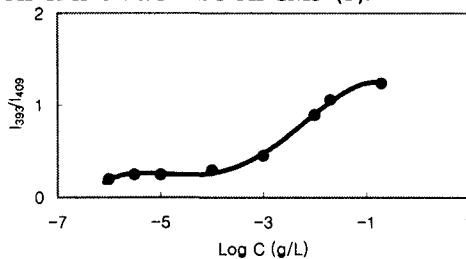


Figure 3. Plot of the intensity ratio  $I_{393}/I_{409}$  (from pyrene fluorescence spectra) vs  $\log C$  for HPCMS-b-PEG 4k-b-HPCMS



Figure 5. TEM images of HPCMS-b-PEG 4k-b-HPCMS micell

Code	$M_{n\text{GPC}}$	PDI	$M_{n\text{NMR}}$	$M_{n\text{HPCMS}}$	Block Ratio (HPCMS/PEG)
PEG 4k macroinitiator	4800	1.05	4800	-	-
HPCMS-b-PEG 4k-b-HPCMS	6100	1.19	7700	3700	0.92/1