# Synthesis and Self-Assembly of Amphiphilic Hyperbranched Poly (aryl ether ketone)-*graft*-poly (ethylene glycol) Copolymer

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**Abstract:** In this work, amphiphilic hyperbranched poly (aryl ether ketone)-*graft*-poly (ethylene glycol) copolymer was synthesized by grafting activated PEG onto hydroxyl-terminated hyperbranched poly (aryl ether ketone) (OH-HPAEK). The molecular structure of HPAEK-*graft*-PEG was confirmed with $^{1}$H NMR. The results of self-assembly investigation demonstrated that the hyperbranched rod-coil diblock copolymer (HPAEK-*graft*-PEG) could self-assemble into regular microspheres with obvious core-shell structure in water/tetrahydrofuran (THF) mixture, and the diameter of the microspheres could be easily controlled by just adjusting the initial concentration of the copolymer in the common solvent of THF. The heat-treated experimental results demonstrated that the polymer microspheres possessed excellent thermal property which could stably exist even if heated at 130 $^{o}$C for 10 h. However, when the polarity of the selective solvents was changed, polymer micelles with various morphologies were obtained. And relevant self-assembly mechanism was discussed.

***Key words*:** Hyperbranched poly (aryl ether ketone); Self-assembly; Morphology.

## 1. Introduction

Self-assembly of amphiphilic copolymers has been demonstrated as an effective and convenient approach to fabricate ordered nanostructures with various morphologies in dilute solution, such as spherical micelles, tubules, cylinders, vesicles, lamellas, and so on.[1-2] Such block copolymer assemblies have potentially technological applications in many research fields, like medicine, biochemistry and material science.[3-4]

Unlike traditional coil-coil copolymers, rod-coil copolymers consist of a flexible coil segment and a rigid rod segment which can be a helical or a stiff conjugated block. The tendency of the rigid segments to aggregate and the high immiscibility and stiffness asymmetry between the rigid rod and flexible coil segments provide extra driving force to control the morphology of the obtained micelles in selective mixed solvents. Much attention has been paid in the research of the self-assembly of copolymers containing rod polymers or oligomers to acquire functional materials with different supramolecular structures both in solution and solid. [5-6]

However, the rigid moieties of rod-coil copolymers reported in the literatures were mainly focused on linear rod polymers or oligomers, which included thiophene, phenylene, quinolone, fluorene, etc.[7] In this work, we presented a novel hyperbranched rod-coil copolymer, HPAEK-*graft*-PEG, which was prepared by grafting linear coil poly (ethylene glycol) (PEG) onto hyperbranched rod hydroxyl-terminated poly (aryl ether ketone) (OH-HPAEK). Afterwards, the self-assembly behavior of the copolymer in solution was investigated.

## 2. Experimental

### *2.1 Preparation of HPAEK-graft-PEG Copolymers*

In this work, we adopted the "core first" method to obtain the hyperbranched rod-coil HPAEK-*graft*-PEG copolymer, and the synthetic route is presented in **Scheme 1**. The process consisted of two steps, activation of PEG and grafting activated PEG onto OH-HPAEK.

*2.2 Micellization of HPAEK-graft-PEG copolymers in water/THF mixtures*

Sample solutions were prepared by first dissolving the amphiphilic hyperbranched rod-coil copolymer in THF with different initial concentrations. 5 mL of distilled water was added dropwise into 1 mL of the copolymer solution with the rate of approximately 1 drop per second, and the mixture was stirred for 2 h to reach equilibrium morphologies for the copolymer assemblies. Finally, excess water was poured into the micelle solution to freeze the morphology and the final volumes of all the solutions maintained 30 mL.

*2.3 Micellization of HPAEK-graft-PEG copolymers in $CHCl_3$/THF mixtures*

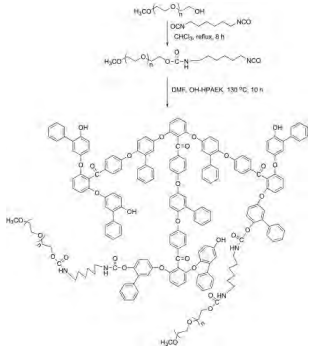
Five of the sample solutions with the same initial copolymer concentration of 2 mg/mL were prepared by dissolving the copolymer in 1 mL THF first. Different quantity of $CHCl_3$ (1 mL, 2 mL, 5 mL, 10 mL, and 20 mL) was added dropwise into the solution to induce the occurrence of the micellization. After magnetic stirring for 2 h, excess $CHCl_3$ was poured into the solutions to ensure the final volumes of 30 mL.

*2.4 Micellization of HPAEK-graft-PEG copolymers in toluene /THF mixtures*

The micellization procedure was similar to that of in water/THF mixtures. The differences were that the initial concentration was only 2.0 mg/mL, and the selective solvent for PEG was toluene.

**3. Results and discussion**

The molecular structure of HPAEK-*graft*-PEG was characterized by $^1$H NMR spectra, as shown in **Figure 1**, both signal (l) (4.24 ppm) and (d) (5.71 ppm) belonged to the hydrogen in the urethane group generated from the reaction of hydroxyl groups in OH-HPAEK and isocyanate groups (-NCO) in PEG-HMDI.



**Scheme 1.** Synthetic route of HPAEK-*graft*-PEG

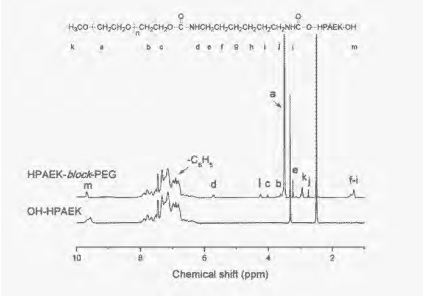



**Figure 1.**NMR spectra of HPAEK-*graft*-PEG

TEM and SEM measurements of the obtained aggregates indicated that HPAEK-*graft*-PEG generated microspheres in water/THF mixtures, as shown in **Figure 2**. From the TEM micrographs (**Fig. 2a**), it could be seen that the microspheres had obvious core-shell structure, and the diameter was about 100 nm, which was well agreed with the result of SEM characterization (**Fig. 2b**).

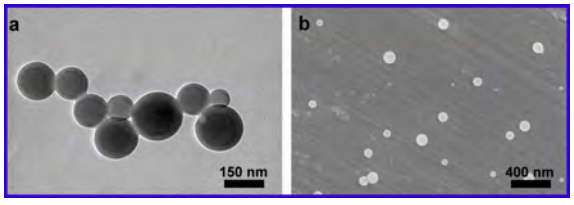



**Figure 2.** TEM (a) and SEM (b) micrographs of the microspheres in water/THF mixture

To better characterize the diameters of the obtained spherical micelles in solution, DLS measurement was carried out, as shown in **Figure 3.** It could be seen clearly that the diameter of the spherical micelles increased from 109.0 nm to 159.0 nm with the increase of HPAEK-*graft*-PEG concentration from 0.6 mg/mL to 10.0 mg/mL.

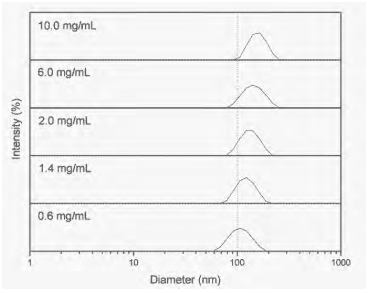



**Figure 3.** DLS plots of HPAEK-*graft*-PEG micelle solutions of water/THF

A few drops of the microsphere solution based on HPAEK-*graft*-PEG were dropped on the aluminum foil, and dried at room temperature. Then the dried microspheres were heated in a vacuum oven to evaluate their thermal stability. The corresponding SEM micrographs were given in **Figure 4**. It could be clearly seen that the microspheres could exited stably at 130 $^{o}$C for 10 h.

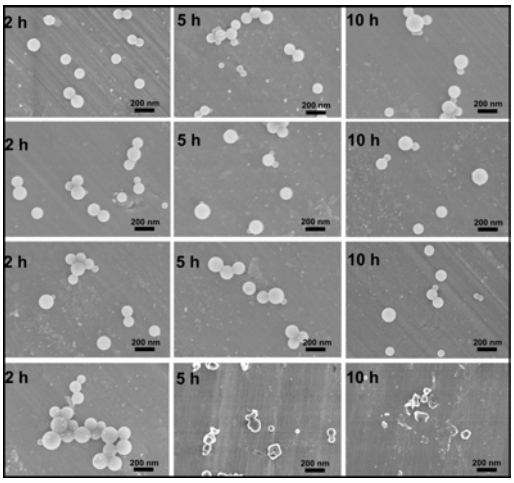



**Figure 4.** SEM micrographs of heat-treated microspheres. From top to bottom, the heat-treated temperature is 25 $^{o}$C, 100 $^{o}$C, 130 $^{o}$C, 150 $^{o}$C, respectively.

Another selective solvent for PEG segments, $CHCl_3$, was used for the further study of the self-assembly behavior of rod-coil HPAEK-*graft*-PEG copolymer in solution. As shown in **Figure 5**, nonspherical micelles were obtained when the selective solvent was changed to $CHCl_3$ whose polarity was much lower than that of water. Based on relevant polymer physics knowledge and our experimental phenomena, a possible self-assembly mode was proposed, as shown in **Figure 6.**

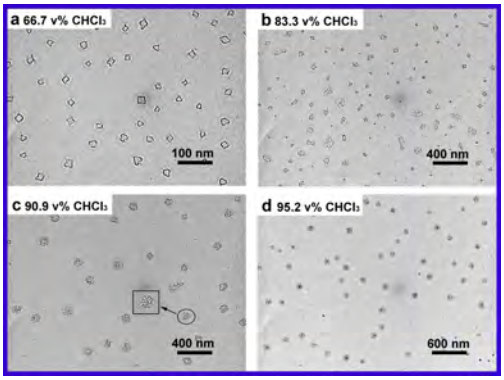



**Figure 5.** TEM micrographs of HPAEK-*graft*-PEG aggregates in $CHCl_3$/THF mixtures

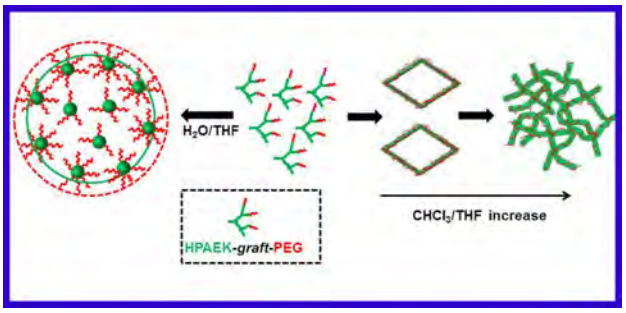



**Figure 6.** A possible self-assembly mechanism of micelles based on HPAEK-*graft*-PEG

As can be seen from **Figure 7**, the aggregates of HPAEK-*graft*-PEG in toluene/THF were large compound micelles with wide size distribution. And the bigger ones were even spindle-shaped rather than spherical.

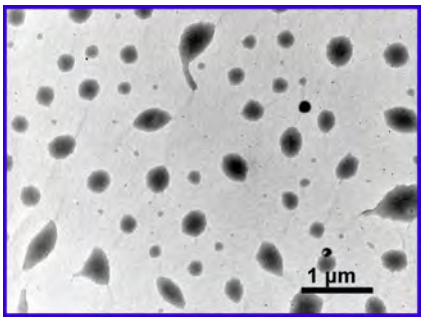



**Figure 7.** Large compound micelles made from HPAEK-*graft*-PEG in toluene/THF mixture

In summary, a novel amphiphilic hyperbranched rod-coil copolymer (HPAEK-*graft*-PEG) was synthesized, then the self-assembly behavior of HPAEK-*graft*-PEG in different mixed solvents was investigated.

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