



Study on the Morphologies of Poly(ethylene glycol)-*block*-poly(γ -benzyl L-glutamate)-*graft*-poly(ethylene glycol) Aggregates Deposited from the Dilute Solution

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Poly(ethylene glycol)-*block*-poly(γ -benzyl L-glutamate)-*graft*-poly(ethylene glycol) (PEG-*block*-PBLG-*graft*-PEG) copolymer was synthesized by the ester exchange reaction of PBLG-*block*-PEG copolymer with mPEG. The surface morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer aggregates from the dilute solution were studied by scanning electron microscopy. The effects of the solution concentration, the precipitation temperature and various solvent system on the surface morphologies of the polypeptide block-*graft* copolymer aggregates from the dilute solution were investigated.

Key Words: PEG-*b*-PBLG-*g*-PEG, Aggregate, Morphology, Dilute solution.

INTRODUCTION

Polypeptides and their copolymers with excellent biocompatible and biodegradable properties have received lots of attention for their potential applications¹⁻⁷. As known, the synthesized polypeptides and their copolymers have been studied widely in the fields of functional biomaterials, protein simulation, polymer carriers for protein conjugates, macromolecular conformational research, catalysis and artificial skin substrates, etc.⁸⁻¹².

In order to understand the properties of polypeptides, it is important to characterize their morphologies and structures and to elucidate the relationship between their properties and the morphologies and structures¹³⁻¹⁵. Geil *et al.*^{14,15} have reported the surface morphologies of poly(γ -benzyl L-glutamate) homopolymer aggregates deposited from dilute solution. However, to our best of knowledge, no experimental work has been done on the studies of the surface morphologies of PEG-*b*-PBLG-*g*-PEG copolymer aggregates deposited from dilute solution so far. Owing to different molecular structure of polypeptide block-*graft* copolymer and polypeptide homopolymer, it is still interesting to study the aggregates morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer from dilute solution. In the present work, PEG-*block*-PBLG-*graft*-PEG copolymer was synthesized. SEM technique was used to study the aggregates morphologies of PEG-*b*-PBLG-*g*-PEG from the dilute solution. The effects of the solution concentration, the precipitation temperature and various solvent system on the surface morphologies of the polypeptide block-*graft* copolymer aggregates from the dilute solution were investigated.

EXPERIMENTAL

Amine-terminated α -methoxy- ω -amino poly(ethylene glycol) (AT-PEG, $M_w = 10000$) and poly(ethylene glycol methyl ether) (mPEG, $M_w = 350$) were purchased from Sigma Inc. (USA) and used without further purification. Hexane, tetrahydrofuran (THF) and 1,4-dioxane are of analytical grade and dried with sodium to remove water before use. All other solvents are of analytical grade and used without further purification.

Preparation of polypeptide copolymer and its solution: PBLG-*block*-PEG copolymer was prepared by a standard *N*-carboxyl- γ -benzyl-L-glutamate anhydride (NCA) method⁷. Molecular weight of the PBLG-*block*-PEG copolymer was estimated by NMR method². The molecular weight of PBLG-*block*-PEG used in the study was about 90000. PEG-*block*-PBLG-*graft*-PEG copolymer was obtained by the ester exchange reaction of PBLG-*block*-PEG with mPEG ($M_w = 350$) in 1,2-dichloroethane with *p*-toluenesulfonic acid as a catalyst according to the described method⁷. The grafting percentage of PEG-*block*-PBLG-*graft*-PEG was 10.5 % calculated according to the document². PEG-*block*-PBLG-*graft*-PEG copolymer solution was prepared according to the previous documents^{14,15}. Fig. 1 shows the schematic representation of PEG-*block*-PBLG-*graft*-PEG copolymer structure.

Test method: Aggregates morphologies of polypeptide block-*graft* copolymer were observed by a scanning electron microscope (SEM) (Sirin 200, FEI, Holland). Testing specimens were obtained by depositing drops of precipitate suspension onto clean glass plates and drying them at room temperature^{14,15}.

Gold was sprayed on samples in vacuum. Acceleration voltage was 10 kV.

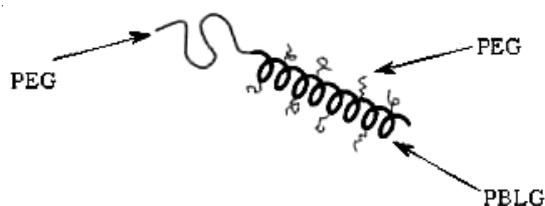


Fig. 1. Schematic representation of PEG-*block*-PBLG-*graft*-PEG copolymer structure

RESULTS AND DISCUSSION

Effects of solution concentration on the surface morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer aggregates from the dilute solution: Fig. 2 shows the aggregates morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer in dilute mesitylene/xylene solution with different solution concentrations. As seen from Fig. 2, with the increase of the solution concentration, the aggregates morphologies of polypeptide block-*graft* copolymer in dilute solution changed from dispersed spheres to tightly congregating spheres, indicating that the increase of the solution concentration changed the surface morphologies of polypeptide block-*graft* copolymer aggregates from dilute solution^{14,15}. This phenomenon also proves that the solution concentration is a factor of influencing the aggregates morphologies of polypeptide block-*graft* copolymer in dilute solution.

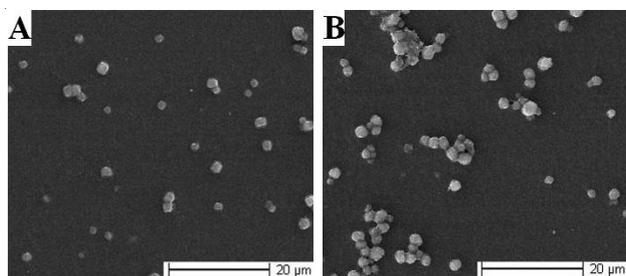


Fig. 2. SEM photographs of PEG-*b*-PBLG-*g*-PEG copolymer aggregates deposited at 40 °C from mesitylene/xylene (vol ratio: 1:1) solutions: (a) 2×10^{-4} g/mL solution and (b) 9×10^{-4} g/mL solution, where the precipitation time is 72 h

Effects of precipitation temperature on aggregates morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer from dilute solution: Fig. 3 presents the aggregates morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer from dilute toluene solution at various precipitation temperatures. As is shown in Fig. 3, the polypeptide block-*graft* copolymer aggregated to form fibrillar strands in dilute solution^{14,15}. With the increase of the precipitation temperature, the fibrillar strands became thinner, shorter and having a lower aggregating density. This phenomenon indicates that the precipitation temperature is also a factor of influencing the surface morphologies of polypeptide block-*graft* copolymer aggregates in dilute solution.

Effects of solvent/nonsolvent mixed system on aggregates morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer in dilute solution: Fig. 4 indicates the aggregates

morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer in dilute mesitylene/hexane solution with different hexane (as nonsolvent) volume contents. As it can be seen from Fig. 4, the surface morphologies of polypeptide block-*graft* copolymer aggregated to form spheres in dilute mesitylene/hexane solution. With the increase of the hexane volume content in the mixed system, the shape of the spheres became more irregular and the aggregating density increased. This phenomenon shows that the introduction of the nonsolvent into the mixed system changed the surface morphologies of the polypeptide block-*graft* copolymer aggregates from the dilute solution.

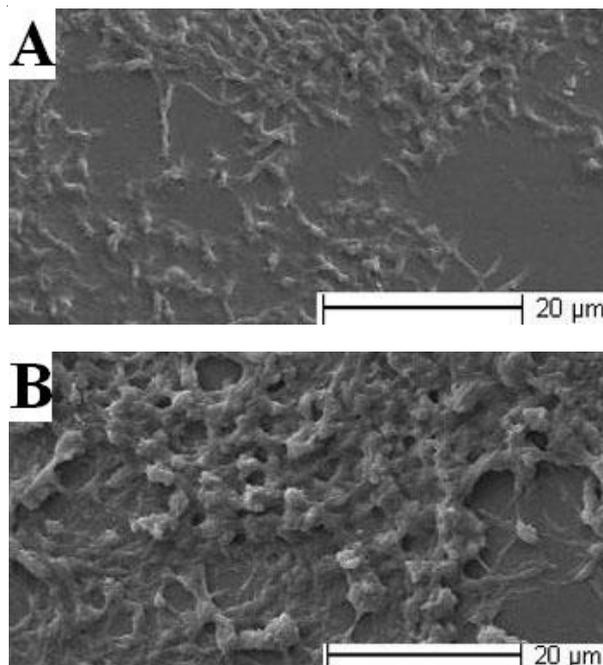


Fig. 3. SEM photographs of PEG-*b*-PBLG-*g*-PEG copolymer aggregates deposited from 7×10^{-4} g/mL various solutions: (a) toluene solution at 80 °C and (b) toluene solution at 20 °C, where the precipitation time is 72 h

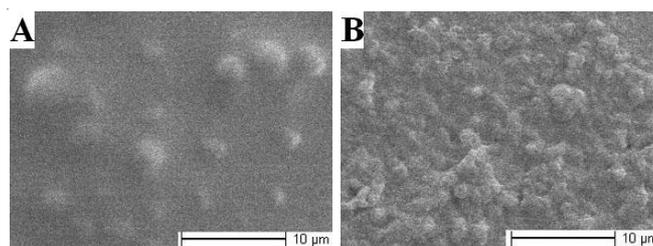


Fig. 4. SEM photographs of PEG-*b*-PBLG-*g*-PEG copolymer aggregates deposited at 30 °C from 6×10^{-4} g/mL various solutions: (a) mesitylene/hexane (vol ratio: 49:1) and (b) mesitylene/hexane (vol ratio: 9:1), where the precipitation time is 72 h

Conclusion

PEG-*block*-PBLG-*graft*-PEG copolymer was synthesized. The aggregates morphologies of PEG-*block*-PBLG-*graft*-PEG copolymer deposited from dilute solution were investigated by SEM technique. Experimental results demonstrated that the solution concentration, the precipitation temperature and various solvent system could exert marked effects on the aggregates morphologies of the polypeptide block-*graft* copolymer from dilute solution.

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