Asian Journal of Chemistry; Vol. 25, No. 6 (2013), 3501-3502

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13485

NOTE

Aggregates Morphologies of Poly(γ-benzyl *L*-glutamate)-*graft*-poly(ethylene glycol) and Poly(γ-benzyl L-glutamate) Mixtures in Dilute Solution

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(*Received*: 21 January 2012; *Accepted*: 28 December 2012) AJC-12625

Poly(γ-benzyl L-glutamate) (PBLG) homopolymer and poly(γ-benzyl L-glutamate)-*graft*-poly(ethylene glycol) (PBLG-*graft*-PEG) copolymer were synthesized by a standard *N*-carboxyl-γ-benzyl-L-glutamate anhydride method and by ester exchange reaction, respectively. The aggregates morphologies of PBLG-*graft*-PEG and PBLG mixtures in dilute solution were studied by scanning electron microscopy. The effects of the weight (wt) ratio of PBLG-*graft*-PEG to PBLG, various solvent system and the addition of denaturant acid on the aggregates morphologies of the PBLG-graft-PEG and PBLG mixtures in the dilute solution were investigated.

Key Words: Polypeptide mixture, Aggregate, Morphology, Dilute solution.

Because of the outstanding biocompatible and biodegradable properties, polypeptides and their copolymers have received much attention for their potential applications[1-5]. 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*.[6-8].

To understand the properties of polypeptides and control them, it is important to characterize their morphology and structure and to elucidate the relationship between their properties and the morphology and structure[9-11]. Geil *et al*.[10,11] have reported the morphologies of PBLG homopolymer aggregates in dilute solution. However, to the best of our knowledge, no experimental work has so far been reported on the studies of the aggregates morphologies of PBLG-*graft*-PEG and PBLG mixtures in dilute solution. As the molecular structure of polypeptide graft copolymer and homopolymer is different, it is interesting to study the aggregates morphologies of PBLG-graft-PEG and PBLG mixtures in dilute solution. In the present study, PBLG-*graft*-PEG and PBLG were synthesized. SEM technique was used to study the aggregates morphologies of PBLG-*graft*-PEG and PBLG mixtures in the dilute solution. The effects of the weight ratio of PBLG-*graft*-PEG to PBLG, various solvent system and the addition of denaturant acid (*e.g.*, trifluoroacetic acid) on the aggregates morphologies of PBLG-*graft*-PEG and PBLG mixtures in the dilute solution were studied.

Polyethylene glycol monomethylether (mPEG, $M_w = 750$) was purchased from Sigma Inc. (USA) and used without further purification. Hexane, tetrahydrofuran 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 mixtures and its solution: The PBLG sample was prepared by a standard *N*-carboxyl-γ-benzyl-*L*-glutamate anhydride method[1]. Molecular weight of PBLG was estimated from the intrinsic viscosity measured in dichloroacetic acid (DCA)[12]. PBLG-*graft*-PEG copolymer was obtained by the ester exchange reaction of the PBLG homopolymer with mPEG ($M_w = 750$) in 1,2-dichloroethane with *p*-toluenesulfonic acid as a catalyst according to the described method[1]. The molecular weight of the PBLG used in the ester exchange reaction was 90,000. The grafting percentage of PBLG-*graft*-PEG was 14.5 % calculated according to the document[1]. Polypeptide mixture solutions were prepared according to the previous documents[10,11]. Fig. 1 shows the schematic representations of (a) PBLG structure and (b) PBLG-graft-PEG structure.

Test method: Aggregates morphologies 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[10,11]. Gold was sprayed on samples in vacuum. Acceleration voltage was 10 kV.

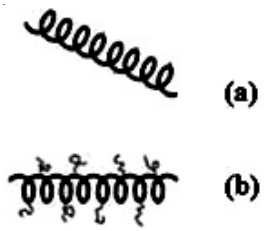

Fig. 1. Schematic representations of (a) PBLG structure and (b) PBLG-graft-PEG structure

Effects of the weight ratio of PBLG-*graft*-PEG to PBLG on aggregates morphologies of PBLG-*graft*-PEG and PBLG mixtures in dilute solition: Fig. 2 shows the aggregates morphologies of PBLG-*graft*-PEG and PBLG mixture in dilute mesitylene/xylene solution with different PBLG-*graft*-PEG/PBLG wt ratios. As seen from Fig. 2, with the increase of PBLG wt content, the aggregates morphologies of polypeptide mixture in mesitylene/xylene solution changed from lath-like shape to spherical shape, indicating that the PBLG homopolymer chains tended to congregate with PBLG segments of PBLG-*graft*-PEG to form various shaped aggregates[10,11]. This phenomenon also shows that the addition of PBLG exerts marked effect on the aggregate morphology of polypeptide mixture in dilute solution.

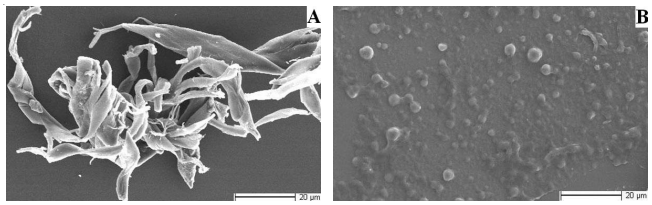

Fig. 2. SEM photographs of PBLG-*graft*-PEG and PBLG mixture aggregates deposited at 20 ºC from mesitylene/xylene (volume ratio: 1:1) solution: (a) PBLG-*graft*-PEG/PBLG (wt ratio is 4:1) and (b) PBLG-*graft*-PEG/PBLG (wt ratio is 2:1), where the precipitation time is 72 h and the solution concentration is 7×10^{-4} g/mL

Effects of solvent/nosolvent mixed system on aggregates morphologies of PBLG-*graft*-PEG and PBLG mixtures in dilute solition: Fig. 3 presents the aggregates morphologies of PBLG-*graft*-PEG and PBLG mixture in dilute xylene/hexane solution with different hexane volume (vol) contents. As shown in Fig. 3, with the increase of hexane volume content, the aggregates morphologies of polypeptide mixture in xylene/hexane solution changed from loose sphere with core/shell structrure to dense sphere with core/shell structure, suggesting that the PBLG homopolymer chains tended to congregate with PBLG segments in PBLG-*graft*-PEG to form the core of the sphere and the increase of hexane as nonsolvent promotes the density of the sphere. The situation also proves that the addition of hexane changed the aggregating behaviour of the polypeptide mixture in dilute solution.

Effects of the addition of denaturant acid on aggregates morphologies of PBLG-*graft*-PEG and PBLG mixtures in dilute solition: Fig. 4 indicates the aggregates morphologies of PBLG-*graft*-PEG and PBLG mixture in dilute toluene/trifluoroacetic acid solution with different trifluoroacetic acid volume contents. As it can be seen from Fig. 4, with the addition of trifluoroacetic acid, the aggregates morphologies of polypeptide mixture in toluene/trifluoroacetic acid solution changed from regular lamellar crystals to irregular block-like crystals, suggesting that the addition of trifluoroacetic acid changed the molecular conformation of PBLG segments from α-helix conformation to random coil conformation[13]. The phenomenon also attests that the addition of denaturant acid could affect the aggregating behaviour of the polypeptide mixture in dilute solution.

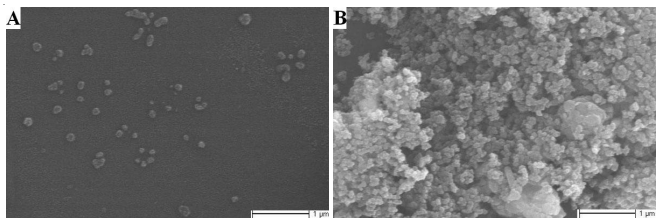

Fig. 3. SEM photographs of PBLG-*graft*-PEG/PBLG (wt ratio: 3:1) mixture aggregates deposited at 20 ºC from various solutions: (a) xylene and (b) xylene/hexane (vol ratio is 9:1), where the precipitation time is 72 h and the solution concentration is 6×10^{-4} g/mL

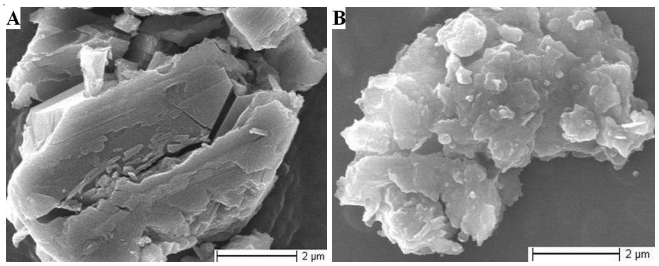

Fig. 4. SEM photographs of PBLG-*graft*-PEG/PBLG (wt ratio: 2:1) mixture aggregates deposited at 5 ºC from various solutions: (a) toluene and (b) toluene/trifluoroacetic acid (vol ratio is 19:1), where the precipitation time is 72 h and the solution concentration is 8×10^{-4} g/mL

Conclusion

The results showed that the weight ratio, the solvent system and the denaturant acid could affect the aggregates morphologies of the polypeptide mixtures in dilute solution.

ACKNOWLEDGEMENTS

This work is supported by the Natural Science Foundation of Shandong Province (No. ZR2011EMM009).

REFERENCES

1. D.M. Tang, J.P. Lin, S.L. Lin, S.N. Zhang, T. Chen and X.H. Tian, *Macromol. Rapid Commun.*, **25**, 1241 (2004).
2. C.S. Cho, J.B. Cheon, Y.I. Jeong, I.S. Kim, S.H. Kim and T. Akaike, *Macromol. Rapid Commun.*, **18**, 361 (1997).
3. C.S. Cho, J.W. Nah, Y.I. Jeong, J.B. Cheon, S. Asayama, H. Ise and T. Akaike, *Polymer*, **40**, 6769 (1999).
4. G.Q. Zhu, *Chem. Pap.*, **63**, 683 (2009); **64**, 34 (2010).
5. G.Q. Zhu, *Fiber. Polym.*, **10**, 425 (2009).
6. M. Moffitt and A. Eisenberg, *Macromolecules*, **30**, 4363 (1997).
7. K. Jokei, M. Oka, T. Hayashi and Y. Miyachi, *Eur. Polym. J.*, **35**, 945 (1999).
8. Y. Miyachi, K. Jokei, M. Oka and T. Hayashi, *Eur. Polym. J.*, **35**, 767 (1999).
9. J. Sun, X.S. Chen, J.S. Guo, Q. Shi, Z.G. Xie and X.B. Jing, *Polymer*, **50**, 455 (2009).
10. F. Rybnikar and P.H. Geil, *Biopolymers*, **11**, 271 (1972).
11. J.J.B.P. Blais and P.H. Geil, *J. Ultrastruct. Res.*, **22**, 303 (1968).
12. A. Abe and T. Yamazaki, *Macromolecules*, **22**, 2138 (1989).
13. Y. Tajima, J.M. Anderson and P.H. Geil, *Int. J. Biol. Macromol.*, **2**, 186 (1980).