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Poly(ethylene glycol)-*block*-poly(γ-benzyl *L*-glutamate)-*graft*-poly(ethylene glycol) (PEG-*b*-PBLG-*g*-PEG) copolymer was synthesized by the ester exchange reaction of PBLG-*block*-PEG copolymer with mPEG. The self-association behaviors of PEG-*b*-PBLG-*g*-PEG and its blends with PBLG homopolymer in the mixtures of ethanol and dimethylformamide (DMF) were investigated by transmission electron microscopy (TEM), dynamic light scattering (DLS), and viscometry. Effects of the introduction of PBLG homopolymer, the grafting ratio, and the DMF content on the self-association behaviors of PEG-*b*-PBLG-*g*-PEG copolymer in the mixtures of ethanol and DMF were mainly researched. It was revealed that PEG-*b*-PBLG-*g*-PEG copolymer could self-assemble to form polymeric micelles with a core-shell structure in various shapes from different preparation conditions. The critical micelle concentration (CMC) and the average particle diameter of the micelles formed by PEG-*b*-PBLG-*g*-PEG copolymer in the mixed solvents also changed with different preparation conditions.

Keywords: Aggregation behavior, PEG-*b*-PBLG-*g*-PEG, blends, mixed solvents

1 Introduction

Amphiphilic block or graft copolymers could self-assemble to form micelles or nanoparticles with a core-shell structure in selective solvents (1–14). Various micelle morphologies such as spheres, rods, vesicles, spindles, tubules, cylinders, toroids, and other complex structures have been found (15–19). The structures formed in aqueous media have attracted widespread interest for the great potential applications in drug delivery systems, catalysis, cosmetics, and nanoreactors (20–25).

Recently, increasing interest has been given to the polypeptide-based self-assemblies because of their excellent biocompatibility and significant advantages in controlling both the function and the structures of the supramolecular self-assemblies (2,26–32). Lecommandoux et al. (27,28) have reported the self-association behavior of poly(L-glutamic acid) (PLGA)- and poly(L-lysine) (PLL)-based amphiphilic diblock copolymers in aqueous solution. It was revealed that vesicles or spherical micelles are formed by different block ratios, and the change of solution pH value has marked effects on the aggregate size. Kwon et al. (33) have reported that poly(β-benzyl L-aspartate) (PBLA)/ poly(ethylene oxide) (PEO) diblock copolymers could self-assemble to form polymeric micelles consisting of an outer shell of PEO and an inner core of PBLA in aqueous medium. Cho et al. (34) have reported the formation of polymeric micelles composed of poly(γ-benzyl L-glutamate) and poly(ethylene oxide) in aqueous medium and the drug delivery system based on the core-shell nanoparticles with PBLG as the hydrophobic inner core and PEO as the hydrophilic outer shell.

Relative to pure water or ethanol system, the self-association behaviors of polypeptide copolymers in the mixed solvents system have received less attention. Lin et al. (4) have studied the aggregation behavior of polypeptide graft copolymer in the mixtures of water, tetrahydrofuran (THF), and *N*, *N*′-dimethylformamide (DMF). It was revealed that the introduction of THF or DMF into water could affect the morphologies of the micelles formed by polypeptide graft copolymer in the mixed water

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system. However, to the best of our knowledge, no experimental work has so far been reported on the studies of the self-association behaviors of polypeptide block-graft copolymer and its blends with PBLG homopolymer in the mixtures of ethanol and DMF. In the present work, the self-association behaviors of PEG-*b*-PBLG-*g*-PEG copolymer and its blends with PBLG homopolymer in the mixtures of ethanol and DMF were studied by TEM, DLS, and viscometry techniques. Effects of the introduction of PBLG homopolymer, the grafting ratio, and the DMF content on the self-association behaviors of PEG-*b*-PBLG-*g*-PEG copolymer in the mixtures of ethanol and DMF were mainly researched. It was revealed that PEG-*b*-PBLG-*g*-PEG copolymer could self-assemble to form polymeric micelles with a core-shell structure in various shapes from different preparation conditions. The critical micelle concentration (CMC) and the average particle diameter of the micelles formed by PEG-*b*-PBLG-*g*-PEG copolymer in the mixed solvents also changed with different preparation conditions.

2 Experimental

2.1 Materials

The 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., 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.

2.2 Syntheses of Polypeptide Homopolymer and Copolymer

PBLG homopolymer was prepared by a standard *N*-carboxyl-γ-benzyl-*L*-glutamate anhydride (NCA) method (35, 36). The molecular weight of the PBLG homopolymer was estimated from the [η] value measured in dichloroacetic acid (DCA) according to the document (37). The molecular weight of PBLG homopolymer used in the study is 35000. PBLG-*block*-PEG copolymer was prepared by a standard *N*-carboxyl-γ-benzyl-*L*-glutamate anhydride (NCA) method (18). Briefly, PBLG-*block*-PEG copolymer was obtained by the ring-opening polymerization of γ-BLG NCA initiated by AT-PEG (M_w = 10000) in 1, 4-dioxane at room temperature. The molecular weight of PBLG-*block*-PEG copolymer was estimated by nuclear magnetic resonance (NMR) measurements (Avance 550) (18). It was calculated by the peak intensities of the methylene proton signal of polypeptide and the ethylene proton signal of PEG in the ^{1}H-NMR spectra (14, 18). The molecular weight of PBLG-*block*-PEG used in the study is 120000.

PEG-*b*-PBLG-*g*-PEG copolymer was obtained by the ester exchange reaction of PBLG-*block*-PEG with mPEG (M_w =350) (8, 14, 38–40). The reaction was performed at 55–60°C in 1, 2-dichloroethane(DCE) with *p*-toluenesulfonic acid (TSA) as a catalyst. Then the reaction mixture was precipitated into a large volume of anhydrous ethanol. The resulting product was purified twice by repeated precipitation from a chloroform solution into a large volume of anhydrous methanol, and then dried under vacuum. The grafting ratio of PEG-*b*-PBLG-*g*-PEG copolymer was estimated by nuclear magnetic resonance (NMR) measurements (Avance 550). It was calculated by the peak intensities of the methylene proton signal of polypeptide and the ethylene proton signal of PEG in the ^{1}H-NMR spectra (8,14). By the variation of molar ratio of BLG unit to mPEG and the reaction time, the grafting ratio could be adjusted (4). The polypeptide copolymers denoted as PEG-*b*-PBLG-*g*-PEG1, PEG-*b*-PBLG-*g*-PEG2, PEG-*b*-PBLG-*g*-PEG3, and PEG-*b*-PBLG-*g*-PEG4, respectively, the corresponding grafting ratios are 14.6%, 20.4%, 29%, and 34%, respectively.

2.3 Preparation of Polypeptide Copolymer Micelles

The obtained polypeptide copolymer samples were first dissolved in DMF to make a 2 g/l polymer solution. Subsequently, a given volume of ethanol was added into the polymer DMF solution with stirring. Formation of the PEG-*b*-PBLG-*g*-PEG copolymer micelles occurred indicated by the appearance of turbidity in the solution, when about 25 vol% of ethanol were added (41). By adjusting the initial polymer solution concentration and the volume ratios of ethanol to DMF, the desired polymer micelle solutions were obtained.

2.4 Observation of Transmission Electron Microscope

The morphology of the micelles was obtained by TEM (JEM-1200-EXII). Drops of micelle solution were placed on a carbon film coated copper grid, and then were dried at room temperature. Before the observations, the sample was stained by aqueous phosphotungstic acid solution (1.0 wt%) (14,18). The TEM bright field imaging was performed with 120 kV accelerating voltage.

2.5 Dynamic Light Scattering Measurements

Dynamic light scattering (DLS) was measured using a S4700 (Malvern Instrument, UK) with an argon laser beam at a wavelength of 488 nm at 25°C. A scattering angle of 90° was used. The polymer micelle concentration was 0.1 g/l.

2.6 Viscosity Measurements

Viscosity measurements of the micelle solution were made in an Ubbelohde viscometer, which was placed in a thermostatically controlled bath with a precision of ±0.1°C. The measurements were repeated at least three times and the times obtained were arithmetically averaged and converted to the relative viscosity (η_γ); η_γ was further converted to the specific viscosity (η_{sp}). The experiments were carried out by diluting the micelle solution step by step. The curve of η_{sp}/C vs. the concentration (C) of the micelle solution was drawn. By analyzing the curve of η_{sp}/C vs. C, the critical micelle concentration of PEG-*b*-PBLG-*g*-PEG in the mixtures of ethanol and DMF could be obtained (42).

3 Results and Discussion

3.1 Effects of the Introduction of PBLG Homopolymer on the Morphology of the Micelles Formed by PEG-*b*-PBLG-*g*-PEG in the Mixed Solvents

Figures 1a and b present the morphologies of the micelles formed in the mixtures of ethanol and DMF: (a) by PEG-*b*-PBLG-*g*-PEG1 (DMF content: 1 vol%, polymer micelle solution concentration: 0.1 g/l) and (b) by PEG-*b*-PBLG-*g*-PEG1/PBLG blend (PBLG content: 30 wt%, DMF content: 1 vol%, polymer micelle solution concentration: 0.1 g/l). As is shown in Figure 1a, regular thin spindly shaped micelles are presented with a length of about 100–130 nm. Due to the difference in molecular architecture (14), it is a very different morphology compared with the spherical micelles of polypeptide block copolymer as described by Cho et al. (43). Figure 1b shows an example of the morphology of the micelles based on the blend of PEG-*b*-PBLG-*g*-PEG1 and PBLG homopolymer. Some micelles change from a spindly shape to a cylindrical shape with the similar length (14), and other micelles change from a spindly shape to a ring-like shape (4). The morphologies of the micelles formed by the blends with other ratios of PEG-*b*-PBLG-*g*-PEG1 to PBLG homopolymer (PBLG content: 10–50 wt%) exhibit similar shapes to that of Figure 1b. The change of the morphology with adding PBLG homopolymer proves that the PBLG homopolymer could self-assemble to form polymeric micelles together with PEG-*b*-PBLG-*g*-PEG1 copolymer by the interaction with PBLG chains in PEG-*b*-PBLG-*g*-PEG1 copolymer (14).

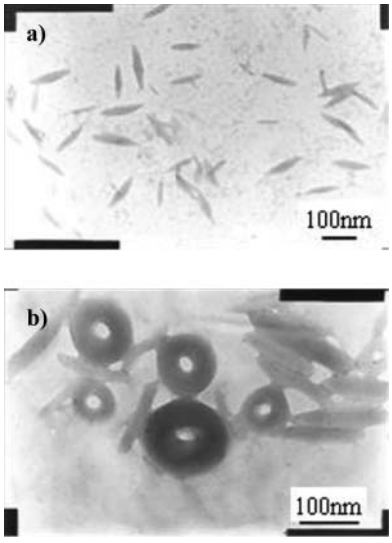

Fig. 1. TEM photographs of the micelles formed in the mixtures of ethanol and DMF: (a) by PEG-*b*-PBLG-*g*-PEG1 (grafting ratio: 14.6%) (DMF content: 1 vol%, polymer micelle solution concentration: 0.1 g/L) and (b) by PEG-*b*-PBLG-*g*-PEG1/PBLG blend (PBLG content: 30 wt%, DMF content: 1 vol%, polymer micelle solution concentration: 0.1 g/L).

3.2 Effects of the Grafting Ratio on the Morphology of the Micelles Formed by PEG-*b*-PBLG-*g*-PEG in the Mixed Solvents

Figure 2 shows the morphologies of the micelles formed in the mixtures of ethanol and DMF: (a) by PEG-*b*-PBLG-*g*-PEG2 and (b) by PEG-*b*-PBLG-*g*-PEG3 (polymer micelle solution concentration: 0.1 g/l, DMF content: 1 vol%). As seen from Figure 2a, PEG-*b*-PBLG-*g*-PEG2 self-assembles into short and plump spindly shaped micelles (8,14). Also seen from Figure 2b, PEG-*b*-PBLG-*g*-PEG3 self-assembles into irregular sphere-like micelles (4). As the grafting ratio increases, the molecular architecture changes, the micelle morphology transforms from spindle-like shape to sphere-like shape (4). This situation also demonstrates that the grafting ratio exerts marked effects on the morphology of

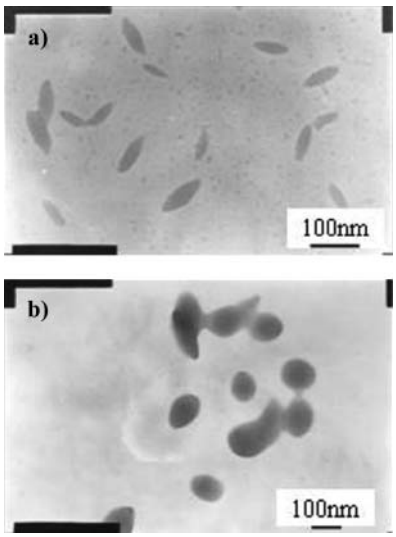

Fig. 2. TEM photographs of the micelles formed in the mixtures of ethanol and DMF: (a) by PEG-*b*-PBLG-*g*-PEG2 (grafting ratio: 20.4%) and (b) by PEG-*b*-PBLG-*g*-PEG3 (grafting ratio: 29%). The polymer micelle solution concentration is 0.1 g/L and the DMF content is 1 vol%.

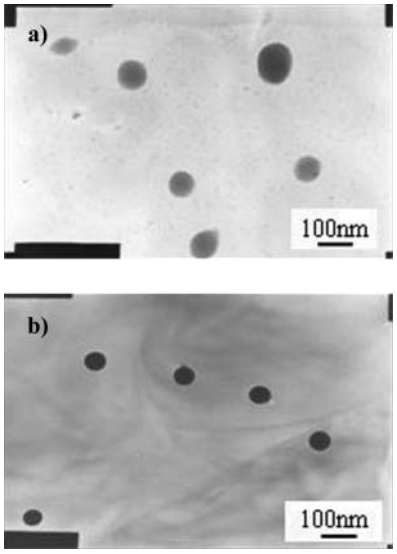

Fig. 3. TEM photographs of the micelles formed by PEG-*b*-PBLG-*g*-PEG4 (grafting ratio: 34%) in the mixtures of ethanol and DMF: (a) the DMF content is 1 vol % and (b) the DMF content is 4 vol%. The polymer micelle solution concentration is 0.05 g/L.

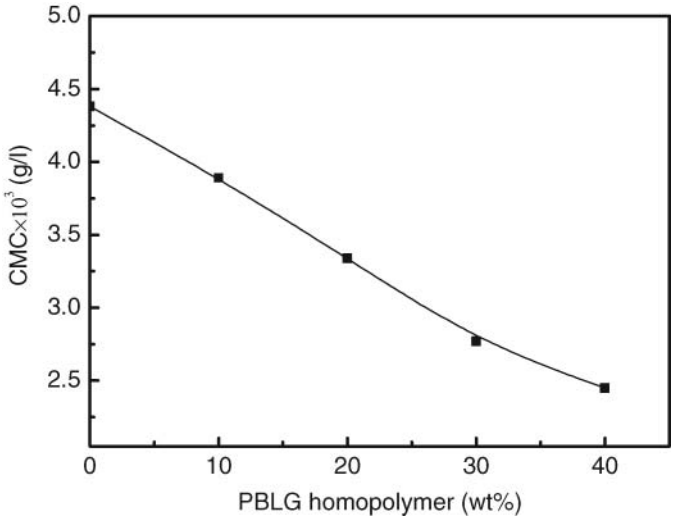

Fig. 4. Curve of the critical micelle concentration of PEG-*b*-PBLG-*g*-PEG2 (grafting ratio: 20.4%) in the mixtures of ethanol and DMF vs. the content (wt%) of PBLG homopolymer (DMF content: 1 vol%, test temperature: 25°C).

the micelles formed by PEG-*b*-PBLG-*g*-PEG copolymer in the mixed solvents.

3.3 Effects of the DMF Content on the Morphology of the Micelles Formed by PEG-*b*-PBLG-*g*-PEG in the Mixed Solvents

Figure 3 presents the morphologies of the micelles formed by PEG-*b*-PBLG-*g*-PEG4 in the mixtures of ethanol and DMF: (a) the DMF content is 1 vol% and (b) the DMF content is 4 vol% (polymer micelle solution concentration: 0.05 g/l). As seen from Figure 3, regular sphere-like micelles with a core-shell structure are shown. By comparing Figure 3a with Figure 3b, it is found that the diameter of the sphere-like micelles becomes smaller with the increase of DMF content in the mixed solvents. This phenomenon could be attributed to the increase of the interfacial area between the PBLG core and PEG shell (4). As described by Lin et al. (4), due to the long chain nature, copolymers have very low mobility in solution; therefore, in the self-association process they are easy to form kinetically trapped structures, as a result, different preparation conditions could give rise to different metastable structures.

3.4 Effects of the Introduction of PBLG Homopolymer on the Critical Micelle Concentration of PEG-*b*-PBLG-*g*-PEG in the Mixed Solvents

The critical micelle concentrations of PEG-*b*-PBLG-*g*-PEG2 and its blends with PBLG homopolymer in the mixtures of ethanol and DMF were confirmed according to the document (42). Figure 4 shows the curve of the critical micelle concentration of PEG-*b*-PBLG-g-PEG2 in the mixtures of ethanol and DMF vs. the content (wt%) of PBLG homopolymer (DMF content: 1 vol%, test temperature: 25°C). As seen from Figure 4, the critical micelle concentration of PEG-*b*-PBLG-*g*-PEG2 in the mixed solvents decreases with increasing PBLG homopolymer content, indicating that PBLG homopolymer promotes the formation of the micelles (7, 14). For a mixed system (14), PBLG homopolymer starts to aggregate first due to its stronger hydrophobic properties with the increase of the blend concentration, and the aggregation of the PBLG chains of PEG-*b*-PBLG-g-PEG2 are probably induced by the intermolecular interaction between the PBLG homopolymer and the PBLG chains of the PEG-*b*-PBLG-g-PEG2 copolymer with a further increase of the blend concentration. The PBLG homopolymer and the PEG-*b*-PBLG-g-PEG2 copolymer could self-assemble to form polymeric micelles with the PBLG chains as the inner core of the micelles and PEG chains as the outer shell of the micelles (7, 14).

3.5 Effects of the Grafting Ratio on the Critical Micelle Concentration of PEG-*b*-PBLG-*g*-PEG in the Mixed Solvents

Figure 5 indicates the curve of the critical micelle concentration of PEG-*b*-PBLG-*g*-PEG in the mixtures of ethanol and DMF vs. the grafting ratio (%) (DMF content: 1 vol%, test temperature: 25°C). As shown in Figure 5, the critical micelle concentration of PEG-*b*-PBLG-*g*-PEG in the

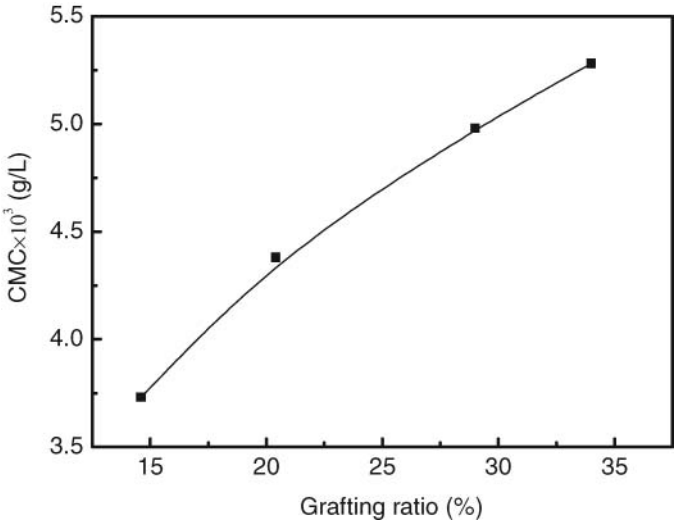

Fig. 5. Curve of the critical micelle concentration of PEG-*b*-PBLG-*g*-PEG in the mixtures of ethanol and DMF vs. the grafting ratio (%) (DMF content: 1 vol%, test temperature: 25°C).

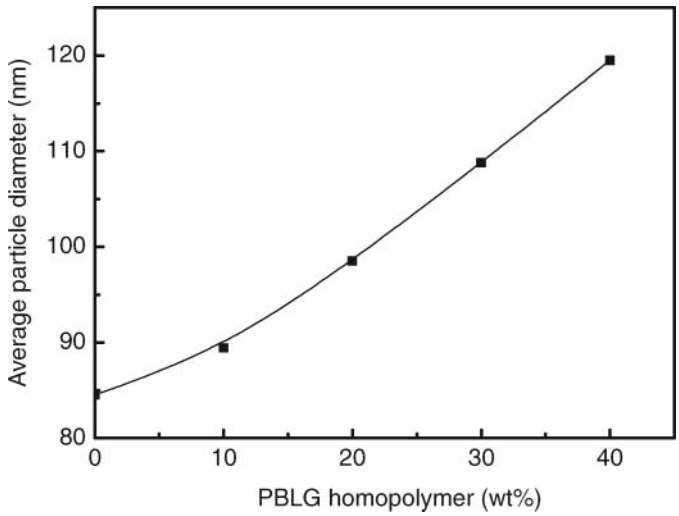

Fig. 6. Curve of the average particle diameter of the micelles formed by PEG-*b*-PBLG-*g*-PEG4 (grafting ratio: 34%) in the mixtures of ethanol and DMF vs. the content (wt%) of PBLG homopolymer (DMF content: 1 vol%, polymer micelle solution concentration: 0.1 g/L).

mixed solvents increases with increasing the grafting ratio. As known, PEG chains hold better hydrophilicity, the higher the grafting ratio, the stronger the hydrophilicity of PEG-*b*-PBLG-*g*-PEG copolymer. This obviously suggests that the grafting ratio decreases the hydrophobic capability of the polypeptide copolymer and promotes the critical micelle concentration of the copolymer (4).

3.6 Effects of the Introduction of PBLG Homopolymer on the Average Particle Diameter of the Micelles Formed by PEG-*b*-PBLG-*g*-PEG in the Mixed Solvents

Figure 6 presents the curve of the average particle diameter of the micelles formed by PEG-*b*-PBLG-*g*-PEG4 in the mixtures of ethanol and DMF vs. the content (wt%) of PBLG homopolymer (DMF content: 1 vol%, polymer solution concentration: 0.1 g/l). As can be seen from Figure 6, the average particle diameter of the micelles of PEG-*b*-PBLG-*g*-PEG4 in the mixed solvents increases with increasing the content of PBLG homopolymer. Because of the same hydrophobic property, PBLG homopolymer could self-assemble into polymeric micelles together with PEG-*b*-PBLG-*g*-PEG4 by the interaction with PBLG chains of PEG-*b*-PBLG-*g*-PEG4 copolymers (8, 14). For a mixed system, the higher the PBLG homopolymer content, the larger the average particle diameter of the micelles.

3.7 Effects of the DMF Content on the Average Particle Diameter of the Micelles Formed by PEG-*b*-PBLG-*g*-PEG in the Mixed Solvents

Figure 7 shows the curve of the average particle diameter of the micelles formed by PEG-*b*-PBLG-*g*-PEG4 in the mixtures of ethanol and DMF vs. DMF content (vol%) (polymer micelle solution concentration: 0.1 g/l). As seen from Figure 7, the average particle diameter of the micelles of PEG-*b*-PBLG-*g*-PEG4 in the mixed solvents decreases with the increase of the DMF content. As described by Cai et al. (4), the higher the DMF content, the larger the interfacial area between the PBLG core and PEG shell, and the smaller the average particle diameter of the micelles formed by PEG-*b*-PBLG-*g*-PEG4 in the mixed solvents. This phenomenon indicates that the introduction of DMF exerts marked effects on the average particle diameter of

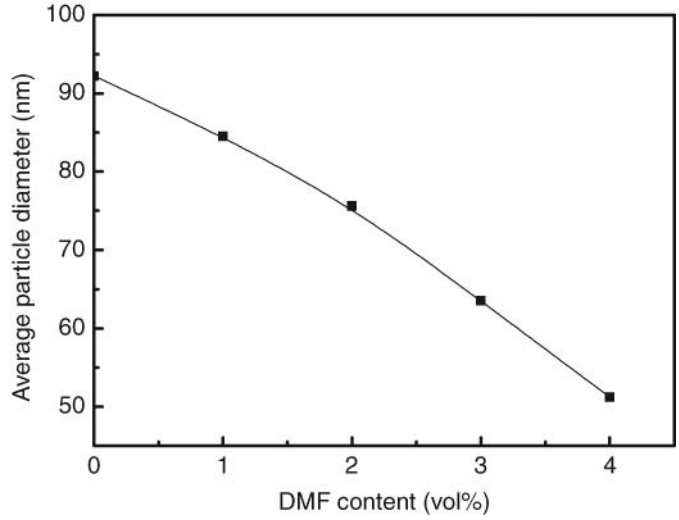

Fig. 7. Curve of the average particle diameter of the micelles formed by PEG-*b*-PBLG-*g*-PEG4 (grafting ratio: 34%) in the mixtures of ethanol and DMF vs. DMF content (vol%) (polymer micelle solution concentration: 0.1 g/L).

the micelles of the polypeptide copolymer in the mixed solvents.

4 Conclusions

Poly(ethylene glycol)-*block*-poly(γ-benzyl *L*-glutamate)-*graft*-poly(ethylene glycol) copolymer has been synthesized. TEM, DLS, and viscometry techniques were used to study the aggregation behaviors of PEG-*b*-PBLG-*g*-PEG copolymer and its blends with PBLG homopolymer in the mixtures of ethanol and DMF. TEM observations revealed that the introduction of PBLG homopolymer, the grafting ratio, and the DMF content could exert marked effects on the morphology of the micelles formed by PEG-*b*-PBLG-*g*-PEG in the mixed solvents. DLS measurements demonstrated that the introduction of PBLG homopolymer increases the average particle diameter of the micelles of PEG-*b*-PBLG-*g*-PEG in the mixed solvents, while the increase of the DMF content in the mixed solvents decreases the average particle diameter of the micelles of the polypeptide copolymer. Viscosity measurements proved that the introduction of PBLG homopolymer decreases the critical micelle concentration of PEG-*b*-PBLG-*g*-PEG in the mixed solvents, while the increase of the grafting ratio increases the critical micelle concentration of the polypeptide copolymer in the mixed solvents.

Acknowledgments

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