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Synthesis and Micellization Behaviour of Polyethylene Glycol-*B*-Poly *B*-Benzyl *L*-Aspartate

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Abstract: *Amphiphilic block copolymers, polyethylene glycol-b-polyβ-benzyl L-aspartate (PEG-b-PBLA) with same PEG chain length and different PBLA chain length were synthesized by ring opening polymerization. Fourier transform infrared (FTIR) spectroscopy was used to confirm the formation of PEG-b-PBLA block copolymers. Effect of polymer chain length and polymer concentrations on the self-assembly behaviours of these block copolymers in the mixed solvents such as dimethyl sulfoxide and deionized water have been investigated. Hydrodynamic properties of the PEG-b-PBLA micelles were investigated by dynamic light scattering technique. Scanning electron microscopy was utilized to reveal the surface morphologies of PEG-b-PBLA micelles.*

Key words: *Amphiphilic block copolymers, PEG-PBLA, hydrodynamic behavior, scanning electron microscopy and dynamic light scattering*

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I. Introduction

Amphiphilic block copolymers are one of the macromolecules that can self-assemble in different forms namely, spherical micelles, cylindrical micelles or vesicles in aqueous media depending on their relative chain length between the polymer blocks [1, 2]. Further they can able to self-assemble in to various ordered nanostructures such as lamellar, cylinder, gyroid and sphere in the form of melt [3, 4]. Inspired by their peculiar properties and interesting applications in the areas of drug delivery, emulsifiers etc, investigations on the block copolymers are still in progress [3].

For example, poly(ethylene glycol)-block-poly(b-benzyl L-aspartate) (PEG-*b*-PBLA) is being used as polymeric micelles for the drug delivery [5, 6]. It is easier to solubilize the drug inside the core of the micelles because of side chain of PEG-*b*-PBLA. Akashi and co-workers [7] have successfully synthesized ABA triblock copolymers comprised of poly(*β*-benzyl-L-aspartate) (PBLA) and prepared thin films using these triblock copolymers. That study showed that these films exhibited enhanced strength and flexibility upon thermal treatment and hence the films could be used for biomedical applications.

Generally, PEG-*b*-PBLA was converted in to anionic or cationic polymers by hydrolysis or aminolysis and then used for micelle preparation. In the present work, we report the synthesis of block copolymers, PEG-*b*-PBLA using ring opening polymerization. We have also explored the micellazation behaviours of these block copolymers in the mixed solvents such as DMSO and distilled water. This is because the block copolymers are not directly soluble in water. To confirm the formation of the structure of the block copolymers, FTIR studies were carried out. DLS and SEM measurements were used to determine the hydrodynamic size of the micelles and morphologies respectively.

II. Materials and methods

β-benzyl *L*-aspartate N-carboxy anhydride (BLA-NCA) and methoxypolyethylene glycol amine (MeO-PEG-NH_2) were used as monomer and initiator respectively. Distilled dichloromethane (DCM) and N, N, dimethyl formamide (DMF) were used for the synthesis of PEG-*b*-PBLA block copolymers.

Synthesis and characterization of PEG-PBLA block copolymers

PEG-PBLA block copolymers were synthesized according to previous report [6]. Initially 20 mg of MeO-PEG-NH_2 was freeze dried from benzene and used as the initiator. Initiator solution was prepared by dissolving freeze dried MeO-PEG-NH_2 in 10 ml distilled dichloromethane (DCM) with constant stirring. Monomer solution was prepared by dissolving 600 mg of BLA in 12 ml distilled DCM and 3 ml distilled N,N, dimethyl formamide (DMF) with stirring. The ring opening polymerization was carried out by mixing these two solutions under argon atmosphere. Reaction was conducted at 35 °C for 72 hours. After polymerization, block copolymers were precipitated by 100 ml of diethyl ether and then dried under vacuum. Perkin-Elmer Spectrum 2 model spectrometer was used to record the FTIR spectra of the block copolymers by KBr pellet method.

Preparation of PEG-PBLA micelles and thin films

PEG-PBLA micelles with three different concentrations of 0.1, 0.5 and 1.0 M were prepared by dissolving 6 mg of PEG-PBLA in 1 ml of dimethyl sulfoxide (DMSO) and 2 ml of distilled water with stirring and allowed to equilibrate at room temperature for overnight. Then the micelles were used for characterization.

PEG-PBLA micellar thin films were prepared on the glass substrate by pouring the micellar solution on the glass substrate. Then the films were subjected to dry at room temperature for several days. After drying, the films were used for SEM observations.

Characterization of PEG-PBLA micelles

Particle analyser-Nano plus was used to study the effect of concentration on the hydrodynamic size of PEG-*b*-PBLA micelles. Surface morphologies of PEG-*b*-PBLA micelles were observed by Scanning electron microscope (Carl-Zeiss, EVO-18).

III. Results and Discussion

Characterization of block copolymers

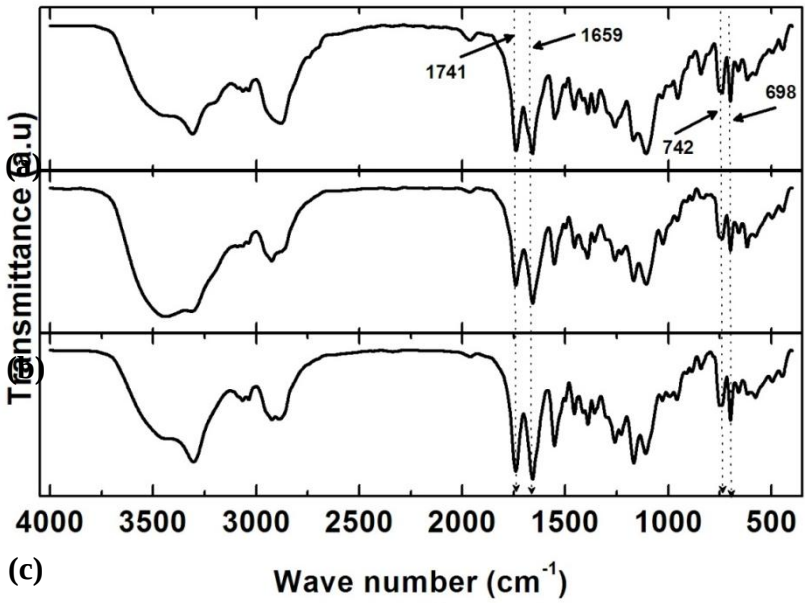

Figure 1. FTIR spectra of (a) PEG-PBLA 1:2, (b) PEG-PBLA 1:3 and (c) PEG-PBLA 1:4.

FTIR studies were performed to confirm the formation of block copolymers, PEG-*b*-PBLA. FTIR spectra for different block copolymers are shown in Figure 1. From the FTIR spectra, it is found that a strong peak at 1741 cm^{-1} is attributed to the ester bond stretching absorption of the benzyloxycarbonyl groups. The peak at 1659 cm^{-1} suggest that the existence of amide carbonyl absorbance. FTIR peaks at 742 and 698 cm^{-1} are due to the presence of C–H bond of benzene. Presence of these different peaks corresponds to functional groups of PEG-*b*-PBLA indicating that the block polymer, PEG-*b*-PBLA was successfully synthesized.

Hydrodynamic behaviours of PEG-*b*-PBLA micelles

DLS measurements were carried out on the PEG-*b*-PBLA micelles to find out the how the block copolymer chain length and polymer concentrations affect size of the micelles. Micellar particle size distributions for different block copolymers with different concentrations are shown in Figure 2. Table 1 summarizes the average diameter of micelles and corresponding polydispersity index. DLS studies showed that size of the micelles increased with increase in chain length of the block copolymers. It was also found that size of the micelles increased with increase in concentration for PEG-*b*-PBLA 1:2. But for PEG-*b*-PBLA 1:4, opposite trend was observed. From the DLS studies it can be concluded that size of micelles found to dependent on the block copolymer chain length and polymer concentrations. We have also found that polydispersity index slightly increases with increase in polymer concentrations irrespective of polymers.

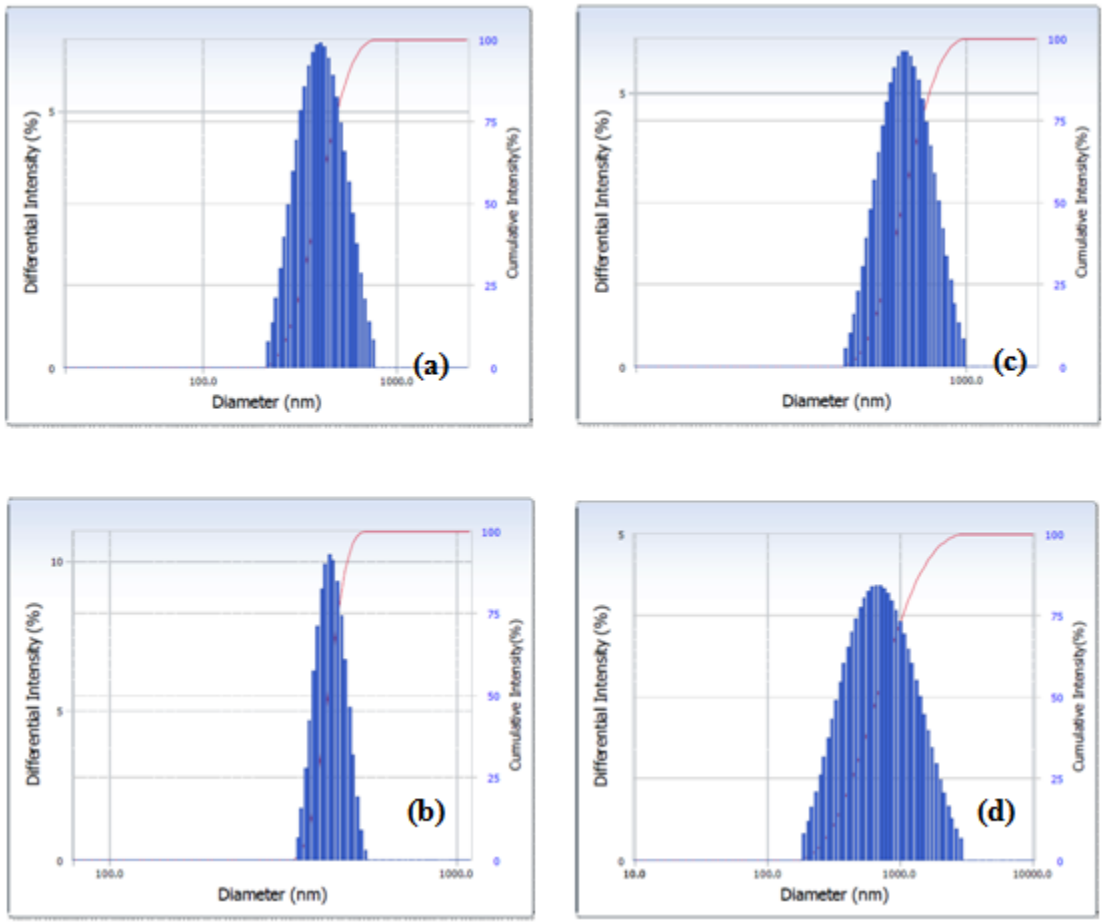

Figure 2. Effect of polymer chain length and concentrations on the hydrodynamic behaviours of PEG-*b*-PBLA micelles in the mixed solvents DMSO and deionized water. (a) 0.5 M PEG-*b*-PBLA 1:2, (b) 1 M PEG-*b*-PBLA 1:2, (c) 0.5 M PEG-*b*-PBLA 1:4, (d) 1 M PEG-*b*-PBLA 1:4.

Table 1. Effect of polymer concentration on the size and polydispersity index (PDI) of micelles

Polymer	Concentration			
	0.5 mg/ml		1 mg/ml	
	Diameter	PDI	Diameter	PDI
PEG-*b*-PBLA 1:2	389	0.026	476	0.366
PEG-*b*-PBLA 1:4	699	0.199	596	0.221

Surface morphologies of PEG-*b*-PBLA micelles

Morphologies of PEG-*b*-PBLA micelles were monitored by SEM observations. SEM images of the micelles are illustrated as shown in the Figure 3. It was noticed from this figure that irregular shaped particles were seen. In the case of PEG-*b*-PBLA 1:2, smaller particles were noticed whereas bigger aggregates were formed for the case of PEG-*b*-PBLA 1:4. These values are almost four times smaller than that of size that determined by DLS. Smaller size could be attributed to the difference in sample preparation of DLS and SEM. For DLS measurements, suspension was used but dried thin films were used for SEM observations.

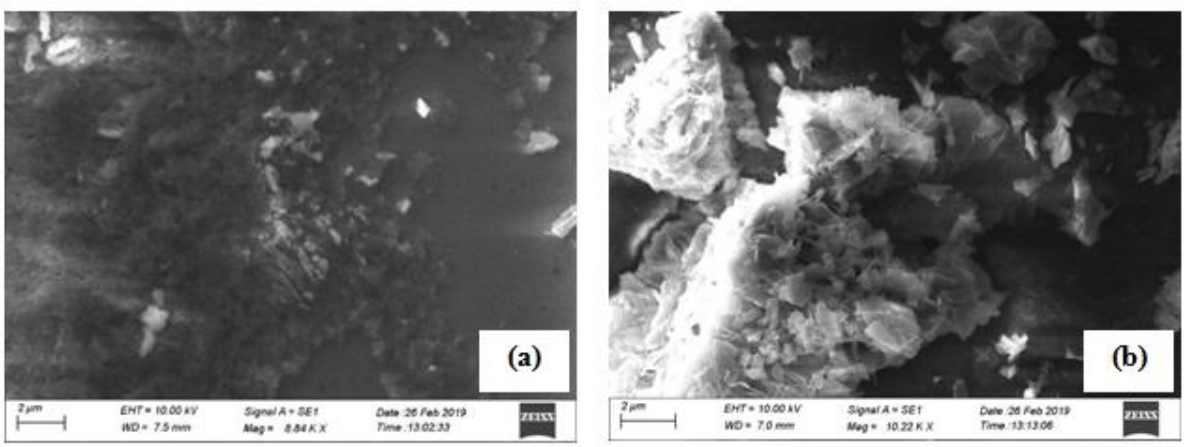

Figure 3. Effect of polymer chain length on the surface morphologies of PEG-*b*-PBLA micelles. (a) PEG-*b*-PBLA 1:2 and (b) PEG-*b*-PBLA 1:4.

IV. Conclusions

Ring opening polymerization was successfully employed to synthesize the block copolymers PEG-*b*-PBLA with different PBLA block length but with same PEG block length. FTIR studies revealed the formation of block copolymers. From the DLS studies it was found that size of the PEG-*b*-PBLA micelles was found to dependent on polymer concentrations and chain length of block copolymers. SEM observations showed that surface morphologies of the PEG-*b*-PBLA micellar thin film depend on the chain length of block copolymers.

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