論文 / 著書情報
Article / Book Information

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Citation	International Workshop on Photonics Polymer for Innovation proceedings, , , p. 61
Pub. date	2016, 10

Structure of Poly(γ-Benzyl–L-Glutamate) Polymerized Using Amine-Terminated Poly(Ethylene Glycol) as a Macroinitiator

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Solution-cast α-helical poly-γ-benzyl-L-glutamate (PBLG) forms two types of aggregation depending on the solvent. The first is "Form B" in which two PBLG chains arranging the dipole as well as the helix axis in one direction are packed in two-dimensional (2D) monoclinic lattice. The other is "Form C" in which PBLG chains packed in 2D hexagonal lattice and arranges only the helix axis in one direction [1]. It has been known that casting PBLG from high- and low-polarity solvent solution yield form B and form C, respectively [2]. The form B transforms to the form C gradually by heating the sample up to 95 °C. In this work, we synthesized PBLG-*block*-polyethylene glycol (PEG) copolymers and investigated the aggregation of PBLG block and micro-segregation morphology characteristic to block copolymers. The self-assembly of block copolymer can provide nanostructures which have potential applications for photonics.

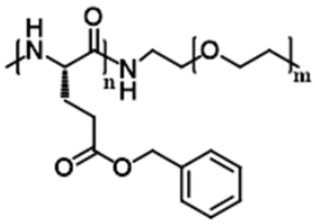

Fig. 1 Chemical structure of PBLG-*b*-PEG

PBLGm-*b*-PEGn copolymers (Fig. 1) were synthesized by the ring-opening polymerization of γ-benzyl-Lglutamate N-carboxy-anhydrides (NCA) using amine-terminated PEG as macroinitiator. Here m and n are the numbers of the number-average molecular weights (M_n) of the PBLG and PEG blocks, respectively, divided by 100.

Interesting is that copolymer films cast from 1,2-dichloro ethane (DCE) has PBLG block in form B whilst PBLG forms form C in DCE solution cast films [3]. The DCE cast films of PBLGm-*b*-PEG20 copolymers have PBLG blocks in form B with 2D monoclinic lattice as revealed by wide-angle X-ray diffraction (Table 1). PBLG36-*b*-PEG20 exhibited a small-angle X-ray scattering pattern including a broad reflection with a spacing of 8 nm which corresponds to molecular length of the copolymer, suggesting that the blocks in the copolymer are not strongly segregated from each other, i.e., the PEG block is compatible to PBLG block. The PEG block is high polarity so as to make the PBLG block compose the form B even in low polarity DCE solution cast film. The form B in the PBLG block is similar to that in the PBLG homopolymer in that heating induces form B-to-form C transition; however, it is different from the homopolymer in that the form C remains partially in the sample cooled to room temperature.

Table 1. X-ray spacing of PBLGm-*b*-PEG_{20} films (m = 36, 50, 69, 100) cast from DCE solutions

m = 36			m = 50			m = 69			m = 100		
	Monoclinic lattice a = 15.6 Å, b = 13.3 Å, γ = 114°			Monoclinic lattice			Monoclinic lattice a = 15.8 Å, b = 13.5 Å, γ = 115°			Monoclinic lattice a = 15.9 Å, b = 13.6 Å, γ = 115°	
d(Å)	Calc. d(Å)	hkl	d(Å)	Calc. d(Å)	hkl	d(Å)	Calc. d(Å)	hkl	d(Å)	Calc. d(Å)	hkl
14.6	14.6	100	14.5	14.5	100	14.3	14.4	100	14.4	14.4	100
12.5	12.5	010	-	-	010	12.3	12.3	010	12.3	12.3	010
7.93	7.95	110	-	-	110	-	7.82	110	7.82	7.82	110
6.94	6.87	120	-	-	120	7.28	7.15	200	6.81	6.81	120
6.22	6.23	020	-	-	020	5.91	6.15	020	6.10	6.15	020

Reference

[1] C. C. Yen, M. Tokita, B. Park, H. Takezoe, J. Watanabe, Macromolecules, 39, 1313-1315 (2006).

[2] A. J. McKinnon and A. V. Tobolsky, J. Phys. Chem. 72, 1157-1161 (1968).

[3] J. Watanabe, I. Kazumichi, R. Gehani, I. Uematsu, J. Polym. Sci., Polym. Phys. Ed. 19, 653-665 (1981)