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Preparation and Evaluation of Poly(Ethylene Glycol)-B-Poly(Caprolactone) Diblock Copolymers with Zwitterionic End Group for Thermo-Responsive Properties

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Abstract : Thermo-responsive materials are viscoelastic materials that undergo a sol-to-gel phase transition at a specific temperature and many materials have been developed. MPEG-b-PCL (MPC) as a thermo-responsive material contained hydrophilic and hydrophobic segments and it formed an ordered crystalline structure of hydrophobic PCL segments in aqueous solutions. The ordered crystalline structure packed tightly or aggregated and finally induced an aggregated gel through intra- and inter-molecular interactions as a function of temperature. Thus, we introduced anionic and cationic groups into the end positions of the PCL chain to alter the hydrophobicity of the PCL segment. Introducing anionic and cationic groups into the PCL end position altered their solubility by changing the crystallinity and hydrophobicity of the PCL block domains. These results indicated that the properties of the end group in the hydrophobic PCL blockand the balance between hydrophobicity and hydrophilicity affect thermo-responsivebehavior of the copolymers in aqueous solutions. Thus, we concluded that determinant of the temperature-dependent thermo-responsive behavior of MPC depend on the ionic end group in the PCL block. So, we introduced zwitterionic end groups to investigate the thermo-responsive behavior of MPC. Methoxypoly(ethylene oxide) and ε-caprolactone (CL) were randomly copolymerized that introduced varying hydrophobic PCL lengths and an MPC featuring a zwitterionic sulfobetaine (MPC-ZW) at the chain end of the PCL segment. The MPC and MPC-ZW copolymers were obtained formed sol-state at room temperature when prepared as 20-wt% aqueous solutions. The solubility of MPC decreased when the PCL block was increased from molecular weight. The solubilization time of MPC-2.4k was around 20 min and MPC-2.8k, MPC-3.0k increased to 30 min and 1 h, respectively. MPC-3.6k was not solubilized. In case of MPC-ZW 3.6k, However, the zwitterion-modified MPC copolymers were solubilized in 3–5 min. This result indicates that the zwitterionic end group of the MPC-ZW diblock copolymer increased the aqueous solubility of the diblock copolymer even when the length of the hydrophobic PCL segment was increased. MPC and MPC-ZW diblock copolymers that featuring zwitterionic end groups were synthesized successfully. The sol-to-gel phase-transition was formed that specific temperature depend on the length of the PCL hydrophobic segments introduced and on the zwitterion groups attached to the MPC chain end. This result indicated that the zwitterionic end groups reduced the hydrophobicity in the PCL block and changed the solubilization. The MPC-ZW diblock copolymer can be utilized as a potential injectable drug and cell carrier.

Keywords : thermo-responsive material, zwitterionic, hydrophobic, crystallization, phase transition
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