Preparation of poly(ethylene glycol)-b-polyester block copolymers with zwitterionic end group for Thermo-responsive properties

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Statement of Purpose: 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 (MC) 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.
Methods: MC diblock copolymer was prepared using a block copolymerization method. For MC-COOH, glutaric anhydride and acetic acid was added to MC solution at room temperature under nitrogen. For MC-NH2, firstly, 4-Nitrophenyl chloroformate and triethylamine was added to MC solution and stirred for 24 h at room temperature under nitrogen to give a MC polymer with oxy-nitrophenoxy end group. Then, Diamino butane was added to MC polymer with oxy-nitrophenoxy end group in THF solution. A reaction mixture was poured into a mixture of n-hexane and ethyl ether to precipitate a polymer, which was separated from the supernatant by decantation to give each block copolymer.
Results: The MPC and MPC-ZW copolymers thus 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 MPC-2.4k to MPC-3.6k. The solubilization time of MPC-2.4k was around 20 min, whereas the solubilization times of MPC-2.8k and MPC-3.0k increased to 30 min and 1 h, respectively; MPC-3.6kwas not solubilized. However, the zwitterion-modified MPC copolymers were readily solubilized in 3–5 min, even in the case of MPC-ZW-3.6k. This result indicates that the zwitterionic end group of the MPC-ZW block copolymer increased the aqueous solubility of the block copolymer even when the length of the hydrophobic PCL segment was increased.
Conclusions: We successfully prepared a series of MPC and MPC-ZW diblock copolymers featuring zwitterionic end groups. The zwitterionic end groups reduced the hydrophobicity around the PCL block and thus changed the solubilization and the onset temperature of gelation of the copolymers. The MPC-ZW diblock copolymer can be utilized as a potential injectable drug and cell carrier.