

Functionalization of Poly(trimethylene carbonate) and Polylactide by Molecular Technology Approach

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Abstract

Biodegradable polymers, such as polylactide and poly(trimethylene carbonate) (PTMC), has been employed to biomedical application. In order to add the functionalities of the biodegradable polymers, the monomer and polymer structures were designed. In this study, molecular design of monomer structures, block copolymer structures, and chain end modification approaches were employed.

At first, the monomer structure was designed in order to introduce functionality. Molecular design of monomer structure is one of approaches to functionalize biodegradable polymers. PTMC is widely employed as biomaterials. Recently, the low-toxic catalyst for trimethylene carbonate (TMC) polymerization has been reported, and numerous studies have reported for PTMC modification by copolymerization, polymer reaction, and novel monomer design. In our laboratory, we designed novel monomers introducing hydrophilic moieties at side group of TMC. It is known that the novel monomer design introducing functional groups via ester and amide linkages. However, we introduced oligo ethylene glycol (OEG) units directly into TMC side group, in order to avoid the possible generation of organic acid compounds after hydrolysis. The homopolymer of PTMC derivatives, bearing OEG units at side chain, shows thermosensitive properties. The lower critical solution temperature (LCST) was varied from 30 °C to 72 °C. When the 3 units of OEG and methyl groups at side chain of TMC was polymerized, the aqueous solution of the homopolymer showed its cloud point at about 33 °C. On the other hand, when the 4 units of OEG and ethyl groups at side chain of TMC was polymerized, the aqueous solution of the homopolymer showed its cloud point at about 72 °C. These results showed the hydrophilic-hydrophobic balance influenced on the cloud point.

Secondly, the block copolymer was synthesized for the functionalization of biodegradable polymers. Block copolymer is also a popular approach to add functionalities to polymers. The hydrophilic modification of PTMC with OEG units were applied to the preparation of hydrophilic and hydrophobic block copolymer. We added methoxyethoxyl group into the TMC as monomer, and the homopolymer of the TMC derivative was used as initiator for ring opening polymerization of lactide. Then the block copolymer of PTMC derivative and PLA was obtained. The copolymer ratios of PTMC and PLA moiety were determined by ¹H NMR as about 2:8. Using the solution of the block copolymer in chloroform, the spin-coated films were prepared on the glass plate. The water droplet was placed to measure contact angle in order to evaluate hydrophilicity. Interestingly, the contact of water droplet caused the contact angles to change from 80 degree to 26 degree, indicating the hydrophilicity increased. The further investigation of the surface were achieved by AFM observation. The surface roughness increased with the estimated value from 3.4 nm to 7.5 nm. This result indicate that the polymer conformation and dynamic change were generated. The elemental analysis of the thin films were achieved by XRD. Compared with the initial thin film, the intensity of carbonate region of the film after increased after water immersion. Similarly, the intensity of ether region increased, suggesting that the TMC moiety with OEG groups were moved onto the surface by the hydrophilic circumstances. On the other hand, the intensity of carbonate region and ester region decreased after the films were immersed into hexane. To add to this, the intensity of ester region increased in the circumstance. The result also implied that the PLA moiety moved onto the surface, and TMC moiety with OEG groups were moved into the film, due to the hydrophobic interaction. Therefore, the thin film of the block copolymer of soft PTMC derivative with OEG and polylactide resulted in a dynamic surface, changing contact angles of a water droplet on the surface. The decomposition behavior of the film were next investigated. The thin films of the block copolymer were prepared onto the quartz crystal microbalance (QCM) substrates. Then, they were immersed into the aqueous solution of proteinase K, which accelerate of the hydrolysis of PLLA moiety. Compared to the film of the amorphous PLLA, the crystalline PLLA showed slower degradation behavior. However, the decomposition of the block copolymer showed much slower behavior than both of amorphous PLLA and crystalline PLLA films. This experiments will contribute to the long-term release of drugs by the degradation of the polymers.

Finally, the chain end modification approach was applied. Chain end modification is also good approach to improve polymer properties. Various functional groups was introduced into initiator for lactide polymerization. After lactide polymerization, the functionality of chain end part was utilized, such as antibacterial properties. We selected catechin as anti-bacterial moiety. Catechin possesses four aromatic hydroxyl groups and one alkyl hydroxyl group, so the aromatic hydroxyl groups were protected for lactide polymerization. The antibacterial properties of the obtained polymer was evaluated. Such multi functionalization of the polymers are expected to produce the novel functional biomedical materials.

Keywords: Trimethylene carbonate, lactide, monomer design, block copolymer, chain end modification