

SYNTHESES OF BIODEGRADABLE POLY(1,4-DIOXAN-2-ONE) AND ITS COPOLYMERS

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Poly (1,4-dioxan-2-one) {poly (*p*-dioxanone), PPDO} is a kind of poly (ether ester) with excellent biodegradability, bioabsorbability, biocompatibility, and mechanical property, and has been applied in biomedical materials¹. Due to the reduction of monomer cost, it will become possible that PPDO finds its use in ecomaterials field. However, owing to the comparatively low activity of the monomer of PPDO (*p*-dioxanone, PDO), an efficient catalyst system is necessary in order to obtain high molecular weight polymers at a higher monomer conversion. A new catalytic system, AlEt₃-H₂O-H₃PO₄, was successfully used as a catalyst for synthesizing PPDO in bulk via the ring-opening polymerization (ROP) of PDO. It has been proved to be a very effective catalyst for ROP of PDO, and high molecular weights of PPDO could be obtained.² AlEt₃-M(AcAc)_n-H₂O, where M is Nd, La, Zn, Fe, Co and Ni, could also initiate the ROP of PDO in bulk and higher-molecular-weight PPDO could be obtained within very short time. Of all those initiator systems, AlEt₃-Nd(AcAc)₃-H₂O was the best one, and it could not only enhance the molecular weight of the polymer but also the monomer conversion. PPDO with a viscosity average molecular weight (M_v) of 3.1×10^5 could be obtained and a monomer conversion of 94.7% could be reached.³ When montmorillonite (MMT) was introduced into the PDO/AlEt₃ system, the ROP of PDO was accelerated. For example, the M_v of product could reach 44,900 only in half an hour. However, after the polymerization was conducted for one hour, the molecular weights did not increase with the increase of polymerization time, and only the monomer conversion became higher and higher.⁴ In order to enhance the polymerization rate, the ROP of PDO was conducted under microwave irradiation. It was found PPDO with a viscosity-average molecular weight of 156,000g/mol could be obtained within 25min at a certain irradiation power.⁵

In order to make PPDO satisfy different needs, its copolymers were synthesized, including a series of amphiphilic copolymers⁶⁻⁸ and some copolymers with other biodegradable polymers^{9,10}. PPDO-poly(ethylene glycol)-PPDO ABA tri-block copolymers (PEDO) were synthesized by ring-opening polymerization (ROP) of PDO using PEG with different molecular weights as macroinitiators. The results indicated that the content and length of PEG chain had a great effect on the thermal behaviors and water absorption properties of copolymers⁶. Poly (vinyl alcohol)-graft-PPDO copolymers with designed molecular structure were synthesized by solid-state polymerization, which was preceded by a graft copolymerization of PDO initiated using PVA as a multifunctional initiator, and SnOct₂ as a coinitiator/catalyst firstly in a homogeneous molten state, then in a solid state. It was found that the crystallization process during the solid-state polymerization could suppress the undesirable inter- or intramolecular side reactions, then resulting in a controlled molecular structure of PVA-g-PPDO, therefore, leading to the controllability of degradability and physical properties via controlling the chemical structure of the graft copolymers by changing polymerization conditions⁸. The copolymers of two kinds of natural macromolecules, starch and chitosan, grafted PPDO were synthesized via two different methods:^{9,10} (1) the grafting reactions were conducted by the ROP of PDO onto the macromolecular backbones and (2) the graft

copolymers were obtained by using 2,4-tolylene diisocyanate (TDI) as a coupling agent to link the prepolymers of PPDO onto the starch or chitosan macromolecules via the reactions between the unreacted NCO groups and the hydroxyls of both PPDO and the starch or chitosan macromolecules. For example, chitosan-g-PPDO could be obtained by ROP of PDO initiated with the hydroxyl group of phthaloyl-protected chitosan in the presence of SnOct₂. Phthaloylchitosan not only enabled the grafting reaction to carry out in a homogeneous system, but also protected the abundant amino groups in the grafting procedure. The structures of copolymers were characterized by one- and two-dimensional NMR spectroscopy. Those amphiphilic copolymers mentioned above have a great potential in drug delivery systems.

The novel triblock copolymers of PPDO block poly(tetrahydrofuran) were synthesized by ROP of PDO in the presence of dihydroxyl poly(tetrahydrofuran) (PTHF) using SnOct₂ as coinitiator/catalyst. The effects of feed ratio, reaction time and reaction temperature were investigated, and it was found that the molar ratio of PDO/catalyst (PDO/cat) had little influence on the inherent viscosity of the copolymers.¹¹ The copolymerizations of PDO with *ε*-CL and LA were also studied systematically. These copolymers can find their applications in biomedical materials.

TDI was used as a chain extender of PPDO, and the chain-extending reactions could still be conducted very well even in the case of quite wide molecular weight range of PPDO prepolymers. In a typical case, PPDO with a viscosity-average molecular weight of 670,000 could be obtained by chain-extending PPDO prepolymers.¹² TDI was also used to prepare the copolymers of PPDO with poly(butylene succinate) (PBS) and with poly(ethylene succinate) (PES) by melt chain-extending reaction of their prepolymers in suitable reactions.¹³

Moreover, a novel star-shaped PPDO was synthesized by the ring-opening polymerization of PDO initiated by pentaerythritol using stannous octoate as catalyst in bulk. The number of initiating hydroxyl groups was close to the theoretical value. The thermal stability of star-shaped PPDO could be improved with the increase of its chain length.¹⁴

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