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Syntheses of biodegradable vinyl polymers by insertion of *N*-benzyl-4-vinylpyridinium chloride into the main chain

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Dedicated to Professor Teiji Tsuruta on the occasion of his 88th birthday (Beiju).

Abstract

Poly(methyl methacrylate), poly(vinyl acetate), polyacrylonitrile, polystyrene, and polyacrylamide were turned biodegradable by insertion of *N*-benzyl-4-vinylpyridinium chloride (BVP) into the main chain. For example, half-life of polyacrylonitrile that contained 3 mol% of BVP was 21 days. Half-life of polyacrylamide that contained 11 mol% of BVP was 2.4 days. Half-life of polystyrene that contained 5 mol% of BVP was expected to be 30–40 days under the conditions where the amount of polymer was very small. Oligomers of vinyl compounds are biodegradable dissimilar to high molecular weight polymers, but they are not useful as polymeric materials. However, connection of oligomers by BVP produced biodegradable polymers. Such bridged polymers are different materials from conventional vinyl polymers, and the utility may be different to some extent, but they are substantially biodegradable.

Keywords: Biodegradability; Functionalization of polymers; Activated sludge; Polystyrene; Poly(methyl methacrylate); Poly(vinyl acetate); Polyacrylonitrile; Polyacrylamide

1. Introduction

In the past 60 years, the polymer industry has provided durable materials adapted to particular uses, but considerable attention has focused on biodegradable polymers for protection of the natural wealthy environment from persistent solid wastes. These biodegradable polymers include naturally occurring polymers and their derivatives, poly(hydroxyalkanoates) produced by bacteria [1], and biodegradable synthetic polymers, such as aliphatic polyesters [2,3] and poly(vinyl alcohol) [4]. However, these polymers do not always possess the necessary characteristics for wide use of synthetic polymers, and it is desirable if general synthetic polymers are turned substantially biodegradable by partial modification of the chemical structure. Different from poly(vinyl alcohol), biodegradation of vinyl polymers having a carbon–carbon bond as the main chain is extremely difficult.

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Insertion of a biodegradable chemical structure into the main chain is effective for making synthetic polymers substantially biodegradable. Matsumura et al. attempted to make poly(carboxylic acid) biodegradable by insertion of vinyl alcohol as a biodegradable unit [5]. On the other hand, rapid digestion of cross-linked poly(*N*-benzyl-4-vinylpyridinium chloride) (cross-linked PBVP) by activated sludge was found during a study on aerobic treatment of wastewater in the presence of cross-linked PBVP [6], and *N*-benzyl-4-vinylpyridinium chloride (BVP) was demonstrated to be a highly biodegradable chemical structure. After this discovery, preparation of biodegradable vinyl polymers was investigated by insertion of BVP as a highly biodegradable chemical structure into the main chain. Poly(methyl methacrylate), poly(vinyl acetate), polyacrylonitrile, polystyrene, and polyacrylamide were turned biodegradable by this methodology. In contrast, however, not-cross-linked poly(*N*-benzyl-4-vinylpyridinium chloride) (linear PBVP) was hygroscopic and showed a strong antibacterial activity [7]. Both of the high biodegradability of cross-linked PBVP and the strong antibacterial activity of linear PBVP appeared to have derived from the strong affinity of BVP with microbial cells [8].

This review briefly surveys the new and effective methodology for making vinyl polymers substantially biodegradable keeping the useful properties of the polymers by partial modification of the chemical structure.

2. Adhesion of bacterial cells by cross-linked poly(*N*-benzyl-4-vinylpyridinium halide)

Cross-linked poly(*N*-benzyl-4-vinylpyridinium halide) was found to have a novel and remarkable ability to remove bacterial cells from water [8]. For example, when 1 g (wet weight) of cross-linked poly(*N*-benzyl-4-vinylpyridinium bromide) (cross-linked PBVP(Br)) was contacted with 20 ml of suspensions of *Escherichia coli* (9.7×10^4–9.7×10^7 cells/ml), *Salmonella typhimurium* (8.0×10^6–1.1×10^7 cells/ml), *Streptococcus faecalis* (5.0×10^5 cells/ml), *Staphylococcus aureus* (8.1×10^7 cells/ml), and *Pseudomonas aeruginosa* (3.2×10^5 cells/ml) with stirring in sterilized physiological saline at 37 °C, 99% of the viable cells of these bacteria were removed in 2–6 h. When suspensions of these bacteria (10^5–10^8 cells/ml) were passed through a column (20 mm by 100 cm) packed with cross-linked PBVP(Br) at 37 °C with a flow rate of 0.8–1.4 bed volumes per h, 97–100% of the viable cells were eliminated from the suspensions during the treatment. Mechanistic studies demonstrated that cross-linked poly(*N*-benzyl-4-vinylpyridinium halide) irreversibly captured these bacterial cells alive during the treatment. That is, total organic carbon (TOC) was removed during the treatment, and the bacterial cells that adhered to the surface of the resin proliferated on the bacterial medium. The adhesion capacity was estimated to be 10^{10} cells per g (dry weight) of the resin. TOC was also removed even when the bacterial cells were killed by heat treatment before the column studies. Scanning electron micrograph of *E. coli* captured on the surface of cross-linked PBVP was reported later [9].

Cross-linked PBVP and cross-linked PBVP(Br) were most effective among a variety of polymers examined for the capture of bacterial cells on the surface, and cross-linked poly(*N*-alkyl-4-vinylpyridinium halides) were much less effective.

Effect of the structure of cross-linked PBVP on its ability to capture bacterial cells in water was investigated in detail [10]. The ability was quantitatively evaluated by the removal coefficient based on the initial rate of decrease of viable cell counts caused by the polymer. The coefficient uniformly increased with content of BVP, and considerably increased when the content of divinylbenzene became smaller. The coefficient also increased with the content of 4-vinylpyridine in the polymer matrix. Based on these observations, presence of BVP was concluded to be essentially important in the affinity of the polymer for bacterial cells, and hydrophilic nature and high degree of swelling in water of the polymer matrix appeared to enhance the ability to capture bacterial cells.

Strength of the interaction between cross-linked PBVP and a variety of bacterial cells was evaluated by the removal coefficient [11]. Hydrophobic bacteria and hydrophilic bacteria showed distinct differences in the capturing interaction. With hydrophobic bacteria, electrostatic interaction as well as hydrophobic interaction between the polymer and the cells appeared to be important. With hydrophilic bacteria, however, other factors such as solvent (water) mediated forces and hydrodynamic forces were suggested.

Adhesion of microbial cells by cross-linked PBVP was used for immobilization of bacterial cells in bioreactors [12,13] and rapid determination