CHEMISTRY LETTERS, pp. 1859-1862, 1992.

Anaerobic Biodegradability of Water-Soluble High Molecular Weight Polycarboxylate by River Sediments

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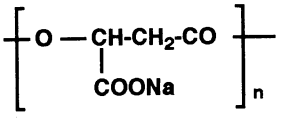
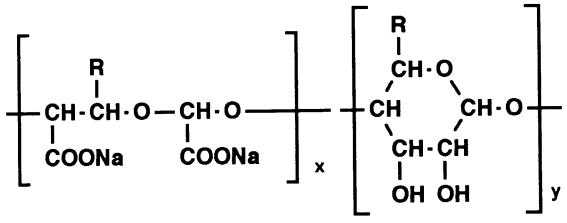
High molecular weight poly(sodium carboxylate)s designed as biodegradable functional polymers were confirmed to be biodegraded under anaerobic conditions using river sediment. They were biodegraded to an extent similar to that under aerobic conditions.

Polymeric polycarboxylates have been reported to provide valuable properties in various fields, such as builder performance in detergent formulations as sodium tripolyphosphate (STPP) substitutes.[1-4] These polymeric compounds, however, are extremely resistant to biodegradation, which is an important criterion for an environmentally acceptable compound as a STPP replacement.[3] Recently, much effort has been concentrated on developing biodegradable polymers in the industrial field. It will be very important to estimate the biodegradability of such a water-soluble polycarboxylate under anaerobic conditions in addition to aerobic conditions. Water-soluble polymeric compounds will be widely diffused into aerobic environments as well as anaerobic environments of soil, river water or sea water of the earth after their use. However, the anaerobic biodegradability of the water-soluble synthetic polymers, so far, has not been studied with a few exceptions.[5-7]

In this report, biodegradability of water-soluble poly(sodium carboxylate)s which were designed and synthesized as biodegradable functional polymers, were evaluated under anaerobic conditions using river sediments and compared to that under aerobic conditions.[8-10]



PMLA



R = CH_2OH : DCAm
= H : DCXy

Poly(sodium carboxylate)s containing biodegradable segments evaluated in this report were poly(sodium β-DL-malate) (PMLA) [8] having a number-average molecular weight ($\bar{M}n$) of 5200, sodium dicarboxy amylose (DCAm) [9] having $\bar{M}n$=29000 and a relative dicarboxylate content of 26 mol%, and sodium dicarboxy xylan (DCXy) [10] having $\bar{M}n$=14500 and a relative dicarboxylate content of 21 mol%. Polymer code and structures are shown above.

The anaerobic biodegradation test was carried out basically according to the literature[11] in a 3 L glass bottle equipped with a sampling tube into the medium and also having a serum cap for gas sampling. The inoculum consists of black river sediments obtained from the river mouth at the industrial area (Fuji River, Fuji City, Japan). All procedures were carried out anaerobically under a stream of nitrogen gas. The river sediments were centrifuged at 1200 g for 10 min, the wet sediments (2 g) were suspended in a 2 L BOD test solution [12] into which nitrogen was previously bubbled, and then the incubation bottle was purged by nitrogen and incubated anaerobically for another 3 weeks in the dark. After a 3 week incubation, the bottle was allowed to stand for 12 h and the supernatant was used as an anaerobic microbial source. Each biodegradation vessel (3 L) containing the BOD test solutions (1.8 L), the anaerobically preincubated microbial source (200 mL) and the test polymers (0.01%) was purged by nitrogen gas and incubated at 27℃ in the dark with one-hour stirring two times a day. Biodegradability was evaluated by gel permeation chromatography (GPC)[13] and total organic carbon (TOC) of the incubation media. The head space gas concentration of H_2, CO_2,and CH_4 was also analyzed using gas chromatography. D-Glucose was used in place of the test polymer for checking the activities of the microbes by analyzing the gas production of H_2, CO_2, CH_4, H_2S, and TOC. From the measurement using D-glucose as a sole carbon source, the test microbes consisted mainly of sulfate-reducing bacteria which are reported to commonly occur in river mouth sediments.[14] Figure 1 shows the CO_2 gas production [11] typical for the sulfate-reducing bacteria.[14]

It will be useful to measure molecular weight and the molecular weight distribution of the polymers by GPC before and after the biodegradation to determine the main-chain scission of the polymer, as well as the amount of the polymer which has been reduced by the microbes. Residual polymers in the biodegradation media were analyzed by GPC after ultrasonication with a small

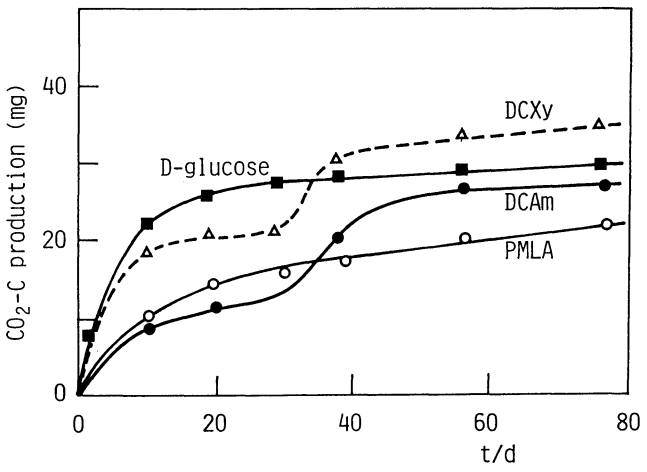


Fig. 1. Time course of CO_2 production.

amount of nonionic surfactant to avoid the adsorption of the polymers onto the microbes.[10] Peak area of polymer fraction on GPC corresponds to the polymer concentration in the biodegradation media. Figure 2 shows the GPC profiles of PMLA, DCAm and DCXy before and after the anaerobic biodegradation test. It was confirmed that the polymers were all biodegraded under the anaerobic conditions.[15] Among the polymers tested in this report, PMLA was biodegraded more quickly than those of DCAm and DCXy. It was also found that the main chain of the partially dicarboxylated polysaccharides containing unreacted sugar blocks (DCAm and DCXy) were biodegraded to yield low molecular weight fractions with subsequent assimilation without further lowering of the molecular weight. GPC profiles also show that the high molecular weight fractions were biodegraded as well as the low molecular weight fractions of the polymer. When compared to the results under aerobic conditions measured using acitivated sludge,[8,10,16] similar tendencies were observed under anaerobic conditions.

Judging from the GPC analysis of the fate of polymer fractions in the incubation media, biodegradation certainly occurred under anaerobic

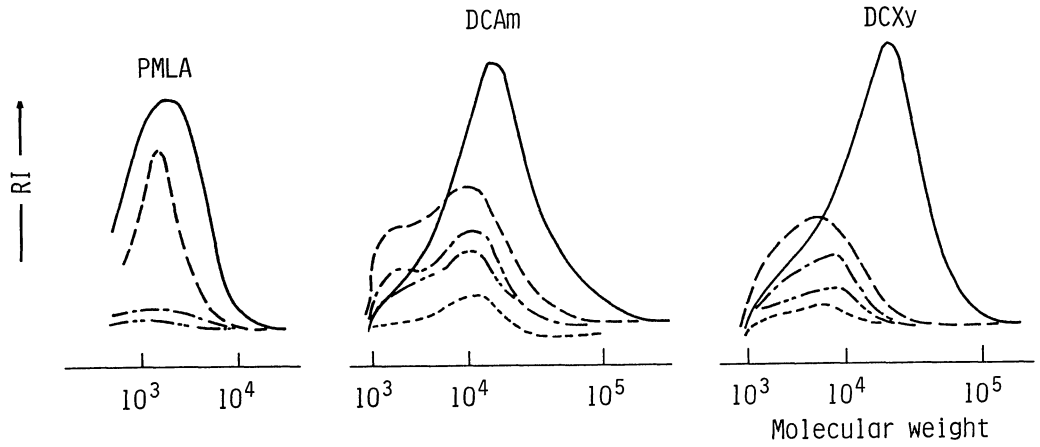


Fig. 2. GPC profiles of PMLA, DCAm and DCXy before and after anaerobic biodegradation test. —— : 0 d, ----: 10 d, — — : 21 d, —·—·— : 35 d, -----: 100 d.

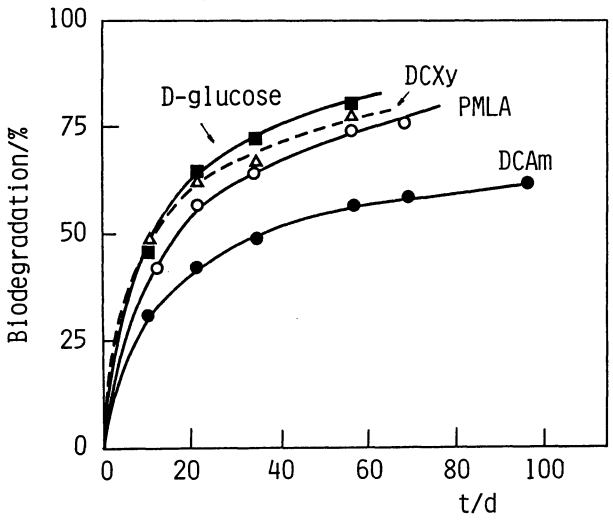


Fig. 3. Biodegradability as determined by the TOC values in the anaerobic incubation media. Biodegradation = $100(1-TOC/TOC_0)$.

conditions. These phenomena were also confirmed by measuring the TOC concentrations in the incubation media. Figure 3 shows the biodegradability as expressed by the ratio of the TOC value after biodegradation and the initial TOC value (TOC/TOC_0 x100) of the culturing media as determined by the TOC analyzer. It was confirmed that the biodegradability of these polymers was comparable to that of D-glucose as a control and more than 60% of the organic carbon was removed from the incubation media by the anaerobic degradation using river sediments. Moreover, the rate of biodegradation was relatively comparable to that under aerobic conditions.

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12) OECD Guidelines for Testing of Chemicals, 301D, Closed Bottle Test, Organization for Economic Cooperation and Development (OECD, 1981). BOD solution contains (mg/L) : KH_2SO_4, 8.5; K_2HPO_4, 21.75; $Na_2HPO_4 \cdot 2H_2O$, 33.3; NH_4Cl, 1.7; $MgSO_4 \cdot 7H_2O$, 22.5; $CaCl_2$, 27.5; $FeCl_3 \cdot 6H_2O$, 0.25. pH=7.2.
13) Number-average molecular weight ($\bar{M}n$) and molecular weight distribution ($\bar{M}w/\bar{M}n$) were measured by a GPC system with commercial GPC columns (TSKgel G5000PW + G2500PW, TOSOH Co. Ltd., 0.1 M phosphate buffer/0.3 M NaCl as eluent). The system was calibrated with a poly(ethylene oxide) standard.
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15) DCAm and DCXy were quite stable in a buffer solution without microbial source (pH 4-9) at 30 ℃ for 60 d. PMLA was slowly hydrolyzed in a buffer solution (pH 6.8) to reduce $\bar{M}n$ in 80% at 30 ℃ for 20 d.
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(Received June 25, 1992)