Builder Performance in Detergent Formulations and Biodegradability of Partially Dicarboxylated Amylopectin

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Amylopectin was partially dicarboxylated so as to retain the unreacted glucopyranose groups as biodegradable segments in the polymer chain; and the bioenzymatic degradability, as well as builder performance in detergent formulations, was evaluated and compared with data obtained from amylose. Dicarboxylation of amylopectin was carried out by conversion of the vicinal diols of the glucopyranose groups of amylopectin into the corresponding dicarboxylates *via* dialdehydes. The aerobic biodegradability of sodium dicarboxyamylopectin (DCAp) was evaluated by measuring the biological oxygen demand (BOD) with activated sludge. The biodegradability, of DCAp depended on the content of unreacted glucopyranose groups in the polymer chain. DCAp containing more than 80 mol% glucopyranose groups showed excellent biodegradability. The biodegradability, obtained by the BOD test, and the enzymatic degradability also correlated well, suggesting that these polymers are first cleaved at the unreacted glucopyranose units with subsequent assimilation of the resultant oligomeric fractions. DCAp, which was biodegradable under aerobic conditions, also biodegraded under anaerobic conditions. Detergency tests were carried out with heavy-duty detergent formulations. The detergency was determined by the content of dicarboxylate groups in the polymer when compared on an equal weight basis. The polymers with high dicarboxylate contents showed better builder performance. DCAp showed better builder performance than the corresponding amylose derivatives. This excellent builder performance is ascribed to the cluster-type structure of amylopectin, in which calcium ion is effectively sequestered. Builder performance in detergent formulation improved greatly with increasing amounts of DCAp used in the detergent formulation.

KEY WORDS: Amylopectin, anaerobic biodegradation, biodegradation, biological oxygen demand, builder, detergency, dicarboxyamylopectin, enzymatic degradation, polycarboxylate, water-soluble polymer.

High-molecular weight polycarboxylates have been considered attractive as water-soluble functional polymers, including dispersants and detergent builders (1–7). However, they are generally highly resistant to biodegradation, which is an important criterion in large-scale application in the industrial field. Environmentally acceptable polycarboxylates are particularly needed, and great efforts have been made to develop such biodegradable polymers. We previously reported that the introduction of biodegradable segments into the functional polymer chain is one way to design a biodegradable functional polymer (4–11).

Amylopectin is the major component of starch, which is one of the most abundant and promising renewable resources as a substitute for petroleum in the next generation. In recent years, this compound has attracted attention as a biodegradable polymeric raw material for the production of biodegradable plastics. Furthermore, amylopectin has a highly branched structure, consisting of hundreds or thousands of short linear amylose chains, connected to each other by α-1,6 linkages (12–15). It is feasible to prepare a novel biodegradable polycarboxylate with a high-molecular weight by partial oxidation of amylopectin. The inherent cluster-structure of dicarboxylated amylopectin may provide greater calcium sequestration capacity than is possessed by linear-type dicarboxylated amylose.

Preparation and calcium complexation of completely dicarboxylated polysaccharides were reported (16–19), but partially dicarboxylated polysaccharides containing sugar residues have not yet been reported. Functionalization of amylopectin as a water-soluble polymer has not yet been extensively studied with respect to biodegradability and functionality.

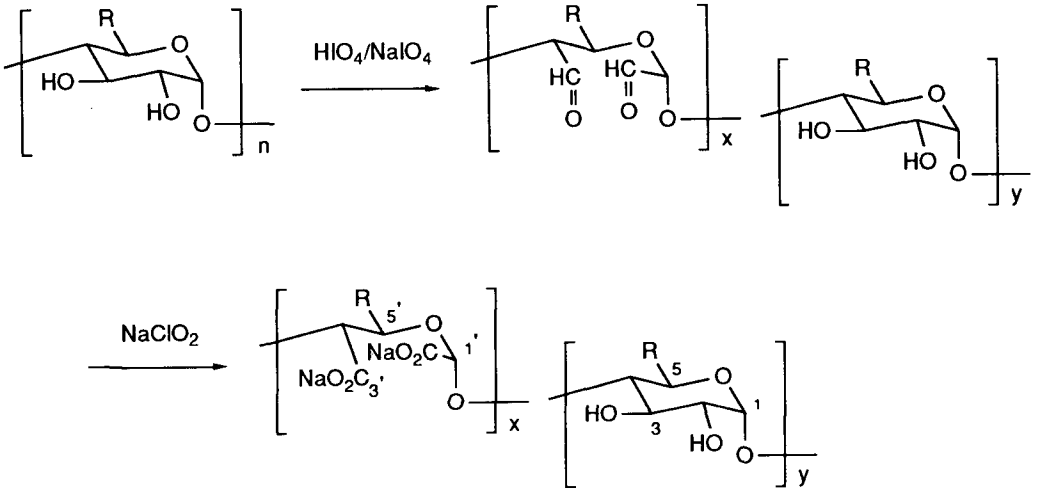
For this report, amylopectin was partially dicarboxylated so as to retain biodegradable glucopyranose groups by the conversion of the vicinal diols of the glucopyranose moieties into dicarboxylates *via* dialdehydes. The relationship between the degree of dicarboxylation and biodegradability, as well as functionality, is discussed.

EXPERIMENTAL PROCEDURES

Materials and measurements. Amylopectin (amylose-free) from waxy corn was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). The other materials were of highest available purity and were used as purchased. ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were determined with a JEOL model JNM-FX90A (90 MHz) Fourier transform spectrometer, operating at 22.5 MHz with complete proton decoupling (JEOL Ltd., Tokyo, Japan). Infrared (IR) spectra were measured with a JASCO Fourier transform infrared spectrometer model FT/IR-5000 (JEOL Ltd.). Number average molecular weight ($\overline{M}n$) and molecular weight distributions ($\overline{M}w/\overline{M}n$) were measured by a gel-permeation chromatographic system (GPC) with commercial GPC columns (TSK gel G5000PW + G2500PW; Tosoh Co. Ltd., Tokyo, Japan) and 0.1 mol/L phosphate buffer/0.3 mol/L sodium chloride, pH 6.8, as eluent). The system was calibrated with a poly(ethylene oxide) standard ($\overline{M}n$: 3000 ≈ 996000, $\overline{M}w/\overline{M}n$: 1.02 ≈ 1.10; Tosoh Co. Ltd.). α-Amylase from *Bacillus* sp. (1,4-α-D-glucan-glucanohydrolase; E.C. 3.2.1.1. 22500 U/g solid) was purchased from the Sigma Chemical Co. (St. Louis, MO). Pullulanase (amylopectin 6-gluconohydrolase; E.C. 3.2.1.41) from *Klebsiella pneumoniae* (2000 U/g solid, according to the supplier) was purchased from Hayashibara Biochemical Laboratories, Inc., (Okayama, Japan).

Preparation of partially dicarboxylated amylopectin (11,19). Dicarboxyamylopectin (DCAp) with variable degrees of dicarboxylation was prepared by the partial conversion of the vicinal diol of the glucopyranose groups into the corresponding dicarboxylates, as shown in Scheme 1.

Preparation of sodium DCAp with an $\overline{M}n$ value of 52000 and a sodium dicarboxylate content of 26 mol% [DCAp-52000(26)] is described as a representative. Amylopectin (5.0 g) was suspended in 0.267 mol/L aqueous periodic



SCHEME 1

acid (145 mL) and stirred at 4°C for 2 h in the dark. After the reaction, the suspension was filtered, washed thoroughly with chilled water, dried in vacuum below 40°C to obtain dialdehyde amylopectin (diformylamylopectin) in 38.9% yield (4.43 g). The dialdehyde content of the product, determined by the method of Nieuwenhuizen (19), was 28.9 mol%. Dialdehyde amylopectin (3.5 g) was suspended in water (123 mL), and a solution of sodium chlorite (21 g) and water (70 mL) was added to the aqueous suspension of dialdehyde amylopectin. The pH value of the solution was adjusted to 4.0 with acetic acid, and the mixture was stirred at 20°C for 24 h. The temperature was then raised to 50°C, and the reaction was allowed to continue for another 1 h. Nitrogen was passed through the solution until a colorless solution was obtained. The pH value of the solution was raised to 11 with 3 mol/L aqueous sodium hydroxide. The solution was slowly poured into a large amount of ethanol (400 mL) with stirring to precipitate the polymer. The precipitated polymer was dissolved in a small amount of distilled water (50 mL), and the solution was then slowly added to a large amount of ethanol (300 mL) with stirring to precipitate the polymer. The precipitated polymer was dissolved in distilled water (100 mL) and freeze-dried. Further drying was carried out at 70°C in vacuum to obtain the sodium salt of dicarboxyamylopectin in 97% yield (3.8 g) as a white powder. The dicarboxylate content, measured according to Neale and Springfellow (20), was 26.4 mol%, and $\overline{M}n = 52000$ and $\overline{M}w/\overline{M}n = 7.3$ by GPC. The following spectral data for DCAp-52000 (26) confirm the structure. Fourier transform IR (KBr): 3360, 1020 (OH), 1616, 1419 (COONa), 2932 (CH_2), 1155 cm^{-1} (C-O-C); ^{13}C NMR (22.5 MHz: D_2O): δ = 177.0 (C2′), 175.8 (C3′), 100.7 (C1, C1′), 76 ≈ 81 (C4, C4′, C5′), 74.2, 72.2 (C2, C3, C5), 61.3 ≈ 62.2 (C6, C6′).

For the preparation of dialdehyde amylopectin with a high degree of dialdehydation, sodium periodate was used in place of periodic acid to avoid the molecular weight reduction by the acidic hydrolytic cleavage caused by periodic acid. The procedure was the same as that of periodic acid. The other DCAp was also obtained by a similar procedure. Typical oxidation conditions and analytical data for DCAp are shown in Table 1.

Detergency test (21). The detergency test was first conducted with a standard heavy-duty detergent formulation that contained 20% sodium dodecylbenzene sulfonate, 25% sodium tripolyphosphate (STPP)/disodium 3-oxapentanedioate (ODA), 5% sodium silicate, 3% sodium carbonate, 0.5% carboxymethyl cellulose and 46.5% sodium sulfate. The test was done to determine the detergency of the STPP/ODA formulation as a basis for comparison with the test polymers. In the experimental formulas, the STPP/ODA was replaced with an equal weight of the test builders unless otherwise stated. The washing efficiency of the polymers was determined in a Terg-O-Tometer (United States Testing Co., Inc., Hoboken, NJ) (22) with improved artificially soiled cotton cloth test pieces prepared by an aqueous dispersion method (21). The washing experiments were performed with water containing 54 ppm $CaCO_3$ with a cloth-to-liquor ratio of 1:30, at a temperature of 25°C and with a detergent concentration of 1.2 g/L. Light reflectance of the test swatches was measured by means of an automatic reflectometer equipped with a green filter. The K/S ratio (K, reflectivity coefficient; S, light scattering coefficient) was calculated with the Kubelka-Munk equations (23), and the detergency was expressed as follows:

$$\text{detergency (\%)} = (A - B)/(A - C) \times 100 \quad [1]$$

where A, B and C are the K/S values of the soiled swatches, the washed swatches and the original unsoiled swatches, respectively. This is illustrated in:

$$K/S = (1 - R)^2/2R \quad [2]$$

where R is the reflectance. The relative detergency was expressed as a value of 10 for STPP and 0 for ODA.

TABLE 1

Typical Preparation Conditions and Analytical Data of Sodium Dicarboxyamylopectin (DCAp)

	Oxidation of amylopectin to dialdehyde by aqueous periodic acid/sodium periodate[b]					Oxidation of dialdehyde to DCAp by aqueous sodium chylorite[c]			
Substance[a]	$HIO_4/NaIO_4$	t (h)	Concentration of $HIO_4/NaIO_4$ (mol/L)	Yield (%)	Dialdehyde content (mol%)	Yield (%)	Dicarboxyl content (mol%)	$\bar{M}n$	$\bar{M}w/\bar{M}n$
DCAp-									
40000(14)	HIO_4	2	0.267	87	23	81	14	40000	8.9
52000(26)	HIO_4	2	0.267	89	29	97	26	52000	7.3
22000(45)	$NaIO_4$	24	0.112	91	54	55	46	22000	8.0
34000(51)	$NaIO_4$	24	0.134	88	63	82	52	34000	7.0
15000(83)	$NaIO_4$	24	0.191	88	92	36	83	15000	7.2

[a]Polymer code indicates number average molecular weight ($\bar{M}n$) and relative dicarboxylate content in mol% in parenthesis.
[b]Dialdehyde amylopectin (diformyl amylopectin) was prepared by the reaction of amylopectin (5.0 g) with aqueous $HIO_4/NaIO_4$ (145 mL) at 4°C.
[c]DCAp was prepared by the reaction of dialdehyde with aqueous sodium chlorite at pH 4.0 for 24 h at 20°C.

Calcium sequestration capacity (24). A calcium ion electrode (Model 93-20; Orion Research, Inc., Boston, MA) and an ion meter (IM-20E; TOA Electronic Ltd., Tokyo, Japan) were used to measure the equilibrium calcium ion concentrations. Ten mg of polymer was dissolved in 50 mL of 1.00×10^{-3} mol/L calcium hardness solution with 0.08 mol/L KCl (ion strength, $\mu = 0.08$), and the pH of the solution was adjusted to 9.0 at 30°C. The electrode was immersed in the solution, which was then stirred. After 10 min, the equilibrium free calcium ion concentrations were measured, and the calcium sequestration capacity was expressed as grams of calcium ion sequestered by 100 g of the polymer.

Aerobic biodegradation. Biochemical oxygen demand (BOD) was determined with a BOD Tester (Model 200F; TAITEC Corp., Koshigaya-shi, Japan) by the oxygen consumption method, according to the Modified MITI Test (25). The activated sludge was obtained from a municipal sewage plant in Yokohama City. The concentration of the test polymer was 25 mg/L. The residual polymers, present in the culture broth before and after the biodegradation test (BOD test), were analyzed directly by GPC after ultrasonic treatment with a small amount of a nonionic surfactant to avoid any adsorption loss of the polymer onto the microbial cell.

Total organic carbon (TOC) concentration in the cell-free culture filtrate was measured to evaluate the aerobic biodegradability of the polymers. The incubation was carried out with 0.1% polymer concentration in an inorganic medium (initial pH = 7.2), containing the activated sludge, in a shaking flask with reciprocal shaking at 25°C. The TOC values were periodically measured by a commercial TOC analyzer.

Anaerobic biodegradation test (26,27). The anaerobic biodegradation test was carried out basically according to the literature (28) 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 consisted of black river sediments obtained from the river mouth in an 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 mineral solution (29) [(mineral 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] into which nitrogen was previously bubbled. Nitrogen was then bubbled into the incubation bottle for two days, and the contents were incubated anaerobically for another two weeks in the dark. After a two-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 mineral solutions (1.8 L), the anaerobically preincubated microbial source (200 mL) and the test polymers (0.01%) was purged with nitrogen gas and incubated at 27°C in the dark and stirred twice a day for one hour with a magnetic stirring bar. Biodegradability was evaluated by GPC and TOC of the incubation media. The headspace gas concentration of H_2, CO_2 and CH_4 was also analyzed with a gas chromatograph (GC) using a stainless-steel column packed with Unibeads C (60/80 mesh).

Enzymatic degradation by α-amylase. A mixture of DCAp (15 mg), α-amylase (3.0 mg) and 0.2 mol/L phosphate buffer (pH 6.9, 15 mL) was stirred for 1 h in a shaking flask with reciprocal shaking at 30°C. Degradation of the polymer was directly analyzed by GPC. Parallel to this reaction, a mixture of DCAp and 0.2 mol/L phosphate buffer (pH 6.9, 15 mL) without α-amylase was stirred at 30°C as a blank test.

Enzymatic degradation by pullulanase. Enzymatic degradation by pullulanase was measured in a similar procedure, except that a mixture of DCAp (20 mg), pullulanase (6.0 mg) and 0.2 mol/L phosphate buffer (pH 6.0, 20 mL) was used and incubated for 48 h with reciprocal shaking at 30°C.

RESULTS AND DISCUSSION

Preparation of DCAp. DCAp with a varying amount of unreacted glucopyranose residue was prepared by the partial oxidation of amylopectin with periodic acid/sodium periodate followed by sodium chlorite. When a longer oxidation time was used, the acidity of the periodic acid tended to reduce the molecular weight of the resultant oxidized amylopectin by hydrolytic cleavage. To avoid the molecular weight reduction by acidic hydrolytic cleavage,

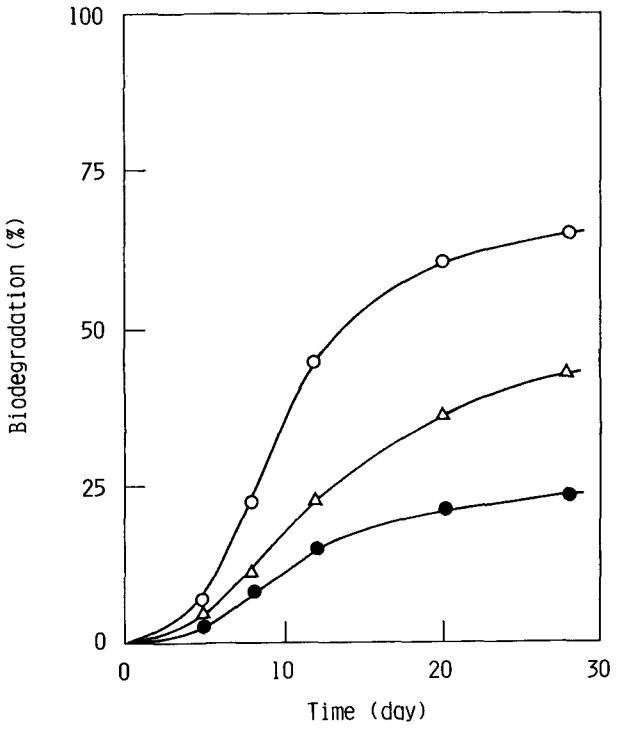


FIG. 1. Aerobic biodegradability of sodium dicarboxyamylopectin (DCAp), calculated from the biochemical oxygen demand (BOD), as measured by the oxygen consumption method in a BOD tester with activated sludge at 25°C and the theoretical oxygen demand. Polymer concentration, 25 mg/L; ○, DCAp-40000(14); △, DCAp-52000(26); and ●, DCAp-34000(51).

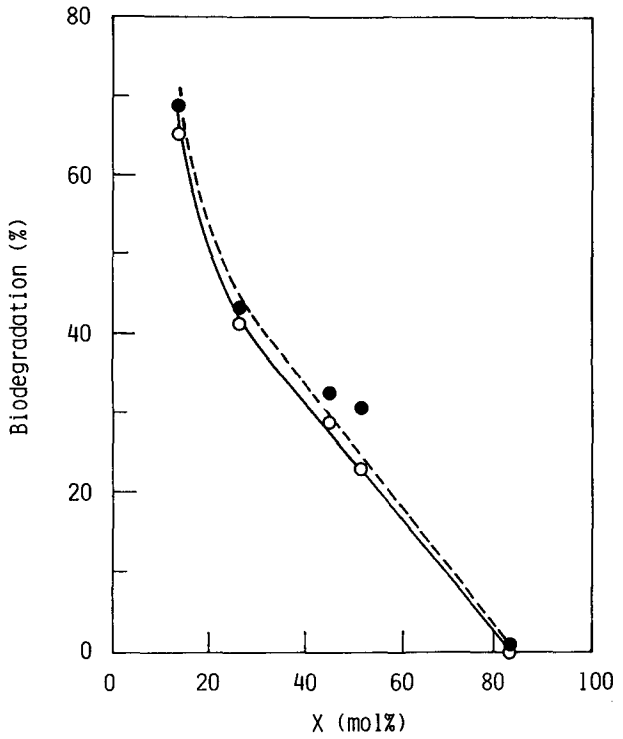


FIG. 2. Biodegradability after 28 d of sodium dicarboxyamylopectin as determined by the biochemical oxygen demand (BOD) and total organic carbon (TOC), as a function of the degree of dicarboxylation (×). Biodegradation conditions are the same as those of Figure 1. ○, BOD_{28}/theoretical oxygen demand × 100; ●, 100 × (1 − TOC_{28}/TOC_0).

sodium periodate was used in place of periodic acid for the preparation of DCAp with a high dialdehyde content. The degree of dicarboxylation was dependent on the reaction time of the amylopectin with periodic acid/sodium periodate and on the concentration of the aqueous periodate. Table 1 shows the typical dicarboxylation conditions and analytical data for DCAp.

Aerobic biodegradability of DCAp. A convenient way of predicting the aerobic biodegradability of the polymers is to measure the BOD values. Figure 1 shows the biodegradation (BOD/TOD) calculated from the BOD values and the theoretical oxygen demand (TOD). The BOD values were measured with a BOD tester, an activated sludge freshly obtained from a municipal sewage treatment plant in Yokohama city, and a test polymer concentration of 25 mg/L. DCAp that contained unreacted glucopyranose groups was biodegraded by the activated sludge. Biodegradation, as measured by BOD value, was accelerated after a one-week incubation, and rapid biodegradation was reduced after about a three-week incubation.

Figure 2 shows the relation between biodegradability (BOD_{28}/TOD), calculated from the BOD value after 28 d incubation and the TOD values, and the degree of dicarboxylation (X). The BOD value of DCAp was dependent on the degree of dicarboxylation or the content of unreacted glucopyranose groups, suggesting that the unreacted glucopyranose groups act as biodegrading segments. DCAp containing less than about 20% dicarboxylate units, or more than about 80% glucopyranose groups in the polymer chain, showed excellent biodegradability. On the other hand, highly dicarboxylated DCAp was resistant to biodegradation.

TOC concentration measurement of the biodegradation medium is one way to learn the ultimate biodegradability of the polymer. Figure 2 also shows the biodegradability [100 × (1-TOC_{28}/TOC_0)], as expressed by the ratio of the TOC value after 28-d biodegradation (TOC_{28}) and the initial TOC value (TOC_0) of the culturing medium. It was confirmed from the TOC measurement that biodegradation of DCAp occurred, and the biodegradability was in agreement with that obtained from the BOD value.

Anaerobic biodegradability of DCAp. Water-soluble polymeric compounds will be widely diffused in anaerobic, as well as in aerobic environments of the earth's soil, river water or seawater after their use. Estimating the biodegradability of these water-soluble polymers under anaerobic conditions in addition to aerobic conditions will be important. Anaerobic biodegradability of the polycarboxylates was demonstrated with anaerobic river sediments. In this anaerobic biodegradation test, D-glucose was used as a control in place of the test polymer for determining the activities of the microbes by analyzing the production of H_2, CO_2, CH_4, H_2S gases and the decrease in TOC in the incubation medium. D-Glucose was assimilated by the anaerobic microbes of river sediments to decrease the TOC value in the incubation medium. GC analysis showed that CO_2 was the main constituent of the evolved gas.

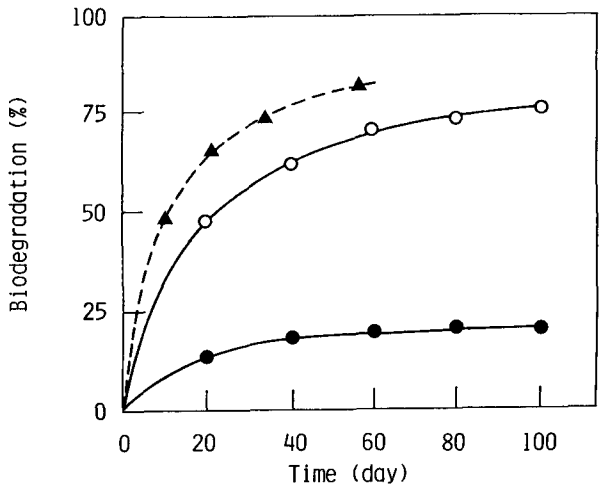


FIG. 3. Anaerobic biodegradability of sodium dicarboxyamylopectin (DCAp) and D-glucose as determined by the total organic carbon (TOC) values in the anaerobic incubation medium with river sediments at 25°C. Biodegradation (%) = 100 × (1 − TOC/TOC_0); ○, DCAp-40000(14); ●, DCAp 34000(51); and ▲, D-glucose.

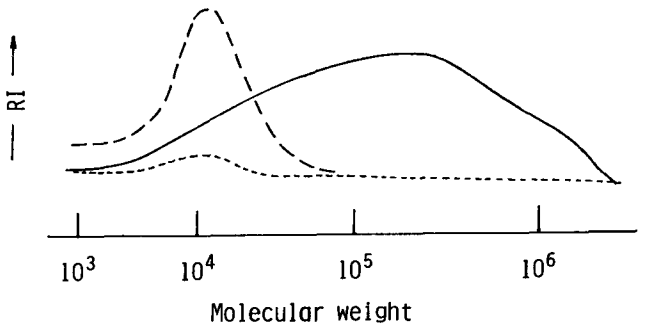


FIG. 4. Gel permeation chromatography profiles of sodium dicarboxyamylopectin [DCAp-40000(14)] before and after anaerobic biodegradation with river sediments (—, 0 d; •••••, 10 d; ·····, 100 d). RI, refractive index.

Evolution of H_2 and H_2S was also detected, but evolution of CH_4 was small. These results suggest that the test microbes consisted mainly of sulfate-reducing bacteria, which commonly occur in river mouth sediments (30). CO_2 gas was also generated when DCAp was used. Figure 3 shows the biodegradability [100 × (1 − TOC/TOC_0)], where TOC is the value after biodegradation and TOC_0 is the initial TOC value of the culturing medium as determined by the TOC analyzer. The biodegradability of the polymers was comparable to that of D-glucose, and more than 60% of the organic carbon of DCAp-40000(14) was removed from the incubation medium by anaerobic degradation with river sediments. However, highly dicarboxylated DCAp was resistant to biodegradation. DCAp containing biodegradable glucopyranose groups, which was biodegradable under aerobic conditions, was also biodegraded under anaerobic conditions. However, the rate of biodegradation of DCAp under anaerobic condition was relatively slower than that under aerobic conditions.

Measuring molecular weight distributions of the polymers by GPC before and after biodegradation is useful to determine the main-chain scission of the polymers as well as the amount of the polymer that has been reduced by the microbes. Residual polymer in the biodegradation media was analyzed by GPC after ultrasonication with a small amount of nonionic surfactant to avoid adsorption of the polymer onto the microbes. Figure 4 shows the GPC profiles of DCAp 40000(14) before and after the anaerobic biodegradation test. The polymers were all biodegraded under anaerobic conditions. The main chain of DCAp was also 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.

Enzymatic degradation of DCAp. DCAp is designed so as to be cleaved at the glucosidic linkage of unreacted glucopyranose moieties by a hydrolytic enzyme (carbohydrase) to reduce the molecular weight to the extent where the environmental microbes can assimilate them. To evaluate the primary biodegradability of DCAp, the enzymatic degradability by carbohydrase was measured and compared with the microbial degradability by the activated sludge. α-Amylase, which cleaves α-1,4-glucosidic bonds, and pullulanase, which cleaves α-1,6-glucosidic bonds, were used as the carbohydrases in this experiment. Degradation of the polymer was directly analyzed by GPC. Figure 5 shows a typical example of GPC profiles of DCAp-40000(14) before and after the enzymatic reaction by α-amylase. The rapid enzymatic degradation was stopped within 1 h, so in this report, degradability was compared after 1-h incubation. The polymer chain of DCAp was cleaved at the unreacted glucopyranose residues by the enzyme to yield lower-molecular weight fractions with narrow molecular-weight dispersions. Similar molecular weight reduction profiles were obtained with both α-amylase and pullulanase.

Figure 6 shows the correlation between the degree of dicarboxylation (X) of DCAp and the molecular weight

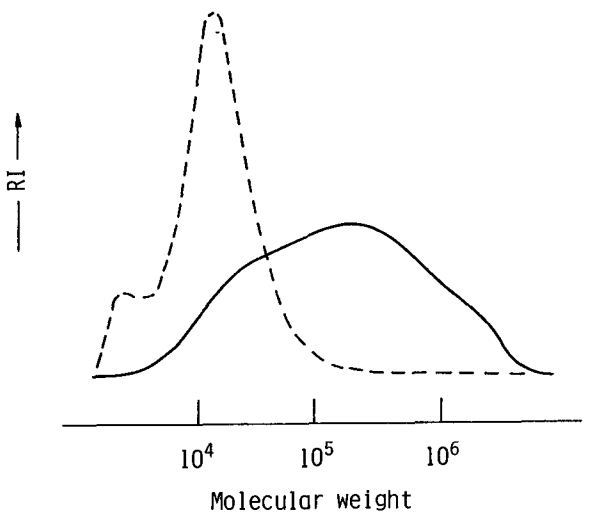


FIG. 5. Gel permeation chromatography profiles of sodium dicarboxyamylopectin [DCAp-40000(14)] before and after enzymatic biodegradation with α-amylase from *Bacillus* sp. after 1-h incubation (—, 0 h; •••••, 1 h). RI, refractive index.

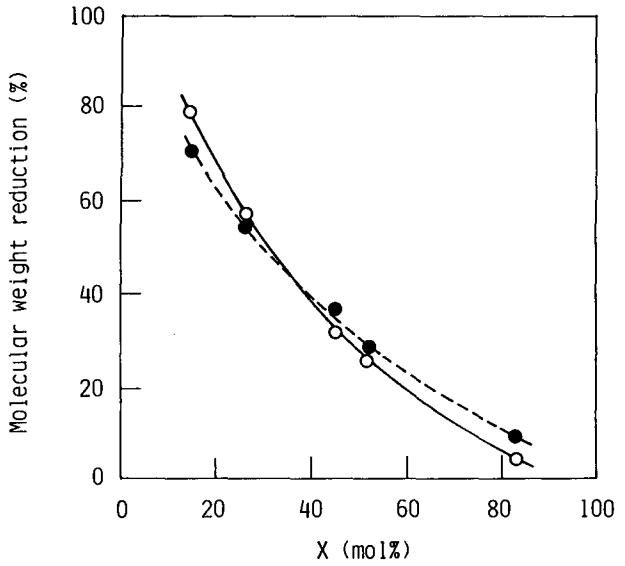


FIG. 6. Molecular weight reduction of sodium dicarboxyamylopectin (DCAp) by α-amylase and pullulanase as a function of the degree of dicarboxylation (X) after 1-h incubation. Molecular weight reduction (%) = 100 × (1 − M_1/M_0); M_1, molecular weight after the enzymatic reaction; M_0, initial molecular weight; ○, DCAp with α-amylase from *Bacillus* sp.; ●, DCAp with pullulanase from *Klebsiella pneumoniae.*

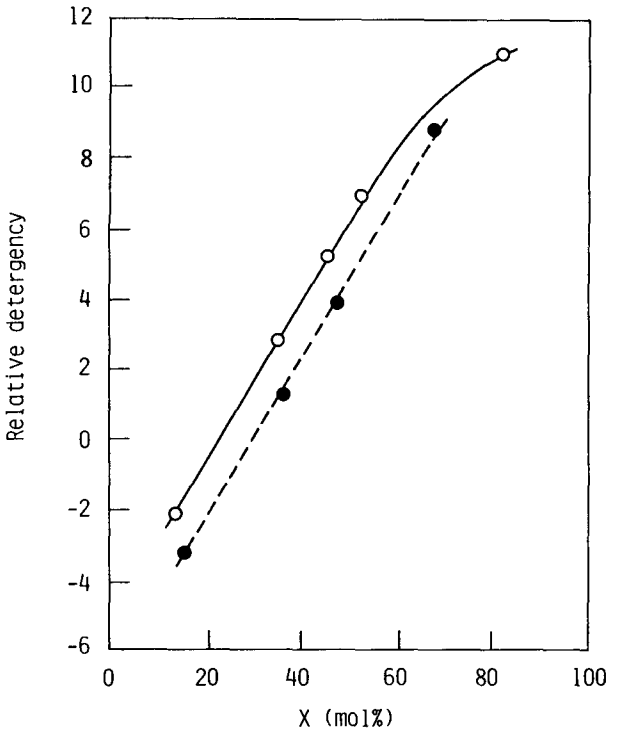


FIG. 7. The relative detergency of sodium dicarboxyamylopectin (DCAp) and sodium dicarboxyamylose (DCAm) (Ref. 5) based on a value of 10 for sodium tripolyphosphate and 0 for disodium 3-oxapentanedioate. (○, DCAp, ●, DCAm).

reduction in percent. Molecular weight reduction, caused by the enzymatically hydrolytic cleavage, is given by:

$$\text{molecular weight reduction (\%)} = 100 \times (1 - M_1/M_0 \quad [3]$$

where M_0 is the initial molecular weight (maximum of the GPC peak) and M_1, is the molecular weight after enzymatic degradation for 1 h (maximum of the GPC peak). Strictly speaking, these values are surely in error because poly(ethylene oxide) standards were used for the calibration curve. However, it was clear that molecular weight reduction by the enzyme was dependent on the content of glucopyranose groups in the polymer chain. The polymers with a higher glucopyranose content tended to be extensively degraded. The biodegradability obtained by the BOD test and the enzymatic degradability as expressed by the molecular weight reduction by the enzymatic reaction are in agreement. These results indicate that DCAp was first biodegraded at the unreacted glucopyranose moieties by the carbohydrase of the environmental microbes to yield low-molecular weight fractions with subsequent assimilation by the microbes.

Builder performance in detergent formulation. Polymeric polycarboxylates have been investigated as STPP substitutes, and a number of polyelectrolytes have been reported to exhibit excellent builder performances in detergent formulations (1–3). The builder performance of DCAp was evaluated on an equal weight basis in a heavy-duty detergent formulation on standard soiled cotton cloths. The detergency, expressed as a value relative to 10 for STPP and 0 for ODA, is shown (Fig. 7) as a function of the degree of dicarboxylation of the DCAp. The detergency was dependent on the content of the carboxylate groups in the polymer, and a clear relation between detergency and the carboxylate groups content was seen when compared on an equal weight basis. The polymers with high carboxylate contents showed better builder performance. DCAp with more than 70% dicarboxylation showed better builder performance than that of STPP. The builder performance of DCAp was also more effective than that of the corresponding sodium dicarboxyamylose (DCAm), which was reported on previously (5). This excellent builder performance is ascribed to the cluster-type structure of amylopectin, in which divalent alkaline earth metals, such as calcium and magnesium ions, are effectively sequestered. On the other hand, DCAm in aqueous solution has a linearly coiled structure in which calcium ion is sequestered. The calcium ion sequestration capacity in the cluster structure of DCAp may be larger than that in the linearly coiled structure of DCAm. Calcium ion sequestration capacity is the most indispensable property for a detergent builder. Figure 8 shows the calcium sequestration capacity of DCAp as a function of the degree of dicarboxylation (X) with the previously reported results for DCAm as comparison. The calcium sequestration capacity of DCAp was better than that of DCAm when compared on an equal weight basis. A correlation between the sequestration capacity for calcium ion and the resulting detergency performance was demonstrated based on these data.

Biodegradability and building performance in detergents containing DCAp varied inversely with the extent of dicarboxylation. DCAp with a high dicarboxylation extent showed better builder performance but showed poor biodegradability. Detergency is dependent on the number of carboxylate groups in the polymer chain when compared on an equal weight basis. Therefore, detergency

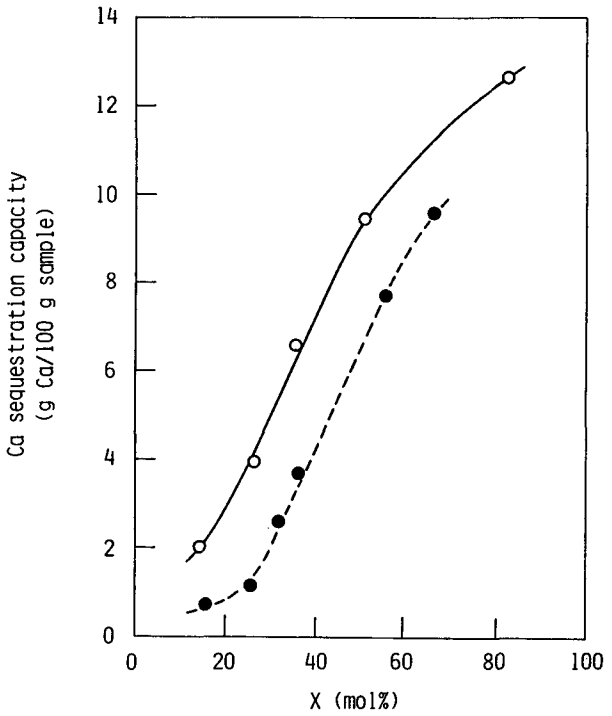


FIG. 8. Calcium (Ca) sequestration capacity of sodium dicarboxyamylopectin (DCAp) and sodium dicarboxyamylose (DCAm) (Ref. 5) as a function of the degree of dicarboxylation (X). Ca^{2+} sequestration capacities of sodium tripolyphosphate and disodium 3-oxapentanedioate were 14.2 and 9.9, respectively. (○, DCAp, ●, DCAm).

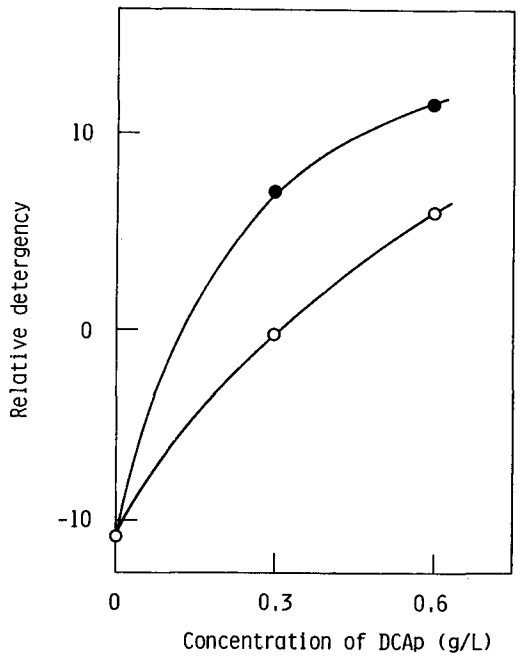


FIG. 9. The relative detergency of sodium dicarboxyamylopectin (DCAp), based a value of 10 for sodium tripolyphosphate and 0 for disodium 3-oxapentanedioate as a function of concentration of DCAp in washing liquor in g/L. Detergency was expressed when the amount of DCAp in the washing liquor was increased. 0.3 g/L of DCAp was used for the standard washing liquor. [○, DCAp-52000(26); ●, DCAp-34000(51)].

performance may be improved when a more polymeric carboxylate is used in the detergent process. Figure 9 shows the correlation between relative detergency and DCAp concentration in the washing liquor. The concentration of the detergent formulation, except for DCAp, remains constant. The concentration of DCAp was 0.3 g/L in the washing solution of standard detergent formulations, but detergency was much improved by increasing the amount of DCAp.

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