Builder Performance in Detergent Formulations and Biodegradability of Poly(Sodium Carboxylate) Containing Vinyl Alcohol Groups

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Two series of poly[(disodium fumarate)*co*-(vinyl alcohol)] and poly[(disodium maleate)-*co*-(vinyl alcohol)], containing vinyl alcohol moieties as biodegradable segments in the polymer chain, were prepared and evaluated for builder performance in detergent formulations as well as for their biodegradability. From the biological oxygen demand test and gel permeation chromatography of the polymer in the biodegradation test media, it was found that biodegradability of the copolymers was dependent on the content of vinyl alcohol moieties in the polymer chain. Significant degradation was observed for fumarate copolymers containing more than 75% vinyl alcohol units and for maleate copolymers containing more than 88≈90% vinyl alcohol units in the copolymer chain. The decisive factor for rapid degradation of the polymer by polyvinyl alcohol (PVA)-degrading microbes seems to be the chainlength of the successive vinyl alcohol groups in the polymer chain. A definite chainlength is needed to become a substrate for the PVA-degrading enzyme. For rapid biodegradation to occur, a copolymer containing more than about five to seven successive vinyl alcohol blocks is needed. Builder performance in the detergent formulation is dependent on the content of carboxylate groups in the polymer. Polymers with high carboxylate content showed better detergency, and the fumarate copolymer was more effective than the maleate copolymer. Detergency performance improved greatly with increasing amounts of polymeric builder used in the detergent formulation.

KEY WORDS: Biodegradation, biological oxygen demand, builder, detergency, fumarate copolymer, maleate copolymer, microbe, polycarboxylate, polyvinyl alcohol.

High-molecular-weight poly(sodium carboxylate)s with carbon-carbon backbones have been reported to show excellent builder performance (1–12). However, it is also known that these polymeric materials are generally highly resistant to biodegradation (3,10). The nonbiodegradability of such compounds restricted their large-scale application in the industrial detergent field. Environmentally acceptable poly(sodium carboxylate)s are particularly needed, and great effort has been made to develop such biodegradable polymers.

The introduction of biodegradable segments into the main chain of the synthetic polymer is one way to design a biodegradable polymer, because such segments are accepted as substrates by the extracellular enzymes of environmental microbes (13–16). A high-molecular-weight polymer chain containing biodegradable segments can be cleaved by the enzyme secreted by environmental microbes to form low-molecular-weight fractions, which are then taken up by the microbes to assimilate them. However, substrate specificity of the enzymatic reaction is generally strict. It seems that the susceptibility of the enzymatic reaction at the biodegradable segment in the polymer chain is influenced by the surrounding polymer chain. A longer biodegradable block acts as a biodegradable segment, whereas a shorter block does not act the same way and is not cleaved by the enzyme during primary biodegradation (16).

Polyvinyl alcohol (PVA) is the only substance that has been confirmed to be biodegradable in the class of polyvinyl-type synthetic polymers (17–21). PVA is first oxidized into β-diketone by PVA-oxidase or PVA-dehydrogenase, followed by hydrolysis by means of β-diketone hydratase to cleave the polymer chain. The minimum PVA chainlength necessary to become a substrate for the PVA-degrading enzyme has not been clearly estimated as yet; however, a definite PVA chainlength will be needed as a biodegradable block in the functional polymer chain as suspected from the estimation of polysaccharide blocks in the polycarboxylate chain (16). As biodegradable segments, vinyl alcohol blocks may be readily incorporated into the functional polymer chain by copolymerization of functional vinyl monomers with vinyl acetate. However, the vinyl alcohol blocks must be incorporated into a functional polymer chain in such a manner that they are accepted as a substrate for the PVA-degrading enzyme present in the environmental microbes. We reported previously on a molecular design to develop a biodegradable poly(sodium carboxylate) and showed that the introduction of biodegradable segments, such as vinyl alcohol, to the polymer chain improved their biodegradability (17,21,22).

In this report, the vinyl alcohol block was selected as a biodegrading segment in the polymer chain, and two series of poly[(disodium fumarate)-*co*-(vinyl alcohol)] [P(FU-VA)] and poly[(disodium maleate)-*co*-(vinyl alcohol)] [P(MA-VA)] were prepared by copolymerization of vinyl acetate with dimethyl fumarate or diethyl maleate. The relationship between the content of vinyl alcohol groups in the polymer chain and its biodegradability, as well as its functionality are discussed.

EXPERIMENTAL PROCEDURES

Materials and measurements. All materials were of the highest available purity and used as purchased. ^{1}H nuclear magnetic resonance (NMR) spectra were determined with a Jeol model JNM-FX90A (90 MHz) spectrometer (Jeol Ltd., Tokyo, Japan). Infrared (IR) spectra were measured in a Jasco Fourier Transform Infrared Spectrometer model FT/IR-5000 (Japan Spectroscopic Co., Ltd., Tokyo, Japan). Molecular weights and molecular weight distributions were measured by a gel permeation chromatographic system (GPC) with commercial GPC columns (TSK-GEL G5000PW + G2500PW, Tosoh Co. Ltd., Tokyo, Japan; 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 glycol) standard ($\bar{M}_n$: 3000≈99600, $\bar{M}_w/\bar{M}_n$: 1.02≈1.10), purchased from Tosoh Co. Ltd.). Viscosity measurements were carried out with an Ostwald viscometer (Sibata Scientific Technology Ltd., Tokyo, Japan) at 25°C.

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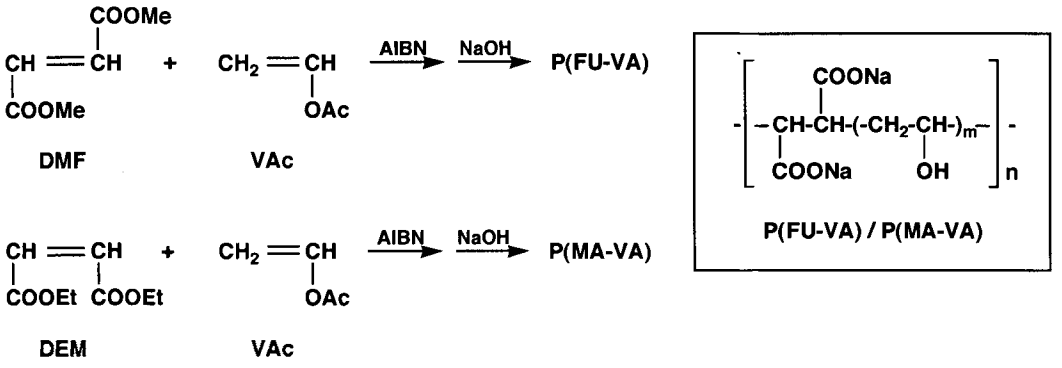

SCHEME 1

Preparation of poly(sodium carboxylate)s containing vinyl alcohol blocks. Two series of P(FU-VA) and P(MA-VA) were prepared by the radical copolymerization of vinyl acetate with dimethyl fumarate or diethyl maleate, with an excess amount of vinyl acetate to incorporate vinyl alcohol blocks into the polymer chain and subsequent saponification as shown in Scheme 1.

Preparation of P(FU-VA) with an $\overline{M}_n$ value of 10500 and disodium fumarate content of 14 mol% [P(FU-VA)-10500(14)] is presented as an example. A mixture of dimethyl fumarate (DMF) (7.2 g, 0.05 mol), vinyl acetate (VAc) (43 g, 0.50 mol) and α, α'-azo-*bis*(isobutyronitrile) (AIBN) (0.54 g, 0.0033 mol) and toluene (100 mL) was stirred slowly at 80°C for 5 h in a glass flask under a nitrogen atmosphere. After the reaction, the crude polymer solution was added slowly to a large amount of hexane (300 mL) while stirring to precipitate the polymer. The precipitated polymer was dissolved in a small amount of acetone (50 mL), and the solution was then added slowly to a large amount of hexane (300 mL) while stirring to precipitate the polymer. This purification procedure was repeated three times to obtain 32.5 g of poly[(DMF)-*co*-(VAc)] in 64.7% yield. ^{1}H NMR (90MHz:$CDCl_3$): δ = 1.3≈1.8 (CH_2 of VAc unit), 3.7 (OCH_3), 2.2≈3.2 (*CH*COOMe), 2.0 (OCO*CH*$_3$), 4.9 (*CH*OAc).

The content of the DMF fraction in the copolymer, determined by ^{1}H NMR, was 14 mol%. Poly[(DMF)-*co*-(VAc)](10 g) was dissolved in methanol (100 mL) and 2N NaOH (100 mL) was added; then the solution was stirred at 65°C for 2 h. After the reaction, the mixture was diluted with distilled water (50 mL), the methanol was evaporated under vacuum and the resultant aqueous solution was dialyzed exhaustively against distilled water for a week, to give P(FU-VA)-10500(14) as a powder (5.4 g). $\overline{M}_n$ = 10500 and $\overline{M}_w/\overline{M}_n$ = 1.7 by GPC. FT-IR: 1572, 1397 (COONa), 3407 (OH), 2943 cm^{-1} (CH_2). ^{1}H NMR (90MHz:D_2O): δ = 1.4 ≈ 2.1 (CH_2), 2.1 ≈ 2.9 [*CH*-(COONa)], 3.8 ≈ 4.2[*CH*(OH)].

The other P(FU-VA) and P(MA-VA) were prepared in a similar way. The polymer code, polymerization conditions and analytical data are summarized in Table 1.

Biodegradation test (15,16,21). Biochemical oxygen demand (BOD) was determined with a BOD Tester (Model 200F, Taitec Corp., Koshigaya-shi, Japan) by the oxygen consumption method, basically according to the Organization for Economic Cooperation and Development (OECD) Guidelines for Testing of Chemicals (301C, Modified MITI Test) (23). The activated sludge was obtained from a municipal sewage plant, with and without additional PVA-degrading microbes (*PVA-IMX*), which were stored in our

TABLE 1

Polymerization Conditions and Analytical Data of Poly[(Disodium Fumarate)-*co*-(Vinyl alcohol)] [P(FU-VA)] and Poly[(Disodium Maleate)-*co*-(Vinyl Alcohol)] [P(MA-VA)][a]

	Polymerization condition			Polymer (sodium salt)				
Code	M_1	M_2	Molar ratio $[M_1]/[M_2]$	Yield (%)	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Content of M_1 (mol%)	$\overline{I}_n$
P(FU-VA)-								
9000(53)	DMF	VAc	1:1	33	9000	1.5	53	1.1
9500(39)	DMF	VAc	1:5	46	9500	1.5	39	1.7
9600(25)	DMF	VAc	1:6	61	9600	1.7	25	3.1
10500(14)	DMF	VAc	1:10	64	10500	1.7	14	5.9
13000(9)	DMF	VAc	1:15	65	13000	2.5	9	9.1
P(MA-VA)-								
15000(49)	DEM	VAc	1:1	20	15000	1.8	49	1.0
18000(20)	DEM	VAc	1:10	40	18000	2.0	20	4.1
16000(12)	DEM	VAc	1:15	52	16000	2.0	12	7.7
18000(11)	DEM	VAc	1:20	44	18000	2.3	11	9.0
8000(5)	DEM	VAc	1:30	70	8000	3.0	5	21.0

[a]The polymer code indicates its number-average molecular weight ($\overline{M}_n$) and its relative dicarboxylate content in mol% in parenthesis. DMF: dimethyl fumarate, DEM: diethyl maleate, VAc: vinyl acetate, $\overline{I}_n$: number-average chainlength of vinyl alcohol block.

laboratory. Residual polymers present in the culture broth before and after the biodegradation test (BOD test) were directly analyzed by GPC after an ultrasonic treatment with a small amount of a nonionic surfactant.

Detergency test (24). 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 (CMC) and 46.5% sodium sulfate, to determine the detergency of the STPP/ODA formulation as a basis for comparison with the test builders. In the experimental formulas, the STPP was replaced with an equal weight percent of the test builders. The washing efficiency of the builders was determined in the Terg-O-Tometer (United States Testing Co., Inc., Hoboken, NJ) using improved artificially soiled cotton cloth test pieces prepared from an aqueous dispersion method (24). The washing experiments were performed with water of 54 ppm $CaCO_3$ with a cloth-to-liquor ratio of 1:50 at a temperature of 25°C and a detergent concentration of 1.2 g/L, unless otherwise stated. Light reflectance of the test swatches was measured by means of an automatic reflectometer equipped with a green filter. The K/S ratio (K, coefficient of reflectivity; S, coefficient of light scattering) was calculated the Kubelka-Munk equations (25), and the detergency was expressed according to Equation 1:

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

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 Equation 2.

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

In Equation 2 R is reflectance. The relative detergency was expressed as a value of 10 for STPP and 0 for ODA.

Calcium sequestration capacity (12). 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 the builders was dissolved in 50 mL of 1.00×10^{-3} M calcium hardness solution with a 0.08M 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 and 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 builder.

Dispersion capacity (12). The dispersion capacity for manganese dioxide was measured according to the titration method (26) and expressed as milligrams of dispersed manganese dioxide in 100 mL of 0.05% aqueous builder solution after 4 h of sedimentation at 25°C.

RESULTS AND DISCUSSION

Preparation of fumarate and maleate copolymers. Two series of P(FU-VA) and P(MA-VA) were prepared by radical copolymerization of DMF or diethyl maleate with an excess amount of VAc and subsequent saponification. From the reactivity ratios of the two monomers (27), the resultant polymer will contain longer or shorter vinyl alcohol chains, which will be separated by a unit of fumarate or maleate at random positions.

Table 1 shows the typical preparation conditions and analytical data for P(FU-VA) and P(MA-VA). For the preparation of P(FU-VA), varying the molar ratio of DMF to VAc from 1 to 15 caused the vinyl alcohol content in the resultant polymer to vary from 47 to 91%. $\overline{I}_n$ gives the number-average chainlength of the vinyl alcohol block in the P(FU-VA) polymer chain as calculated from the reactivity ratios of DMF and VAc and the conversion according to the Mayo and Lewis equations (27,28). The number-average vinyl alcohol chainlength, $\overline{I}_n$, in P(FU-VA) was estimated to be between 1.1 and 9.1. For the preparation of P(MA-VA), varying the molar ratio of diethyl maleate (DEM) to VAc from 1 to 30 caused the vinyl alcohol content in the polymer chain to vary from 51 to 95%. The number-average vinyl alcohol chainlength, $\overline{I}_n$, in P(MA-VA) was estimated to be between 1.0 and 21.

Microbes for the biodegradation tests. Symbiotic PVA-degrading microbes (*PVA-IMX*), comprised mainly of *Arthrobacter* sp., were used for evaluation of the biodegradability of the copolymers containing vinyl alcohol blocks as biodegradable segments. The microbes were obtained from the Fuji river near Fuji City, Japan, and were used with and without fresh activated sludge from a municipal sewage plant in Yokohyama City, Japan, to achieve better reproducibility. The activities of these microbes were measured against the biodegradation of PVA by means of GPC analyses of the polymers before and after the biodegradation test as well as the measurement of the BOD. PVA with a number-average molecular weight of 14000 was confirmed to be completely biodegraded by these symbiotic *PVA-IMX* within two weeks. Details of the PVA-degrading microbes will be analyzed elsewhere.

Biodegradability of the copolymers. It is feasible to predict the ultimate biodegradability of the polymers by measuring the BOD and using it as a preliminary biodegradation predictor. To evaluate the biodegradability of the poly(sodium carboxylate)s containing PVA blocks, the BOD was measured with the previously described PVA-degrading microbes and activated sludge. Figure 1 shows the BOD values of P(FU-VA), P(MA-VA) and PVA ($\overline{M}_n$ = 14000) at a test polymer concentration of 25 ppm. The biodegradability was dependent on the content of vinyl alcohol in the polymer chain. A significant decrease in biodegradability was observed for the P(FU-VA) with less than 75% vinyl alcohol content in the polymer chain. Biodegradability of P(FU-VA) was better than that of P(MA-VA) when normalized for vinyl alcohol content. This probably means that for the maleate copolymer a longer vinyl alcohol block was necessary to become a substrate for the PVA-degrading enzyme when compared to that of the fumarate copolymer.

The molecular-weight distribution of the polymers was measured by GPC before and after biodegradation to determine if the main chain of the polymer has been cleaved by the microbes. Figure 2 shows the GPC profiles of PVA, P(FU-VA) and P(MA-VA) before and after the biodegradation test. Results of the biodegradation test by both evaluation methods are well correlated. For PVA, the GPC peak had completely disappeared after 24 d incubation

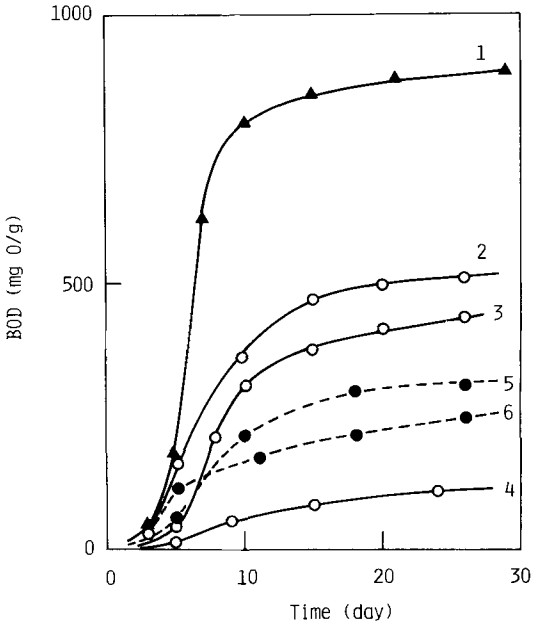

FIG. 1. Biological oxygen demand (BOD) of polyvinyl alcohol (PVA), poly[(disodium fumarate)-*co*-(vinyl alcohol)] [P(FU-VA)] and poly-[(disodium maleate)-*co*-(vinyl alcohol)] [P(MA-VA)] with PVA-degrading strains (*PVA-IMX*) and an activated sludge obtained from a municipal sewage plant. The concentration of the polymer was 25 ppm. 1: PVA ($\bar{M}_n$ = 14000), 2:P(FU-VA)-13000(9), 3: P(FU-VA)-10500(14), 4: P(FU-VA)-9600(25), 5:P(MA-VA)-8000(5), 6: P(MA-VA)-16000(12).

About 70% of the polymer peak area in GPC had disappeared after the biodegradation for P(FU-VA). On the other hand, for P(MA-VA), reduction of the GPC peak area was small.

BOD values for maleate copolymer were low under ordinary conditions. However, the BOD values may be increased for potential biodegradable polymers when more PVA-degrading microbes (*PVA-IMX*) are used. By this method it will then be easier to compare the biodegradability. That is, BOD values of P(MA-VA)s containing 88 to 89% PVA increased rapidly, whereas the P(MA-VA) containing 80% PVA remained at zero when more PVA-degrading microbes (*PVA-IMX*) were adapted to the biodegradation test (ten times the microbial concentration of *PVA-IMX* compared to that in Fig. 2) as shown in Figure 3. It seems that the critical value for rapid biodegradation approaches a 90% PVA content in the maleate copolymer.

These results suggest that the decisive factor for rapid biodegradation is the chainlength of the successive vinyl alcohol groups in the copolymer chain where vinyl alcohol is used as a biodegradable group. Figure 4 shows the relation between biodegradability (BOD/TOD) calculated by the BOD value and the theoretical oxygen demand (TOD) after 21 d incubation and number-average vinyl alcohol chainlength, $\bar{l}_n$, for P(FU-VA) and P(MA-VA). Fumarate copolymers with more than about five successive vinyl alcohol blocks were rapidly biodegraded by the PVA-degrading microbes. On the other hand, a block with more than seven successive vinyl alcohols was needed for the biodegradation of maleate copolymer by the PVA-degrading microbes. It appears that this difference can be attributed to the difference in the conformation in aqueous solution between fumarate and maleate copolymers. Therefore, vinyl alcohol blocks in the fumarate copolymer chain will be more easily accepted as a substrate by the PVA-degrading enzyme.

Builder performance. Polymeric poly(sodium carboxylate)s containing carbon-carbon backbones and a related high charge density of carboxylate groups along the chain have been investigated as STPP substitutes, and a number of polyelectrolytes have been reported to give excellent builder effects.

Builder performances of the poly(sodium carboxylate)s containing vinyl alcohol moieties, as well as poly(disodium fumarate) ($\bar{M}_n$ = 8080) prepared according to the literature (7), were evaluated on an equal weight basis in a heavy-duty detergent formulation. The detergency is shown as a function of vinyl alcohol content in Figure 5. Detergency was dependent on the content of carboxylate groups in the polymer. In addition, a clear relationship between relative detergency and content of carboxylate groups was observed when compared on an equal weight basis. The polymers with high carboxylate content showed better detergency, and the fumarate copolymer was more effective than the maleate copolymer. This difference in detergency can be attributed to their Ca^{2+} sequestration capacity, which is the most indispensable for the detergent builder and is not easily replaced by other substances.

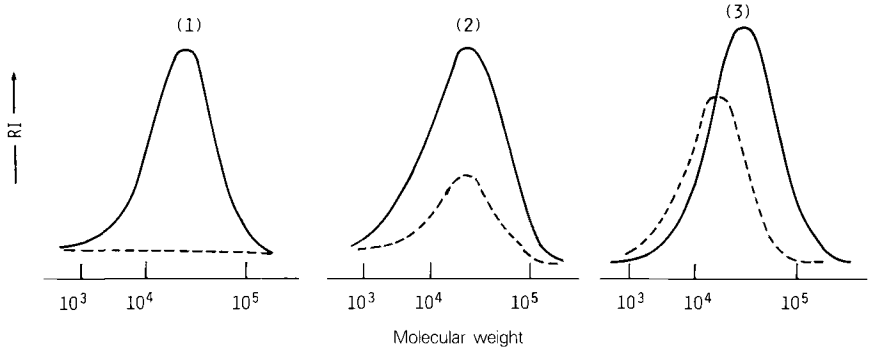

FIG. 2. Gel permeation chromatography profiles before and after the biodegradation test by biological oxygen demand tester. (Sample conditions as in Fig. 1). RI: refractive index. 1: polyvinyl alcohol ($\bar{M}_n$ = 14000), 2: poly[(disodium fumarate-*co*-(vinyl alcohol)]-10500(14), 3: poly[(disodium maleate)-*co*-(vinyl alcohol)]-18000(11), ——: 0 d, ------: 24 d.

Figure 6 shows the calcium sequestration capacities. The complexes of the polymer and calcium were water-soluble. Calcium sequestration capacities of fumarate copolymers were better than those of maleate copolymers when compared on an equal weight basis. A correlation between sequestration capacity for calcium ion and resulting detergency performance was demonstrated from these data.

The difference in builder effects between fumarate and maleate copolymers can also be attributed to the conformation of their copolymers in aqueous solutions. Figure 7 shows the reduced viscosity in aqueous and saline solutions. There was a great difference in their viscosities in aqueous solutions. The reduced visocisty of the maleate copolymer was much higher than that of the fumarate

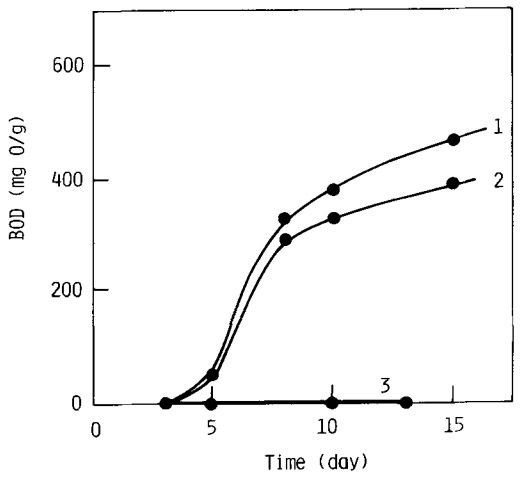

FIG. 3. Biological oxygen demand (BOD) of poly[(disodium maleate)-*co*-(vinyl alcohol)] [P(MA-VA)] with PVA-degrading strains (*PVA–IMX*) and an activated-sludge. Conditions were the same as those of Figure 2 except that ten times the microbial concentration was used. 1: P(MA-VA)-18000(11), 2: P(MA-VA)-16000(12), 3: P(MA-VA)-18000(20).

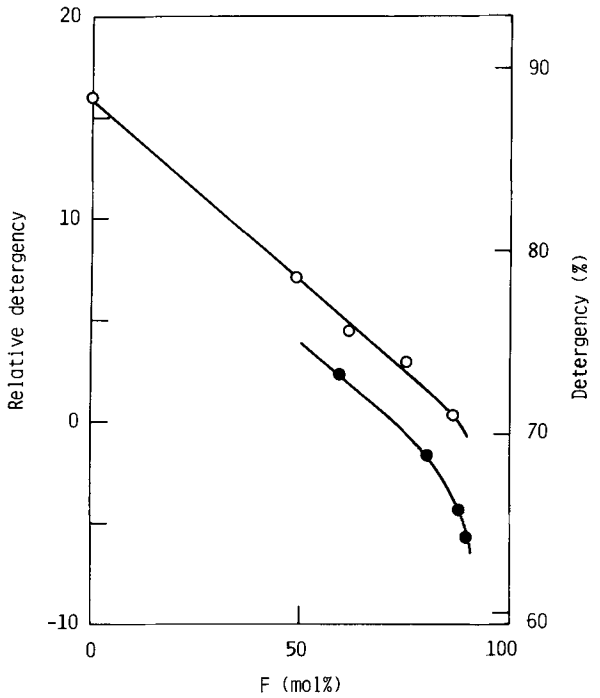

FIG. 5. Relative detergency expressed as a value relative to 10 for sodium tripolyphosphate and 0 for disodium 3-oxapentanedioate, and detergency (washing efficiency) *vs.* vinyl alcohol content (F). ○: poly[(disodium fumarate)-*co*-(vinyl alcohol)], ●: poly[(disodium maleate)-*co*-(vinyl alcohol)].

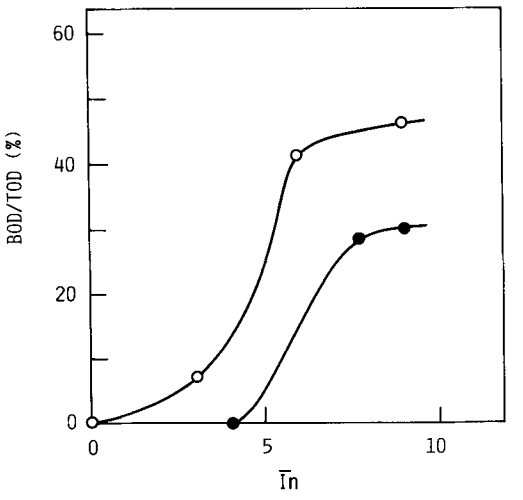

FIG. 4. Biodegradability [biological oxygen demand/(BOD/TOD) in %)] of the polymers by polyvinyl alcohol (PVA)-degrading strains (*PVA–IMX*) and an activated sludge after 21 d incubation, basically according to OECD Guidelines for Testing of Chemicals (301C, Modified MITI Test), as a function of number-average vinyl alcohol chainlength, $\bar{I}_n$, for poly[(disodium fumarate)-*co*-(vinyl alcohol)] [P(FU-VA)] and poly[(disodium maleate)-*co*-(vinyl alcohol)] [P(MA-VA)]. ○: P(FU-VA), ●: P(MA-VA).

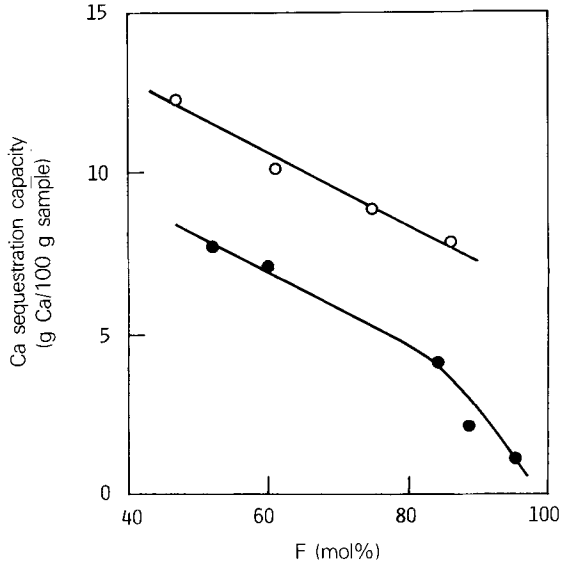

FIG. 6. Calcium sequestration capacity of poly[(disodium fumarate)-*co*-(vinyl alcohol)] [P(FU-VA)] and poly[(disodium maleate)-*co*-(vinyl alcohol)] [P(MA-VA)] *vs.* vinyl alcohol content (F). Ca^{2+} sequestration capacities of sodium tripolyphosphate and ODA were 14.2 and 9.9, respectively. ○: P(FU-VA), ●: P(MA-VA).

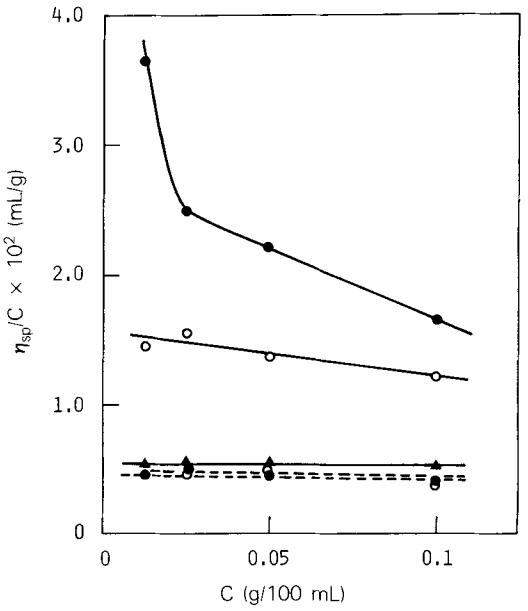

FIG. 7. Reduced viscosity of poly[(disodium fumarate)-*co*-(vinyl alcohol)] [P(FU-VA)] and poly[(disodium maleate-*co*-(vinyl alcohol)] [P(MA-VA)] at 25°C. ○: P(FU-VA)-13000(57), ●: P(MA-VA)-15000(49), ▲: Polyvinyl alcohol ($\bar{M}_n$ = 14000), ——: NaCl, 0 mol/L, – – –: NaCl, 0.05 mol/L.

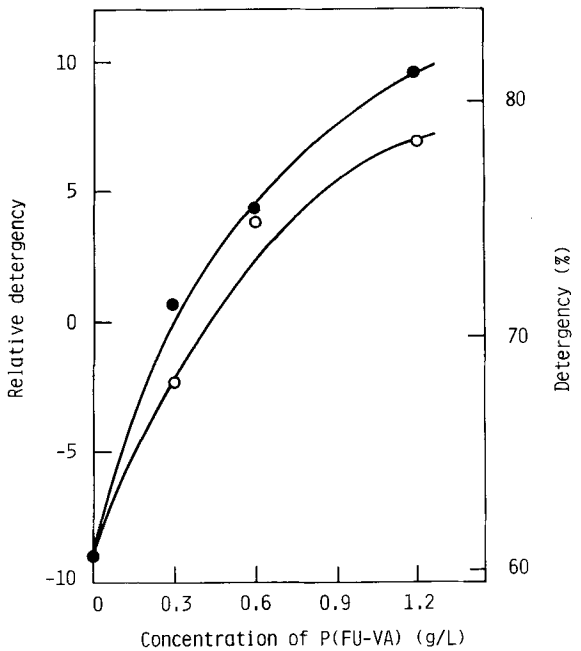

FIG. 8. Relative detergency expressed as a value relative to 10 for sodium tripolyphosphate and 0 for disodium 3-oxapentanedioate, and detergency (washing efficiency) *vs.* concentration of the polymer in washing liquor in g/L. Detergency was expressed when the amount of the polymer in the washing liquor was increased. 0.3 g/L of the polymer was used for the standard washing liquor. ○: Poly[(disodium fumarate)-*co*-(vinyl alcohol)] [P(FU-VA)-13000(9)], ●:P(FU-VA)-10500(14).

copolymer, indicating that the maleate copolymer had a more extended conformation in a diluted solution. Details are now under investigation.

Dispersion capacity for soil particles is one of the most significant properties in a detergent. As shown in Table 2, fumarate copolymers showed excellent dispersion capacities for manganese dioxide, which was selected as a model of a polar substance in the soil.

Biodegradability and building performance in detergents containing these polymers varied inversely with the biodegradable segment content. The polymers with high PVA content showed better biodegradability, but showed poorer builder effect. This declining tendency for detergency can be attributed to the declining number of functional carboxylate groups in the polymer chain when compared on an equal weight basis. Detergency performance may be improved when a more polymeric carboxylate is used in the detergent formulation. Figure 8 shows the correlation between relative detergency and concentration of P(FU-VA). The concentration of the detergent formulation, except for the polymeric builder, remains constant. The detergency was much improved by increasing the amount of polymeric builder used when compared on the standard detergent formulation of 0.3 g/L builder concentration. For example, the detergency of P(FU-VA)-10500(14) was almost the same as that of ODA and trisodium citrate in the standard formulation. When the amount of the polymer was increased four times, that is to 1.2 g/L, the detergency was significantly improved, yielding values comparable to STPP.

TABLE 2

Dispersion Capacity for Manganese Dioxide of the Polymers, Polyvinyl Alcohol (PVA), Disodium 3-Oxapentaedioate (ODA) and Sodium Tripolyphosphate (STPP)

	Dispersion capacity (mg of MnO_2/100 mL of 0.05% builder solution)
P(FU-VA)-[a]	
9000(53)	77
10200(49)	64
9500(39)	63
9600(25)	67
10500(14)	70
P(MA-VA)-[a]	
15000(49)	43
18000(20)	39
16000(12)	39
18000(11)	28
PVA ($\bar{M}_n$ = 14000)	11
ODA	0
STPP	112

[a]See Table 1 for abbreviations.

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