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Synthesis of Biodegradable Detergent Builder by Alternating Copolymerization of 2-Methylene-1,3,6-trioxocane and Maleic Anhydride

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2-Methylene-1,3,6-trioxocane (MTC) and maleic anhydride (MA) were copolymerized in the presence of a radical initiator. Elemental analysis suggested that the obtained copolymer consisted of alternating monomer units. After hydrolysis of the MA carboxylate anhydride functionality, the copolymer exhibited good calcium ion sequestration capacity and good buffer capacity. The biodegradability of the copolymer after hydrolysis was found to be good with a biochemical oxygen demand (BOD)-tester using soil.

Keywords: radical ring-opening polymerization; cyclic ketene acetal; detergent builder; biodegradation

1 Introduction

A number of polyacrylates such as poly(sodium acrylate), sodium salt of maleic anhydride-isobutylene copolymer and maleic anhydride-vinyl acetate copolymer have been reported to give excellent builder performances in detergent formulations as compared with sodium tripolyphosphate (STPP). Since these polymeric compounds are not biodegradable, they do not provide an environmentally acceptable compound to replace STPP. To date, there are a few polycarboxylates that are biodegradable detergent builders such as poly(aspartic acid) (1, 2) and based on carbohydrates (3–9). However, only a few biodegradable polycarboxylates that introduced an ester group as the biodegradable moiety into the backbone, for example, poly(sodium malate) have been reported (10).

We found that MTC polymerizes via ring-opening in the presence of a radical initiator to produce poly(ester-ether) and that the obtained polymer is biodegradable (11). Further, we reported that MTC can copolymerize with various vinyl monomers to make them biodegradable by introduction of an ester group into the backbone (12–17).

We report here on the radical copolymerization of MTC as a biodegradable segment and MA as a builder segment, and also on the detergent builder performance and the biodegradability of the obtained copolymer.

2 Experimental

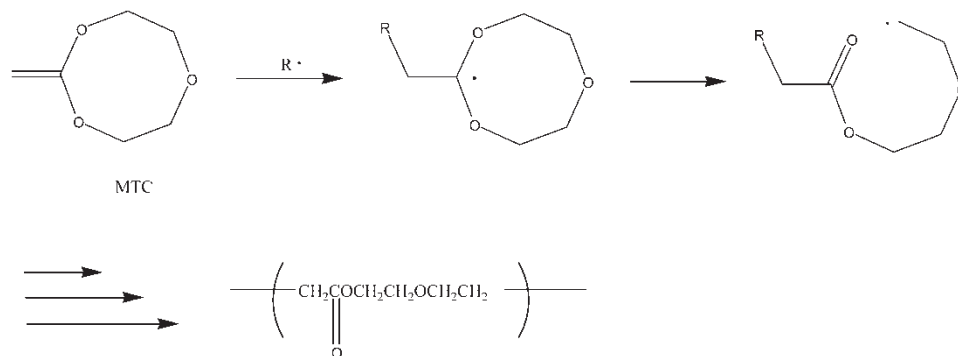
2.1 Materials

MTC was synthesized according to our previous report (11). MA was purchased from Tokyo Kasei Kogyo Co. Ltd. (Japan) and used after sublimation. 2,2'-Azobis(isobutyronitrile) (AIBN) and di-*tert*-butyl peroxide (DTBP) were purchased from Tokyo Kasei Co. Ltd. and used as is. Sodium carbonate was purchased from Wako Pure Chemical Industries Ltd. (Japan). Chlorobenzene (PhCl) was purchased from Wako Pure Chemical Industries Ltd. and used after distillation over calcium hydride. Poly(D-3-hydroxybutyrate) (PHB) with number-average molecular weight (M_n) of 2.1×10^5 was obtained from Mitsubishi Gas Chemical Co. Inc. (Japan).

2.2 Preparation

The copolymerization of MTC and MA was carried out as follows: in a 20 mL sealed polymerization tube, a mixture containing MTC (1.30 g, 1.00×10^{-2} mol), MA (0.98 g, 1.00×10^{-2} mol), AIBN (0.0066 g, 4.00×10^{-4} mol), and PhCl (11.256 g, 1.00×10^{-1} mol) was maintained at 60°C

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Sch. 1. Radical ring-opening polymerization of MTC.

for 24 h. The resulting product was precipitated in diethyl ether. The precipitated material was dried under reduced pressure to give 1.788 g (79%) of a copolymer. When polymerization was carried out at a temperature of 80, 100 or 120°C, DTBP was used as the radical initiator. The acid anhydride moiety of the obtained copolymer was hydrolyzed using 0.01 N sodium carbonate. Hydrolysis of the copolymers' anhydride functionality was carried out as follows: the obtained copolymer (1.00 g) in 50 mL pure water was precipitated using 0.01 N sodium carbonate at a pH not exceeding 8. After the pH was adjusted to 7, the solution was stirred for 16 h. When the pH had decreased to 3.3, 0.01 N sodium carbonate was precipitated again and the pH was adjusted to 7 again. Then, the hydrolyzed copolymer was dialyzed for 48 h against pure water using a dialysis membrane (MWCO:3500, Spectra/Pro Membrane (USA)) and dried under reduced pressure.

2.3 Characterization

The IR spectra of the obtained copolymers before and after hydrolysis were measured using an infrared spectrometer

Table 1. Elemental analysis of MTC-MA copolymers

Anal. Calcd. for C ₁₀ H ₁₂	Found polymerization temperature (°C)				
	60	80	100	120	
Carbon (%)	52.63	51.99	52.64	52.48	52.63
Hydrogen (%)	5.30	5.33	5.56	5.41	5.43

(Shimadzu FTIR-4200). The molecular weight of the copolymer obtained at polymerization temperature of 60°C was determined by GPC with refractive index detector on a TOSOH HPLC chromatograph equipped with an analysis column. TSKgel α -M + α -4000 was used with a mobile phase of DMF at a flow rate of 0.6 mL/min and polymer concentration of 0.3%. Polystyrene was used as the molecular weight standard. Other copolymers obtained at polymerization temperatures of 80, 100, and 120°C were insoluble in DMF.

Calcium ion sequestration capacity was evaluated according to the previous report (18) as follows: calcium chloride dehydrate converted to 0.1% calcium carbonate aqueous solution was calculated using Equation (1):

$$500 \times 0.1/100 \times 1/100.09 \times 147.02 = 734.43 \text{ mg} \quad (1)$$

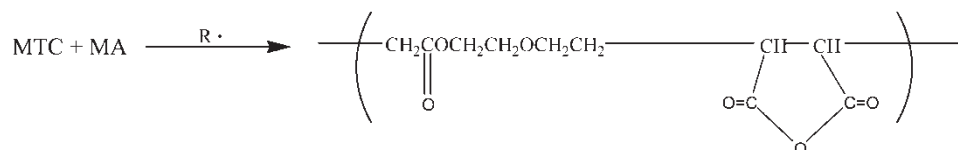
and added to 500 mL pure water, (A). 25 mL aqueous solution, (B) composed of 0.1% MTC-hydrolyzed MA copolymer and 0.1% dodecylsulfuric acid sodium salt was prepared. B was kept in a constant temperature (30°C) room for 3 h and then titrated with A at the rate of 1 drop per 10 seconds using a buret. When B became turbid, the volume of A was measured. Calcium ion sequestration capacity is represented by Equation (2):

$$\text{mg of CaCO}_3/\text{g of MTC-hydrolyzed MA copolymer} \quad (2)$$

In case where the titration volume of A is 2.93, the calcium ion sequestration capacity is indicated by Equation (3):

$$2.93 \times 0.1/100 \times 1000/0.025 = 117 \quad (3)$$

Buffer capacity of MTC-hydrolyzed MA copolymer was measured as follows (18): 50 mL aqueous solution of 0.5% MTC-hydrolyzed MA copolymer was titrated with 0.1255



Sch. 2. Radical alternating copolymerization of MTC and MA.

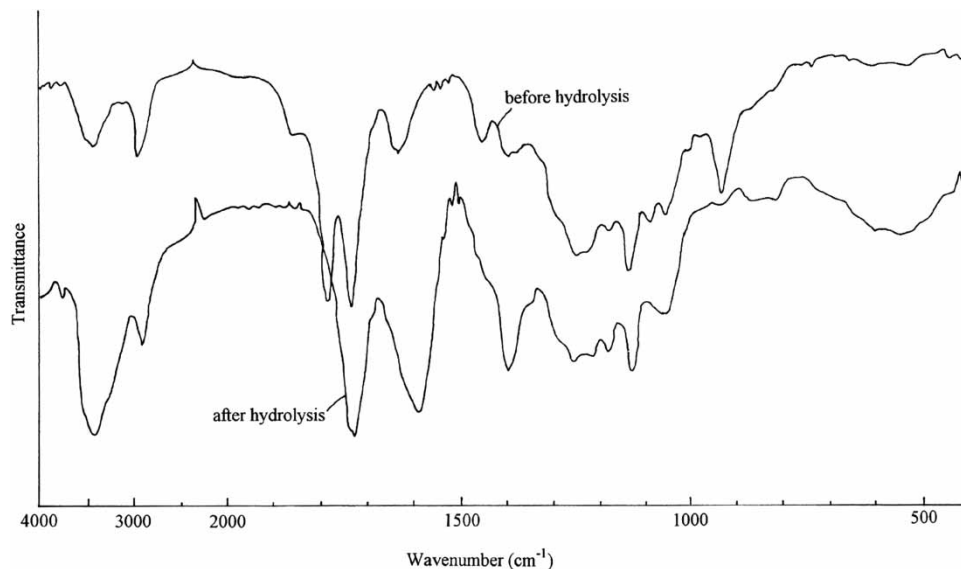


Fig. 1. IR spectra of MTC-MA copolymer before and after hydrolysis.

N HCl using a buret and decrease of pH was measured with a pH meter. dV/dpH was calculated from the pH titration curve (V : volume (mL) of titrated HCl). BOD was determined with a BOD tester (OM8001A; Ohkura Denki Co., Tokyo, Japan) by the oxygen consumption method and basically according to JIS K 6950 at 25°C, using a soil freshly obtained from a forest in Tsukuba City. The incubation medium contained the following (mg/L): K_2HPO_4 , 217.5; KH_2PO_4 , 85.0; Na_2HPO_4 , 260.5; NH_4Cl , 25.0; $CaCl_2 \cdot 2H_2O$, 36.4; $MgSO_4 \cdot 7H_2O$, 22.5; $FeCl_3 \cdot 6H_2O$, 0.25 (pH = 7.4). The concentration of MTC-hydrolyzed MA copolymer in the incubation medium was 100 mg/L.

3 Results and Discussion

Ring-opening polymerization of MTC was carried out in the presence of radical initiator to give poly(ester-ether) (Scheme 1).

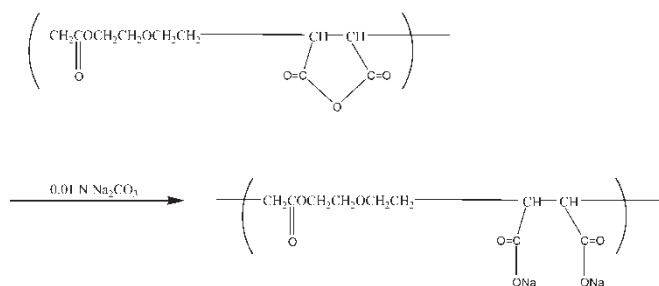
In the case of copolymerization of cyclic ketene acetal as an electron-donating monomer with an electron-accepting

monomer, such as MA, alternating copolymer was obtained (19). The results of elemental analysis of the obtained copolymer are shown in Table 1.

These results strongly suggest that any obtained copolymer is an alternating copolymer as shown in Scheme 2.

The IR spectra of MTC-MA copolymer obtained at polymerization temperature of 80°C before and after hydrolysis are shown in Figure 1.

Before hydrolysis, absorption of the anhydride appeared at 1860 and 1780 cm^{-1} . Absorption of the ester group appeared when MTC underwent ring-opening. After hydrolysis, the absorption of the anhydride group disappeared and absorptions of carboxylic hydroxyl group appeared at 1400, 1590, and 3450 cm^{-1} . The absorption of ester group in the copolymer remained at 1730 cm^{-1} after hydrolysis. These spectral data indicate that MTC ring-opening polymerized to produce an ester group in the presence of radical initiator, MA was hydrolyzed by dilute alkaline, and the ester group remained after the hydrolysis in the mild condition as shown in Scheme 3.



Sch. 3. Hydrolysis of MA moiety.

Table 2. Copolymerization of MTC and MA^a

Temp. (°C)	Initiator (mol%)	Yield ^b (%)	Mn ^c	Mw/Mn
60	AIBN (2)	79	3600	1.5
80	DTBP (2)	50	—	—
100	DTBP (2)	60	—	—
120	DTBP (1)	77	—	—

^aTime: 24 h.

^bInsoluble part in ether.

^cEstimated by GPC.

Table 3. Calcium ion sequestration capacity

MTC-hydrolyzed MA copolymer (Polymerization temperature)	pH	Titration volume (mL)	Sequestration capacity mg of CaCO ₃ /g of MTC-hydrolyzed MA copolymer
60 (°C)	6.5	2.93	117
	7.1	3.46	138
	8.6	4.59	184
80 (°C)	6.8	2.68	107
	8.4	4.31	172

The copolymerization of MTC and MA is summarized in Table 2.

The yields of the obtained copolymers were good.

The results of calcium ion sequestration capacity are summarized in Table 3.

The calcium ion sequestration capacity was over 180 in alkaline condition. This is equal to methyl vinyl ether-hydrolyzed MA copolymer, though it is inferior to that of STPP (about 300) (18).

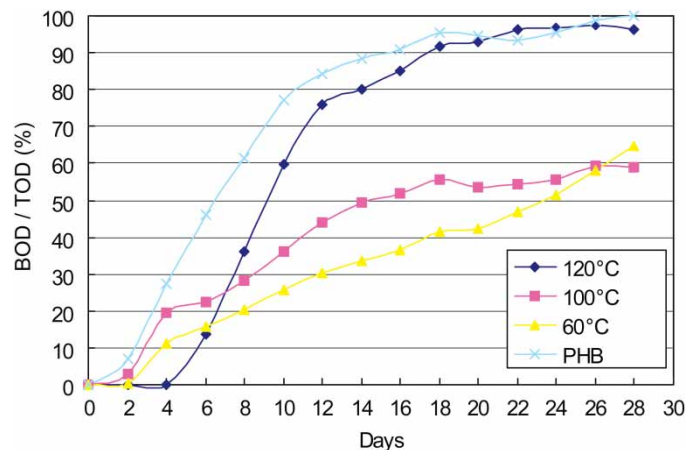
The results of buffer capacity are summarized in Table 4.

The buffer capacity was around 1.0. This capacity is superior to that of methyl vinyl ether-hydrolyzed MA copolymer (0.5) and equal to that of STPP (1.2) (18). Figure 2 shows the biodegradation of MTC-hydrolyzed MA copolymers.

The degradability was 96% in the copolymer synthesized at polymerization temperature of 120°C, 59% in the copolymer synthesized at polymerization temperature of 100°C, and 65% in copolymer synthesized at polymerization temperature of 60°C at 28 days using a soil. It has been reported that a polymer has biodegradability if BOD/TOD is above 60% using soil (20). So it can be concluded that MTC-hydrolyzed MA copolymers are biodegradable. The number-average molecular weight of MTC-MA copolymer synthesized at polymerization temperature of 60°C was 3600. This value was estimated using polystyrene as the molecular-weight standard and is not exact. MTC-hydrolyzed MA copolymer was dialyzed using a dialysis membrane having a fractionated molecular weight of 3500. So, the molecular weight of the obtained copolymers is thought to be about from 1000 to 10000. As the obtained copolymer might be an oligomer, it might have improved biodegradability and also have suitable builder capacity. As the obtained MTC-hydrolyzed

Table 4. Buffer capacity

MTC-hydrolyzed MA copolymer (Polymerization temperature)	dV/dpH
60 (°C)	1.0
80 (°C)	1.3
100 (°C)	0.8
120 (°C)	0.9

**Fig. 2.** Biodegradation of MTC-hydrolyzed MA copolymer.

MA copolymers are alternating copolymers, the hydrolyzed MA moiety can be incorporated into the cell of a microorganism after hydrolysis of the ester moiety by an enzyme and then degraded by microorganism completely. So, the alternating structure might improve biodegradability.

4 Conclusions

MTC and MA were copolymerized in the presence of radical initiator to obtain the alternating copolymer. After hydrolyzing the carboxylate anhydride in MA, the copolymers showed good calcium ion sequestration capacity and buffer capacity. MTC-hydrolyzed MA copolymers were biodegradable in biodegradation experiments conducted with a BOD tester using the oxygen consumption method.

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