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Synthesis of Biodegradable Hydrogel by Radical Ring-Opening Polymerization of 2-Methylene-1,3,6-Trioxocane

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2-Methylene-1,3,6-trioxocane (MTC), maleic anhydride (MA), and poly(ethylene glycol diacrylate) 400 (PEGD) or divinyl adipate (DVA) were terpolymerized in the presence of a radical initiator. Though the obtained gels did not absorb deionized water, the gels could absorb deionized water and saline after hydrolyzing the MA carboxylate anhydride functionality. The absorbing ratios of deionized water and saline were high. The biodegradability of the hydrogels after hydrolysis was found to be good by a biochemical oxygen demand (BOD)-tester using soil.

Keywords radical ring-opening polymerization, cyclic ketene acetal, biodegradation, hydrogel

Introduction

Synthetic materials which can absorb water are desired as water-absorbing agents for plant growing, or medical use such as in disposable diapers, sanitary napkins, and the like. Many papers reporting synthesis of polymeric materials of this type such as by crosslinking poly(acrylic acid)s have been published in the past three decades years (1–3). However, because these water absorbing materials are rarely recovered or collected after use, it is very important to impart biodegradability to them from the standpoint of protecting the natural environment. Though hydrogel derived from amino acids such as poly(asparatic acid), fall in the category of biodegradable hydrogels and methods of preparing them have been investigated recently (4–6). The number of originating amino acids is small.

We have found that MTC polymerizes via ring-opening in the presence of radical initiator to produce poly(ester-ether) and the obtained polymer is biodegradable (7). Further, we reported that MTC could copolymerize with various vinyl monomers to impart them biodegradability (8–11). We also reported that MTC could copolymerize with DVA as a crosslinking agent and the obtained gel was found to be biodegrade (12). We report here on the radical terpolymerization of MTC, and MA as the

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water-absorbing constituents, and PEGD or DVA as the crosslinking agents. We also report on the water-absorbing ability and the biodegradability of the obtained gels.

Experimental

Materials

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

Preparation

The gels were prepared by the radical terpolymerization of MTC, MA, and PEGD or DVA. The terpolymerization of MTC, MA and PEGD [feed ratio: MTC/MA/PEGD = 1.0/0.9/0.1 (mol/mol/mol)] was carried out as follows: in a 20 ml sealed polymerization tube, a mixture containing MTC (1.3 g, 1.00×10^{-2} mol), MA (0.882 g, 9.00×10^{-3} mol), PEGD (0.400 g, 1.00×10^{-3} mol), AIBN (0.0657 g, 4.00×10^{-4} mol), and PhCl (11.256 g, 1.00×10^{-1} mol) was maintained at 60°C for 48 h. The resulting product was precipitated in diethyl ether. The precipitated material was dried under reduced pressure to give 2.369 g (92%) of a gel. The acid anhydride moiety of the obtained gel was hydrolyzed by 0.01 N sodium carbonate. Hydrolysis of the gel's anhydride functionality was carried out as follows: the obtained gel (0.540 g) in 50 ml pure water was precipitated by 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. The hydrogel was dialyzed overnight against pure water using a dialysis membrane (MWCO: 3500, Spectra/Pro Membrane (USA)) and dried under reduced pressure. The same procedure was carried out with DVA as a crosslinking agent.

Characterization

The IR spectra of the obtained gels before and after hydrolysis were measured using an infrared spectrometer (Shimadzu FTIR-4200). The absorbability of dry gels before and after hydrolysis for deionized water and saline was measured by the Tea Bag method according to JIS K7223 except that the immersion time was 30 min., as follows: about 30 mg of sample was added to a small bag made of polypropylene (40 mm \times 50 mm) with 200 mesh, the bag was immersed in deionized water or saline for 30 min. and the increase in weight was examined. So the equilibrium absorption could be expressed as follows:

$$A = W_d/W_0(\text{times}) \quad (1)$$

Where W_0 is the initial weight of the gel, W_d is the weight when the gel was immersed in deionized water or saline, and A is the absorbing degree (times). The rate of the

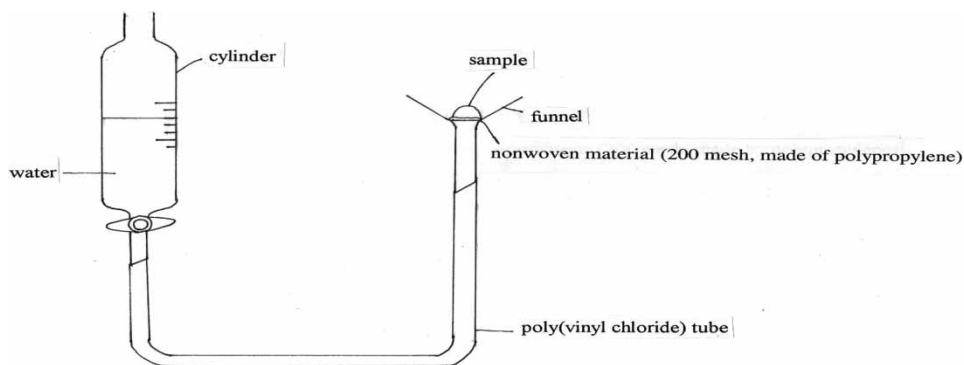


Figure 1. Simplified D/Q method.

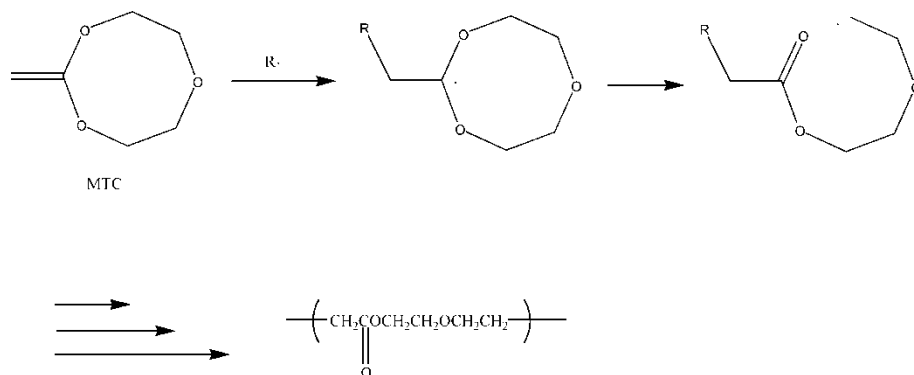
absorbability of dry gels after hydrolysis for deionized water and saline was measured using the simplified D/W method as shown in Figure 1 by reference to JIS K7224-1996.

The decrease in volume of deionized water or saline with elapse of time was measured using the cylinder graduations. 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 gels in the incubation medium was 100 mg/L.

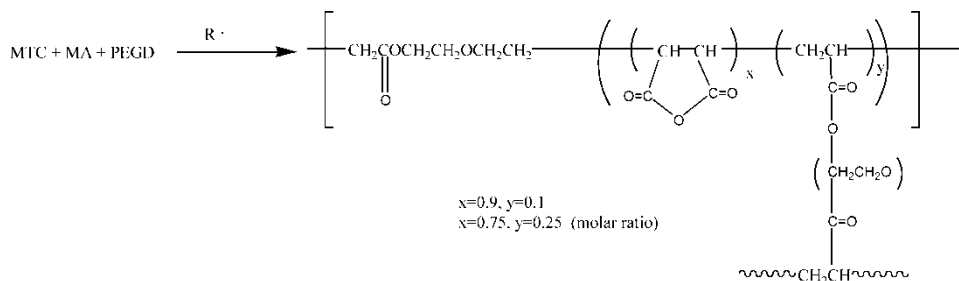
Results and Discussion

Ring-opening polymerization of MTC was carried in the presence of a 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 or cyanoacrylate, alternating copolymers were obtained (13–15). So, in the case of MTC and MA, the copolymer



Scheme 1. Radical ring-opening polymerization of MTC.



Scheme 2. Radical polymerization of MTC, MA and PEGD.

produced might be mostly alternating though a little crosslinking agent was contained in the copolymer, as shown in Scheme 2.

The IR spectrum of the gel-MTC-MA-PEGD before and after hydrolysis is shown in Figure 2.

Before the hydrolysis, absorption of the anhydride appeared at 1850 cm^{-1} and 1775 cm^{-1} . Absorption of the ester groups appeared when MTC underwent ring-opening and the crosslinking agent at 1735 cm^{-1} . After hydrolysis, the absorption of anhydride group disappeared and the absorptions of carboxylic anion and carboxylic hydroxyl group appeared at 1580 cm^{-1} , 1400 cm^{-1} , and 3450 cm^{-1} . The absorption of ester group in the gel remained at 1735 cm^{-1} after hydrolysis. These spectral data indicate that MTC ring-opening polymerizes to produce an ester group in the presence of radical initiator, PEGD acts as crosslinking agent, and MA is hydrolyzed by dilute alkaline and the ester group remains after the hydrolysis in the mild condition, as shown in Scheme 3.

The copolymerization of MTC, MA, and PEGD or DVA is summarized in Table 1.

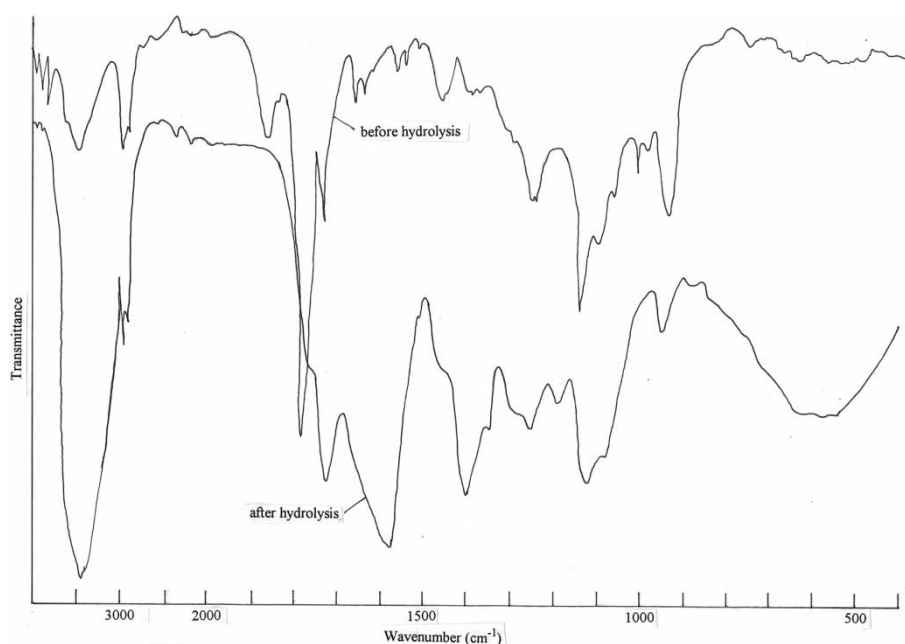
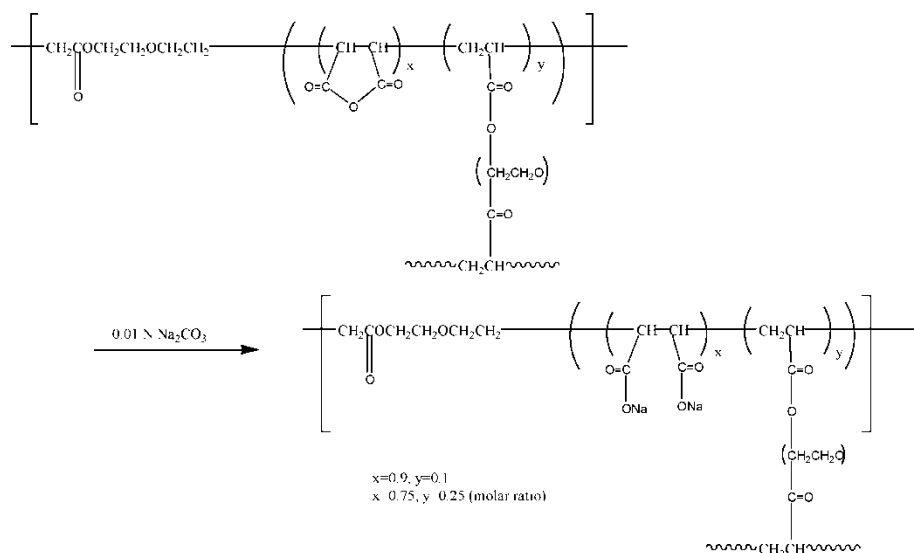


Figure 2. IR spectra of gel MTC/MA/PEGD (1.0/0.9/0.1) before and after hydrolysis.



Scheme 3. Hydrolysis of MA moiety.

Because the yields of the produced gels are high, most monomers are thought to react in the presence of the radical initiator. Therefore, the compositions of the produced gels are thought to be consistent with the monomer feed ratios.

The absorbability of the gels is summarized in Table 2.

No gel absorbed deionized water before hydrolysis. The gel after hydrolysis could absorb deionized water from 29 times to 62 times. The drastic increase of absorbability after hydrolysis is thought to be produced by sodium carboxylate. The absorbability of deionized water in gel (MTC/MA/PEGD = 1.0/0.9/0.1) was higher than that in gel (MTC/MA/DVA = 1.0/0.9/0.1). This is thought to be attributable to the high hydrophilicity of PEGD. The absorbability of deionized water in gel (MTC/MA/PEGD = 1.0/0.9/0.1) was higher than that in gel (MTC/MA/PEGD = 1.0/0.75/0.25). This is thought to be attributable to an increase in the ratio of sodium carboxylate and a decrease in the ratio of crosslinking agent. Deionized water-absorbability after hydrolysis was higher than saline-absorbability. This was due to the high ionic osmotic pressure when contacting the outer solution such as deionized water and saline (3). The rates of deionized water and saline-absorbability of the hydrogel (MTC/MA/PEGD = 1.0/0.9/0.1) after hydrolysis are shown in Figure 3.

Table 1
Terpolymerization of MTC, MA and PEGD or DVA^a

| Monomer feed ratio (mol/mol/mol) | Yield ^b (%) |
|----------------------------------|------------------------|
| MTC/MA/PEGD (1.0/0.9/0.1) | 92 |
| MTC/MA/PEGD (1.0/0.75/0.25) | 86 |
| MTC/MA/DVA (1.0/0.9/0.1) | 86 |

^aInitiator: AIBN 2 mol%, temperature: 60°C, time: 48 h.

^bInsoluble part in diethyl ether.

Table 2
Absorbability of gel

| Gel | After hydrolysis | | Before hydrolysis |
|-----------------------------|-------------------------|----------------|-------------------------|
| | Deionized water (times) | Saline (times) | Deionized water (times) |
| MTC/MA/PEGD (1.0/0.9/0.1) | 62 | 26 | 6 |
| MTC/MA/PEGD (1.0/0.75/0.25) | 29 | 25 | 3 |
| MTC/MA/DVA (1.0/0.9/0.1) | 31 | 13 | 4 |

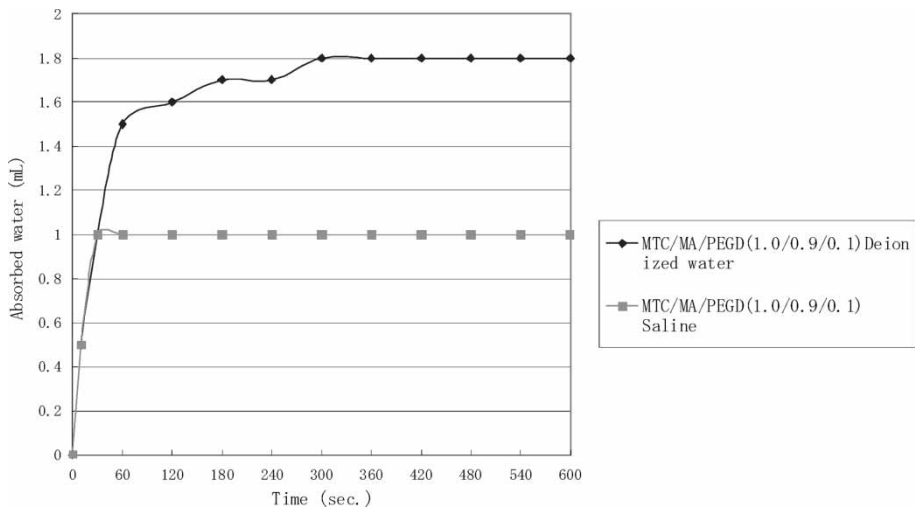


Figure 3. Absorbability ratio of gel after hydrolysis.

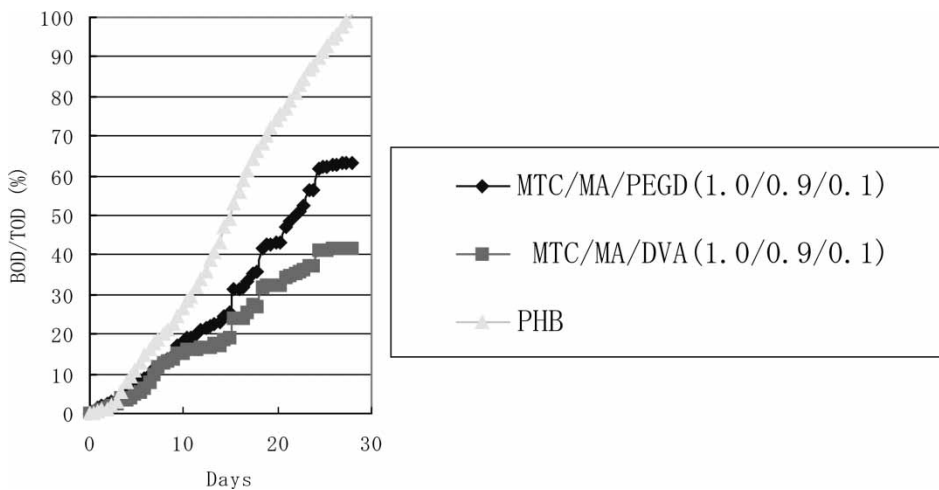


Figure 4. Biodegradation of gel after hydrolysis.

The absorbabilities of the hydrogels reached equilibrium within 60 sec in both cases. This result is compatible with that of poly(acrylic acid) [JIS K7224-1996].

Figure 4 shows the biodegradation of the hydrogels after hydrolysis.

The degradabilities were 64% for hydrogel (MTC/MA/PEGD = 1.0/0.9/0.1) and 42% for hydrogel (MTC/MA/DVA = 1.0/0.9/0.1) at 28 days using a soil. It was reported that a polymer had biodegradability if BOD/TOD was above 60% using soil (16). So, it can be concluded that hydrogel (MTC/MA/PEGD = 1.0/0.9/0.1) is biodegradable after hydrolysis.

Conclusions

MTC, MA, and PEGD or DVA were terpolymerized in the presence of a radical initiator to obtain gels. After hydrolyzing the carboxylate anhydride in MA, the gels could absorb deionized water and saline. The hydrogels, after hydrolysis, were biodegradable in biodegradation experiments conducted with a BOD tester using the oxygen consumption method.

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