

# Deacetylation Behavior of Binary Blend Films of Cellulose Acetate and Various Polymers

Yoichiro Yamashita,<sup>1</sup> Takeshi Endo<sup>2</sup>

<sup>1</sup>*Cigarette Materials R&D Division, Japan Tobacco, Inc., 3-2-34 Sakae-cho, Asaka, Saitama 351-0012, Japan*

<sup>2</sup>*Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan*

Received 28 October 2004; accepted 13 June 2005

DOI 10.1002/app.23079

Published online 24 January 2006 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** For binary blend films of cellulose acetate (CA) and various polymers, the elution behavior of the polymers from the CA films in different environments (i.e., soil, water) was examined. For the CA film containing poly(ethylene glycol) (PEG), the PEG eluted to the periphery of the film completely. On the other hand, polyvinylpyrrolidone blended with CA remained in the CA film. A CA film containing acrylic acid was prepared, and this film was heated. The elution of acrylic acid was inhibited by its polymerization. These results suggested that the internal polymers were capable of remaining in the CA film by polymer entanglement. Second, we examined the deacetylation and biodegradation behavior of CA films containing polymers with a phosphoric acid moiety in the side chain, such as poly(2-hydroxyethyl methacrylate phosphoric acid ester)

[poly(HEMA-P)]. Poly(HEMA-P) had the ability to deacetylate the CA, and the biodegradation rate of the CA films containing poly(HEMA-P) increased in comparison with that of the nonadditive CA films. The elution of internal 2-hydroxyethyl methacrylate phosphoric acid ester was inhibited by the copolymerization with 2-hydroxyethyl methacrylate or crosslinking. In the case of both 2-hydroxyethyl methacrylate phenyl phosphoric acid ester and 10-methacryloyloxydecyl dihydrogen phosphate, the acetone-soluble polymers were obtained by radical polymerization in a mixture of acetone and water. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1816–1823, 2006

**Key words:** additives; blends; films; radical polymerization

## INTRODUCTION

The problem of solid waste disposal, such as compost, wastewater treatment plants, and landfill/litter in the natural environment, has reached a critical stage, and it is a matter of great public concern. The chemical industry is being asked to provide products that will not persist in the environment (i.e., biodegradable products). Cellulose acetate (CA; see Fig. 1), which is made from wood pulp through the acetylation of cellulose, is widely used for textiles, moldings, and cigarette filters. Extensive research on the biodegradability of CA has been conducted by several organizations.<sup>1–5</sup> Research has shown that CA is a biodegradable material and that its biodegradation rate depends on its degree of acetyl-group substitution (DS). As the DS of CA decreases, its biodegradation rate increases. CA has ester bonds and glycosidic linkages in its structure, and it is conceivable that these bonds of CA are susceptible to hydrolysis by acid/base catalysts.<sup>6–9</sup> Research in our laboratory was car-

ried out to clarify the hydrolysis behavior of CA films (DS = 2.5) in acidic or basic solution at room temperature.<sup>10</sup> We found that the CA was deacetylated by acid/base catalysts, depending on the acid/base concentration. Furthermore, we examined the biodegradability of CA films (DS = 2.5) containing acids when they were buried in soil.<sup>11</sup> The biodegradation rate of CA films containing acids, such as phosphoric acid, increased in comparison with that of nonadditive CA film. The CA film containing acids was chemically deacetylated by contact with water in the soil and, consequently, was converted into CA with a lower DS, which had higher biodegradability.

The purpose of this study was to understand the elution behavior of acids from CA films containing acids in the environment (i.e., soil, water). First, we examined the elution rate of chemicals in water for various CA films containing chemicals to clarify the effect of the properties of chemicals on the elution behavior (see Fig. 2). Second, we examined the deacetylation behavior of CA films containing polymers with a phosphoric acid moiety in the side chain whose elution was inhibited. This article describes the results obtained from these experiments and discusses the effects of the additives' properties on the elution behavior and the deacetylation ability of the CA.

Correspondence to: Y. Yamashita (yoichiro.yamashita@ims.jti.co.jp).

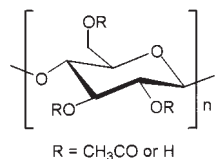


Figure 1 Molecular structure of CA.

## EXPERIMENTAL

### Preparation of the CA films

CA (DS = 2.5) was commercially available from Daicel Chemical Industries, Ltd. (Osaka, Japan). The CA films were prepared with a 20% solution (w/v) of CA in acetone. The insoluble part of the solution was removed beforehand by suction filtration. We cast the films by drawing them on glass plates with a 0.6-mm draw blade. After they were air-dried, the films were cut into circular pieces 5.0 cm in diameter. The thickness of the films was approximately 0.1 mm after the removal of the solvent.

In a typical procedure, the binary blend films of CA with various chemicals were prepared as follows. The indicated amounts of the corresponding chemicals were also added to the solution of CA in acetone. Thereafter, the films were cast in the same way as the nonadditive CA films. All of chemicals were of the highest purity commercially available. The additives used in our examinations were carrageenan (types  $\lambda$  and  $\kappa$ ), polyvinylpyrrolidone [PVP; molecular weight (MW) = 35,000], poly(ethylene glycol) (PEG; MW = 600), acrylic acid, methacrylic acid, *p*-vinylbenzoic acid, 2-acrylamido-2-methylpropane sulfonic acid, 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl methacrylate phosphoric acid ester (HEMA-P), 2-hydroxyethyl methacrylate phenyl phosphoric acid ester (HEMA-PP), 10-methacryloyloxydecyl dihydrogen phosphate (MDP), and 2-hydroxyethyl methacrylate difunctional phosphoric acid ester (di-HEMA-P). Optical microscopy showed that all of the additives were miscible with CA except carrageenan. The trans-

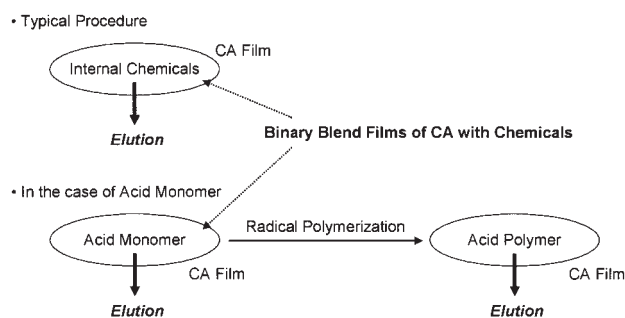


Figure 2 Preparation procedure of the CA films for the elution evaluation of chemicals in the CA films.

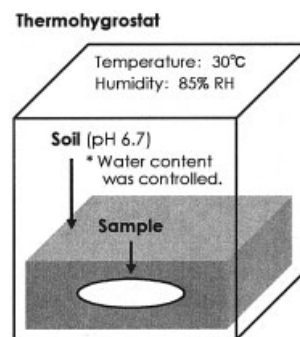


Figure 3 Illustration of the laboratory soil burial test.

parencies of the CA films were as follows: carrageenan and PVP: slightly blooming, and others: transparent.

### Polymerization of the monomers in the CA films

In a typical procedure, the polymerization of the monomers in CA films (shown later in Figs. 8–13 and Tables III and IV) is given as follows (see Fig. 2). CA films containing monomers and 2,2'-azobisisobutyronitrile (AIBN; 3 mol %) as an initiator were prepared with a 20% solution (w/v) of CA in acetone. The indicated amounts of the corresponding monomers and AIBN were also added to the solution of CA in acetone. Thereafter, the films were cast in the same way as the nonadditive CA films. The resulting films were heated at 60°C for 6 h under a nitrogen atmosphere to polymerize the internal monomers.

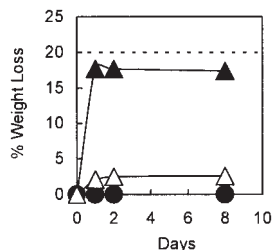
### Synthesis of poly(10-methacryloyloxydecyl dihydrogen phosphate) [poly(MDP)] and poly(2-hydroxyethyl methacrylate phenyl phosphoric acid ester) [poly(HEMA-PP)]

In a typical procedure, the polymerization of MDP and HEMA-PP (shown later in Tables V and VI) is given as follows. A solution of MDP or HEMA-PP (0.25 g) in a mixture of acetone and H<sub>2</sub>O (5 mL; the mixture ratio is indicated as shown later in Tables V and VI) was heated at 60°C for 6 h under a nitrogen atmosphere. AIBN or potassium peroxydisulfate was used as an initiator (3 mol %). The resulting polymer was isolated by precipitation into diethyl ether and filtered.

### Water immersion test

#### Elution

To examine the elution behavior of the additives, the CA films containing additives (ca. 0.4 g) were immersed in 300 mL of neutral water and allowed to stand at 22°C. The CA films, which were collected at predetermined dates, were weighed after drying. The



**Figure 4** Changes in the weights of the CA films containing 25 wt % carrageenan as determined by a water immersion test: (▲) carrageenan- $\lambda$ , ( $\Delta$ ) carrageenan- $\kappa$ , (●) nonadditive, and (- - -) theoretical value of 20.0 wt % loss obtained by additive elution.

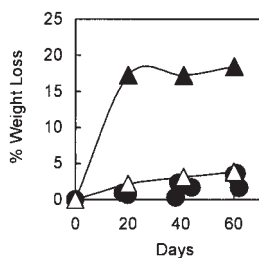
percentage weight loss that indicated the elution of additives was calculated from the difference in the weights before and after the water immersion test.

#### Deacetylation

To examine the deacetylation behavior of CA, the CA films to which predetermined acid had been added were immersed in  $D_2O$  and left for 10 days at room temperature. The detection of free acetic acid, which was generated from the CA film, in  $D_2O$  was determined by  $^1H$ -NMR. The  $^1H$ -NMR spectra were recorded on a JEOL Lambda 500 spectrometer (Tokyo, Japan).

#### Laboratory soil burial test

A soil sample obtained from our company's premises was used as the soil for the examination after pebbles and so on were removed with a sieve. A soil sample 10 cm thick was placed in a square tray 50 cm on a side. The soil water content was set at approximately 36 wt % [67% of the maximum water holding capacity (ca. 53 wt %) of the soil]. The maximum water-holding capacity was determined according to the Hilgard method.<sup>12</sup> Subsequently, circular pieces of the CA films were buried in the soil (20–30 pieces per tray) and left in a thermohygrostat at 30°C for a fixed period of time



**Figure 5** Changes in the weight of the CA films containing 25 wt % carrageenan as determined by a laboratory soil burial test: (▲) carrageenan- $\lambda$ , ( $\Delta$ ) carrageenan- $\kappa$ , and (●) nonadditive.

**TABLE I**  
 $T_g$  for the CA Films Containing PEG<sup>a</sup>

PEG content (wt %)	$T_g$ (°C) <sup>b</sup>
0.0	185.6
10.0	179.9
20.0	166.1

<sup>a</sup> PEG melting temperature = 18.9°C.

<sup>b</sup> Determined by DSC.

(see Fig. 3). During this period, the soil water content was adjusted daily to maintain it at 36 wt %. The CA pieces, which were collected at predetermined dates, were washed extensively with distilled water and subsequently dried at 60°C in vacuo for 24 h before they were weighed. The percentage weight loss was calculated from the difference in the weights before and after the laboratory soil burial test.

#### Measurements

MWs of poly(MDP) and poly(HEMA-PP) were measured by gel permeation chromatography (GPC) on a Tosoh (Tokyo, Japan) HLC-8020 chromatographic system consisting of a liquid chromatograph, a refractive-index detector, and a Tosoh SC-8010 system controller. Three Tosoh TSK-gel columns (7.8 mm i.d.  $\times$  300 mm/column; G2000HXL, G3000HXL, and G4000HXL) were placed in series and operated at a flow rate of 1.0 mL/min. The sample concentration was 10 mg/mL and the injection volume was 50  $\mu$ L. The analysis was performed with tetrahydrofuran (THF; Wako Pure Chemical Industries, Ltd., Osaka, Japan) as an eluent. MWs were calculated relative to polystyrene standards without further correction. The glass-transition temperatures ( $T_g$ 's) of the CA films were measured by differential scanning calorimetry (DSC) on a Seiko DSC 6220/EXSTAR 6000 apparatus (Tokyo, Japan). The calorimetry measurements were made on approximately 5-mg samples at a scanning rate of 10°C/min under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

#### Elution behavior of the additives for the CA films

The elution rate of various chemicals added in the CA films in water was examined by a water immersion

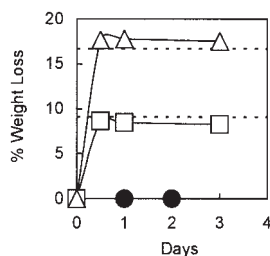
**TABLE II**  
 $T_g$  Values for the CA Films Containing PVP<sup>a</sup>

PVP content (wt %)	$T_g$ (°C) <sup>b</sup>
0.0	185.6
20.0	177.7 <sup>c</sup>

<sup>a</sup> PVP  $T_g$  = 99.1°C.

<sup>b</sup> Determined by DSC.

<sup>c</sup> Single  $T_g$ .



**Figure 6** Changes in the weights of the CA films containing PEG as determined by a water immersion test: (△) 20 wt % PEG, (□) 10 wt % PEG, (●) nonadditive, and (---) theoretical values of 16.7 and 9.1 wt % losses obtained by PEG elution.

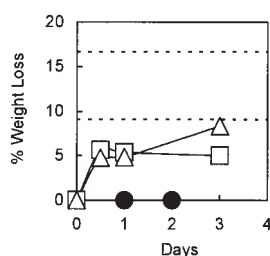
test to clarify the effects of the properties and miscible state of chemicals on the elution behavior in the CA films.

#### Effect of water solubility

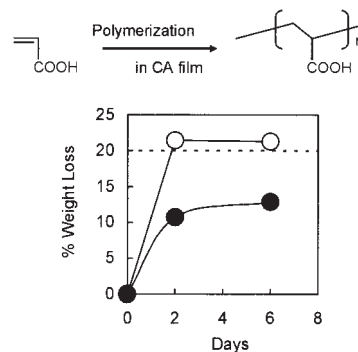
The elution rate of two types of carrageenan, type  $\lambda$  (soluble in water) and type  $\kappa$  (insoluble in water), in the CA films were examined by a water immersion test. The changes in the weights of the CA film containing 25 wt % carrageenan and a nonadditive CA film are shown in Figure 4. The elution rate of carrageenan- $\lambda$  increased in comparison with that of the carrageenan- $\kappa$ . This result indicates that the higher water solubility of the additives promoted the elution rate of the additives. Under a soil environment, the elution behavior of additives was similar to that in the case of water immersion, as shown in Figure 5. Here, we mention the miscibility of carrageenan with CA. The two types of carrageenan were not miscible with CA, and powdered carrageenan was uniformly dispersed in the CA.

#### Effect of miscibility with CA

The elution rate of PEG and PVP in the CA film was examined by a water immersion test to clarify the effect of miscibility with CA. It is well known that



**Figure 7** Changes in the weights of the CA films containing PVP as determined by a water immersion test: (△) 20 wt % PVP, (□) 10 wt % PVP, (●) nonadditive, and (---) theoretical values of 16.7 and 9.1 wt % losses obtained by PVP elution.



**Figure 8** Changes in the weights of the CA films containing 25 wt % acrylic acid as determined by a water immersion test (○) before and (●) after polymerization and (---) the theoretical value of 20.0 wt % loss obtained by additive elution.

PEG<sup>13,14</sup> and PVP<sup>15,16</sup> are miscible with CA. The results of the DSC measurements are shown in Tables I and II and confirm the miscibility of PEG and PVP with CA.  $T_g$  shifted as the PEG or PVP content increased, with a single  $T_g$ , which indicated miscibility with CA. The changes in the weights of CA films containing PEG and PVP are shown in Figures 6 and 7. For PEG, the internal PEG eluted to the periphery of the film completely. On the other hand, the internal PVP remained in the film. PVP was soluble in water, similar to the PEG. It seems that the inhibition of PVP elution was caused by the entanglement of PVP molecules with CA.

#### Effect of polymer entanglement

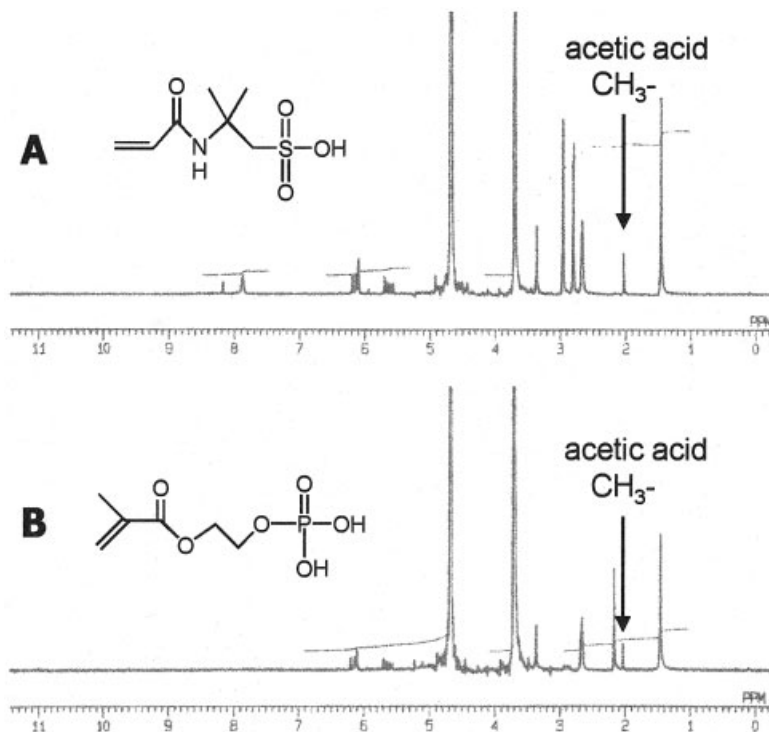
The elution rate of acrylic acid, which was polymerized in the CA film, was examined by a water immersion test to clarify the effect of polymer entanglement. The CA film containing 25 wt % acrylic acid and AIBN (3 mol %) as an initiator was prepared, and this film was heated at 60°C for 6 h under a nitrogen atmo-

**TABLE III**  
Deacetylation of the CA Films Containing 25 wt % Polymer<sup>a</sup> (Indicated Monomers) Immersed in D<sub>2</sub>O after 10 Days

Monomer	Deacetylation <sup>b</sup>
Acrylic acid	Not detected
Methacrylic acid	Not detected
<i>p</i> -Vinylbenzoic acid	Not detected
2-Acrylamido-2-methylpropane sulfonic acid	Detected
HEMA	Not detected
HEMA-P	Detected

<sup>a</sup> Polymerization in the CA films; 60°C, 6 h, 3 mol % AIBN (monomer).

<sup>b</sup> Deacetylation was determined by the detection of free acetic acid (<sup>1</sup>H-NMR).



**Figure 9**  $^1\text{H-NMR}$  spectra of the immersing water collected by a water immersion test for a CA film containing 25 wt % (A) 2-acrylamido-2-methylpropane sulfonic acid and (B) HEMA phosphoric acid ester after polymerization in the CA films.

sphere. The changes in the weights of CA films containing acrylic acid before and after heating treatment as determined by a water immersion test are shown in Figure 8. As shown in Figure 8, the elution of acrylic acid was inhibited by its polymerization. This result suggested that the water-soluble polymer [i.e., poly(acrylic acid)] was capable of remaining in the CA film because of polymer entanglement.

#### Degradation behavior of the CA films containing polymers with an acidic group in the side chain

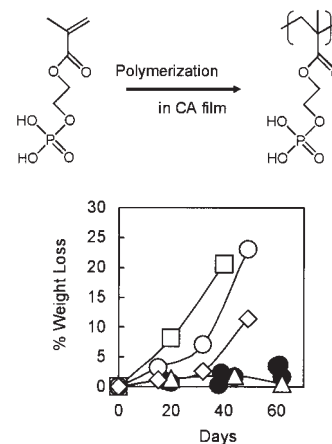
##### Deacetylation and biodegradation behavior

We<sup>11</sup> reported earlier that the biodegradation rate of CA films containing acids, such as phosphoric acid, increased in comparison with that of nonadditive CA film. The CA film containing acids was chemically deacetylated by contact with water in soil and, consequently, converted into a CA with a lower DS and with a higher biodegradability. On the basis of our previous results, the deacetylation and biodegradation behaviors of the CA films containing polymers with an acidic group in the side chain were examined.

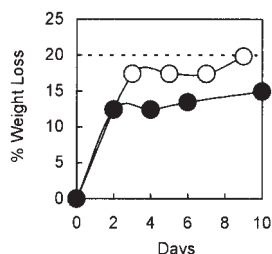
The deacetylation behavior of CA films containing polymers, which were polymerized in the film, was examined by a water immersion test. The detection of free acetic acid, which was generated from the CA film, in  $\text{D}_2\text{O}$  was determined by  $^1\text{H-NMR}$ . The results are shown in Table III and Figure 9. As shown in Table

III, for the CA films containing polymers with a carboxyl group in the side chain, the formation of acetic acid indicated that the deacetylation of CA did not occur. On the other hand, for the CA films containing polymers with a sulfonic acid and a phosphoric acid in the side chain, the CA was deacetylated.

The biodegradation behavior of the CA films containing poly(2-hydroxyethyl methacrylate phosphoric acid ester) [poly(HEMA-P)], which showed the ability



**Figure 10** Changes in the weights of the CA films containing poly(HEMA-P) as determined by a laboratory soil burial test: (□) 13, (○) 5, (◇) 1 wt % poly(HEMA-P), and (△) 25 wt % poly(HEMA) and (●) nonadditive.

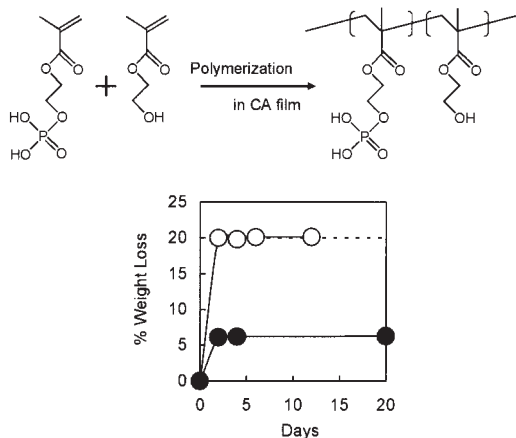


**Figure 11** Changes in the weights of the CA films containing 25 wt % HEMA phosphoric acid ester as determined by a water immersion test (○) before and (●) after polymerization and (---) the theoretical value of 20.0 wt % loss obtained by additive elution.

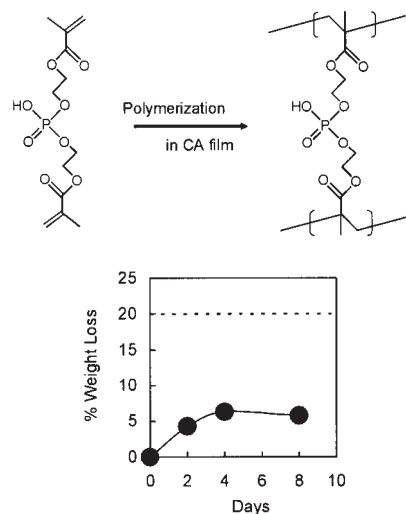
to deacetylate the CA, was examined by a laboratory soil burial test. The changes in the weights of the CA films containing poly(HEMA-P) are shown in Figure 10 along with those obtained from the nonadditive CA films and the CA films containing poly(2-hydroxyethyl methacrylate) [poly(HEMA)]. As shown in Figure 10, the biodegradation rate of the CA films containing poly(HEMA-P) increased in comparison with that of the nonadditive CA films, depending on the poly(HEMA-P) content. On the other hand, for the CA films containing poly(HEMA), the acceleration of the biodegradation rate of the CA films was not observed. This result suggests that the acceleration of the biodegradation rate was caused by a phosphoric acid group in the side chain of HEMA. That is, it seemed that the CA was chemically deacetylated by acid catalysis of a phosphoric acid group and was, consequently, converted into a CA with a lower DS and a higher biodegradability.

#### Elution behavior

The elution behavior of HEMA-P for the CA films containing HEMA-P, which showed the ability to ac-



**Figure 12** Changes in the weights of the CA films containing 25 wt % HEMA phosphoric acid-co-HEMA (1 : 1) as determined by a water immersion test (○) before and (●) after polymerization and (---) the theoretical value of 20.0 wt % loss obtained by additive elution.



**Figure 13** Changes in the weights of the CA films containing 25 wt % di-HEMA-P as determined by a water immersion test (●) after polymerization and (---) the theoretical value of 20.0 wt % loss obtained by additive elution.

celerate the biodegradation rate of CA, was examined by a water immersion test. The changes in the weights of the CA films containing 25 wt % HEMA-P before and after the heating treatment (i.e., polymerization) are shown in Figure 11. Although the elution of HEMA-P was inhibited by its polymerization, HEMA-P more than half eluted to the periphery of the film. As shown in Figure 10, HEMA, which was soluble in water, almost remained in the film. This suggested that HEMA molecules were entangled well with CA in comparison with that of HEMA-P. We believe that the difference in the elution behavior between HEMA and HEMA-P was caused by the degree of polymerization (DP) in the film. That is, HEMA-P had a lower DP, which was caused by the bulk and/or hydrogen bonding of a phosphoric acid group, in comparison with that of HEMA: MW measurement of poly(HEMA-P) in the film was impossible because isolation of the resulting polymer from the film was difficult.

**TABLE IV**  
Deacetylation of the CA Films Containing 25 wt % polymer<sup>a</sup> (Indicated Monomers) Immersed in D<sub>2</sub>O After 10 Days

Monomer	Deacetylation <sup>b</sup>
HEMA-PP	Detected (2.15%)
MDP	Detected (2.53%)
di-HEMA-P	Detected (1.79%)
HEMA-P	Detected (0.12%)

<sup>a</sup> Polymerization in the CA films; 60°C, 6 h, AIBN 3 mol % (monomer).

<sup>b</sup> Deacetylation was determined by the detection of free acetic acid (<sup>1</sup>H-NMR). The degree of deacetylation is given in parentheses.

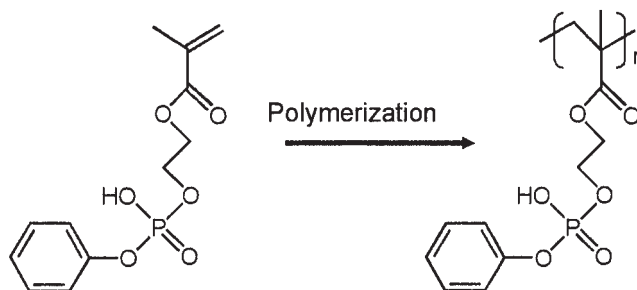


TABLE V  
Relationship Between the Polymerization Conditions and the Acetone Solubility of the Polymers

Entry	Solvent (5 mL)	Ratio of mixture	Initiator	Solubility in acetone <sup>a</sup>
1	H <sub>2</sub> O	—	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	×
2	H <sub>2</sub> O (1 mL)	—	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	×
3	H <sub>2</sub> O, acetone	10 : 1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	×
4	H <sub>2</sub> O, acetone	1 : 1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	○
5	H <sub>2</sub> O, acetone	1 : 1	AIBN	○
6	H <sub>2</sub> O, acetone	1 : 10	AIBN	○
7	H <sub>2</sub> O, acetone	0.4 : 10	AIBN	○ <sup>b</sup>
8	Acetone	—	AIBN	×

Monomer = 0.25 g; 60°C, 6 h, initiator-3 mol %. ○ = soluble; × = insoluble.

<sup>a</sup> Containing 4% H<sub>2</sub>O.

<sup>b</sup> Number-average molecular weight = 5000, estimated by GPC (THF, polystyrene standard).

To inhibit the elution of HEMA-P, the effect of copolymerization with HEMA was examined. CA films containing 25 wt % monomer, which were HEMA-P and HEMA (1:1), and AIBN (3 mol %) as an initiator was prepared, and this film was heated at 60°C for 6 h under a nitrogen atmosphere. The changes in the weights of the CA films containing HEMA-P and HEMA before and after heating treatment as determined by a water immersion test are shown in Figure 12. The elution of HEMA-P was inhibited by copolymerization with HEMA in comparison with that of the homopolymerization of HEMA-P. It seemed that HEMA worked effectively as a spacer for the DP in the film.

As another technique for the inhibition of the HEMA-P elution, to increase the polymer entanglement, the effect of crosslinking was examined. A CA film containing 25 wt % di-HEMA-P and AIBN (3 mol %) as an initiator was prepared, and this film was heated at 60°C for 6 h under a nitrogen atmosphere. The changes in the weights of CA films containing di-HEMA-P after heating treatment as determined by a water immersion test are shown in Figure 13. As shown in Figure 13, the elution of HEMA-P was inhibited by crosslinking in comparison with that of normal poly(HEMA-P).

#### Solubility in acetone of the polymers with a phosphoric acid moiety in the side chain

Poly(HEMA-P), which showed the ability to accelerate the biodegradation rate of CA, had poor sol-

ubility in various solvents. It seemed that this poor solubility was caused by intermolecular hydrogen bonding between phosphoric acid groups in the side chain. In this section, we briefly summarize the use of poly(HEMA-Ps) for the typical spinning process of CA fibers. CA (DS = 2.5) fibers are generally obtained from a solution of CA in acetone by dry spinning. If poly(HEMA-P) is soluble in acetone as a spinning solution, it is possible to spin the CA fibers containing poly(HEMA-P) with the typical spinning process. To find the acetone-soluble poly(HEMA-Ps), the relationship between the acetone solubility and the side chain structure of poly(HEMA-Ps), which were obtained by the radical polymerization of HEMA-PP and MDP, was examined. To inhibit the intermolecular hydrogen bonding between phosphoric acid groups, HEMA-PP with a bulk substituent in the phosphoric acid moiety and MDP with a spacer between the main chain and the phosphoric acid moiety were used.

First, the deacetylation behaviors of the CA films containing poly(HEMA-Ps), which were polymerized in the film, were examined by a water immersion test. The detection of free acetic acid, which was generated from the CA film, in D<sub>2</sub>O was determined by <sup>1</sup>H-NMR. As shown in Table IV, it was observed that every HEMA-Ps had the ability to deacetylate the CA. Considering the results described previously, we expected HEMA-PP and MDP to accelerate the biodegradation rate of CA under the soil environment.

