Biodegradability of Poly(vinyl acetate) Containing a Pyridinium Group

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SYNOPSIS

An attempt has been made to give biodegradability to poly(vinyl acetate) by partial modification of the chemical structure. Poly(vinyl acetate) containing a small amount of *N*-benzyl-4-vinylpyridinium chloride (PVAc-*co*-VPC) and that containing 16 mol % of methyl acrylate and a small amount of the pyridinium group (PVAc-*co*-MA-*co*-VPC) showed significant degradation when placed in an aeration tank of sewage works. Control polymers possessed of no pyridinium group did not show significant degradation under these conditions, and the extent of weight reduction during the treatment increased with the content of the pyridinium group. The weight reduction exhibited an uppermost limit after 7 days of the treatment, and the pyridinium group disappeared from the polymer during the early period. Incorporation of the pyridinium group into poly(vinyl acetate) appeared to have improved the biodegradability. Gel permeation chromatographic analysis showed that the low molecular weight fraction was more easily degraded than was the high molecular weight fraction. In the degradation of PVAc-*co*-MA-*co*-VPC, the unit of methyl acrylate was more easily removed than that of vinyl acetate. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, considerable attention has focused on the development of biodegradable polymers, mainly because pollution of the environment by waste polymers has become a worldwide social problem. Reports available in the literature can be classified into three categories: (i) utilization of polymers produced by microorganisms; (ii) utilization of natural polymers and their derivatives; and (iii) development of biodegradable synthetic polymers. Synthetic polymers, especially hydrophobic high molecular weight polymers, generally exhibit strong resistance to the biological degradation. However, several synthetic polymers are known to be biodegradable. For example, high molecular weight polymers of such aliphatic polyesters as poly(ethylene adipate),[1,2] poly(tetramethylene adipate),[3] and poly(caprolactone)[4,5] are reported to undergo biological degradation. Biodegradation of high molecular weight poly(vinyl alcohol) has been investigated in detail.[6–11] Oligomers of poly(ethylene glycol)[12–16] and poly(sodium acrylate)[17,18] are also reported to be biodegradable.

For chemical industry, development of biodegradable synthetic polymers would be most important. If possible, it is favorable to give biodegradability to synthetic high polymers by partial modification of the chemical structure, because the methodology is anticipated to make useful polymeric materials biodegradable without severe damage of physicochemical properties and utilities. Polymer chemists are skillful at the contrivance of synthetic methodology for high polymers. Molecular design has been used to develop biodegradable synthetic polymers by incorporation of a biodegradable unit, such as vinyl alcohol, to the polymer chain.[19–21] This report describes an approach to give biodegradability to poly(vinyl acetate) by partial modification of the chemical structure based on a new concept.

In a previous report from this laboratory, we observed that poly(methyl methacrylate) containing a small amount of *N*-benzyl-4-vinylpyridinium chloride in the polymer chain showed a remarkable re-

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duction in molecular weight and gravimetric weight when placed in an aeration tank of sewage works.[22] A synthetic hydrophobic polymer of high molecular weight consisted of a carbon–carbon bond as the main chain turned biodegradable by partial modification of the chemical structure through incorporation of the pyridinium group into the polymer chain. Since an insoluble pyridinium-type polymer can capture many bacterial cells alive on its surface[23] and is of wide application in the field of biotechnology and water purification,[24] we assumed that poly(methyl methacrylate) turned biodegradable by enhancement of the affinity to the cells of microorganisms through incorporation of the pyridinium group into the polymer chain.[22] Based on the experimental results, we are continuing improvement of the biodegradability of synthetic polymers based on a novel concept, i.e., we are attempting to make hydrophobic synthetic high polymers biodegradable by partial modification of the chemical structure through incorporation of a small amount of the pyridinium group into the polymer chain. In this work, we investigated the biodegradability of poly(vinyl acetate) containing the pyridinium group in the polymer chain in a similar manner.

EXPERIMENTAL

Chemicals

Vinyl acetate and methyl acrylate were purified by washing with aqueous sodium hydroxide solution followed by drying. 4-Vinylpyridine was purified by distillation before polymerization, as reported previously.[25] Other chemicals and solvents were used without further purification.

Poly(vinyl acetate) Containing a Pyridinium Group

Poly(vinyl acetate) containing a small amount of *N*-benzyl-4-vinylpyridinium chloride in the polymer chain (PVAc-*co*-VPC) was prepared as follows: Copolymer of vinyl acetate with a small amount of 4-vinylpyridine (PVAc-*co*-VP) was prepared by free-radical copolymerization of vinyl acetate with a prescribed small amount of 4-vinylpyridine using 2,2′-azobisisobutyronitrile (AIBN) as an initiator in ethanol at 85–87°C for 12–21 h under a nitrogen atmosphere. The thus-obtained PVAc-*co*-VP was allowed to react with benzyl chloride in ethanol at 80°C for 4 h. The amount of benzyl chloride was set to be equimolar to 4-vinylpyridine contained in PVAc-*co*-VP. The resulting polymer (PVAc-*co*-VPC) was isolated by pouring the reaction mixture into water and was dried to constant weight. The composition of PVAc-*co*-VPC and the amount of the pyridinium group contained in the polymer were ascertained based on nitrogen and chlorine contents determined by elementary analyses of the polymer. For comparison, the homopolymer of vinyl acetate (PVAc) was prepared by free-radical polymerization of vinyl acetate using AIBN as an initiator at 65°C for 10 h.

Poly(vinyl acetate) Containing Methyl Acrylate and a Pyridinium Group

Poly(vinyl acetate) containing 16 mol % of methyl acrylate and a small amount of the pyridinium group in the polymer chain (PVAc-*co*-MA-*co*-VPC) was prepared as follows: A copolymer of vinyl acetate with 16 mol % of methyl acrylate and a prescribed small amount of 4-vinylpyridine (PVAc-*co*-MA-*co*-VP) was prepared by free-radical copolymerization of vinyl acetate, methyl acrylate, and 4-vinylpyridine using AIBN as an initiator in ethanol at 75–80°C for 10–28 h under a nitrogen atmosphere. The thus-obtained PVAc-*co*-MA-*co*-VP was allowed to react with benzyl chloride in ethanol at 80°C for 4 h. The amount of benzyl chloride was set to be equimolar to 4-vinylpyridine contained in PVAc-*co*-MA-*co*-VP. The resulting polymer (PVAc-*co*-MA-*co*-VPC) was isolated by pouring the reaction mixture into water and was dried to constant weight. The composition of PVAc-*co*-MA-*co*-VPC was determined as follows: The content of the pyridinium group was determined based on the chlorine content obtained from elementary analyses. The molar ratio of the unit of vinyl acetate to that of methyl acrylate was determined based on the ratio of acetyl protons (appearing at δ 1.84 ppm) to methoxyl protons (appearing at δ 3.66 ppm) that was obtained from the ^{1}H-NMR spectrum. Acetyl and methoxyl protons were regarded to be derived from the monomer units of vinyl acetate and methyl acrylate, respectively.

For comparison, a copolymer of vinyl acetate containing 16 mol % of methyl acrylate that did not contain the pyridinium group at all (PVAc-*co*-MA) was prepared by free-radical copolymerization of vinyl acetate with methyl acrylate using AIBN as an initiator in a similar manner.

Degradation of Polymers When Placed in an Aeration Tank of Sewage Works

Sheets of PVAc-*co*-VPC and PVAc-*co*-MA-*co*-VPC were prepared by a conventional casting method us-

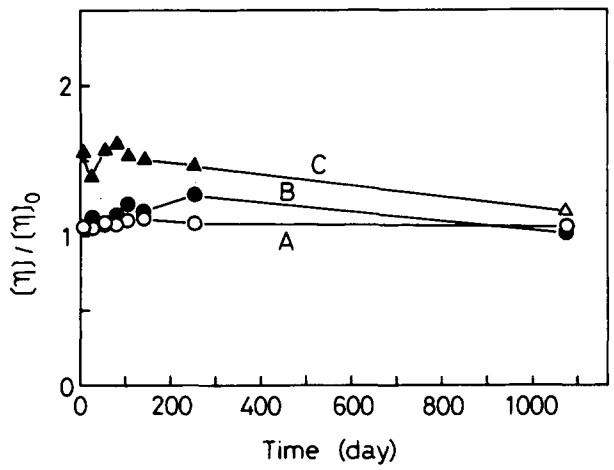

Figure 1 Ratio of the intrinsic viscosity of PVAc-*co*-VPC recovered after placing in an aeration tank of sewage works to that before the biological treatment. Content of the pyridinium group (mol %): (A) 0; (B) 1.6; (C) 3.9. Intrinsic viscosity of the polymer determined in toluene at 25°C before the treatment (dL/g): (A) 0.212; (B) 0.184; (C) 0.188.

ing acetone as the solvent. The sheets of 2.5 cm wide, 3.5 cm long, and 0.5 mm thick were placed in a cage made of 100-mesh nylon net, and the cage was placed in an aeration tank of Kawamata Sewage Works of Osaka Prefecture by hanging with a rope. After a prescribed time, samples of the polymer sheets were taken from the aeration tank, washed with deionized water, and dried to constant weight and then submitted for the analyses.

Analytical Methods

Elementary analyses were performed at the Elemental Analyses Center of Kyoto University. Proton NMR spectra were recorded using deuteriodimethylformamide [$DCON(CD_3)_2$] as a solvent on a General Electric QE-300 spectrometer. Infrared spectra were obtained with a Shimadzu FTIR-4100 spectrophotometer.

The intrinsic viscosity of PVAc-*co*-VPC and PVAc was measured using toluene as the solvent at 25°C. The molecular weight of the polymer was estimated based on the relationship between molecular weight and intrinsic viscosity.[26] The intrinsic viscosity of PVAc-*co*-MA-*co*-VPC and PVAc-*co*-MA was measured using a 1 : 1 (vol/vol) mixture of toluene and methanol as the solvent at 25°C. The intrinsic viscosity of PVAc-*co*-MA-*co*-VPC containing 20.4 mol % of the pyridinium group was measured in the presence of 1 g/dL of magnesium chloride.

A gel permeation chromatogram of poly(vinyl acetate) containing the pyridinium group was obtained using a Shimadzu LC-10AD high-performance liquid chromatograph system with an RID-6A refractive index detector and a Shimpack GPC-803D as the column at 30°C. Dimethylformamide was used as the eluate.

RESULTS AND DISCUSSION

Biodegradability of Poly(vinyl acetate) Containing a Pyridinium Group

Biodegradability of poly(vinyl acetate) containing a small amount of *N*-benzyl-4-vinylpyridinium chloride in the polymer chain (PVAc-*co*-VPC) was investigated. Sheets of the polymer of 2.5 cm wide, 3.5 cm long, and 0.5 mm thick were placed in an aeration tank of domestic sewage works. After a prescribed time, the polymer was taken from the aeration tank, washed with deionized water, and dried to constant weight. The intrinsic viscosity and gravimetric weight of the recovered polymer were measured and compared with those observed before the biological treatment. For reference, control experiments were also performed using a homopolymer of vinyl acetate that did not contain the pyridinium group at all. Figure 1 shows the ratio of the intrinsic viscosity of PVAc-*co*-VPC recovered after placing in the aeration tank to that before the biological treatment as a function of the treatment time. Figure 2 shows the weight reduction of PVAc-*co*-VPC during the biological treatment.

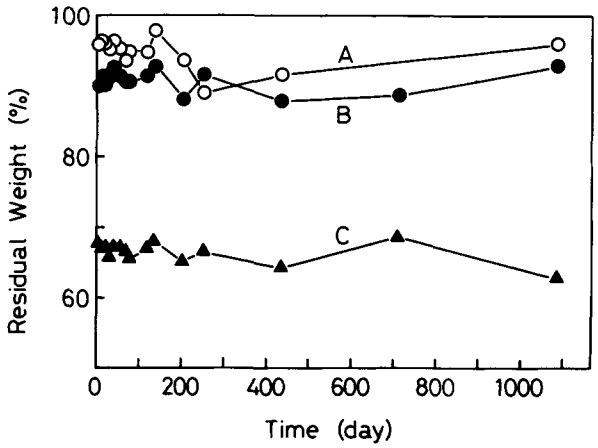

Figure 2 Weight reduction of PVAc-*co*-VPC during placing in an aeration tank of sewage works. Content of the pyridinium group (mol %): (A) 0; (B) 1.6; (C) 3.9. Intrinsic viscosity of the polymer determined in toluene at 25°C before the treatment (dL/g): (A) 0.212; (B) 0.184; (C) 0.188.

In the control experiments using a homopolymer of vinyl acetate (PVAc), a change of intrinsic viscosity as well as that of gravimetric weight were not very significant even after 1072 days of the treatment, as can be seen in Figures 1(A) and 2(A).

On the other hand, PVAc-*co*-VPC containing 3.9 mol % of the pyridinium group showed a significant reduction in gravimetric weight during the biological treatment, as can be seen in Figure 2(C). After 7 days of the treatment, e.g., the polymer showed a 32% reduction in gravimetric weight. Comparison of Figure 2(B) and (C) indicates an obvious increase of the rate of weight reduction with the content of the pyridinium group in PVAc-*co*-VPC. The result would suggest that incorporation of the pyridinium group into the polymer chain improved the biodegradability of poly(vinyl acetate). Unexpectedly, however, a further weight reduction was not observed after this period of the treatment. In other words, a tendency of the uppermost limit of the weight reduction was observed in the degradation of PVAc-*co*-VPC by activated sludge.

Chlorine was predominantly removed from PVAc-*co*-VPC at the early period of the biological treatment. For example, elementary analysis of PVAc-*co*-VPC containing 3.9 mol % of the pyridinium group showed the presence of 1.51% chlorine before the treatment. However, chlorine was not detected in the residual polymers recovered after 28 and 715 days of the treatment. Disappearance of chlorine indicates a loss of the pyridinium group. The uppermost limit of weight reduction during the treatment [Fig. 2(C)] could be attributed to the absence of the pyridinium group in the residual polymer. Based on these observations, we became inclined to consider that the presence of the pyridinium group is essentially necessary for the degradation of PVAc-*co*-VPC by activated sludge.

Although chlorine disappeared from PVAc-*co*-VPC at the early period of the biological treatment, nitrogen remained in the residual polymers recovered after the treatment. For example, elementary analysis of PVAc-*co*-VPC containing 3.9 mol % of the pyridinium group showed the presence of 0.84% nitrogen before the biological treatment and a remainder of 0.33 and 0.68% nitrogen after 28 and 713 days of the treatment, respectively. The presence of nitrogen and the absence of chlorine could suggest that the pyridyl group was included in the residual polymer recovered after the biological treatment and that the presence of the pyridyl group is not very helpful for the improvement of biodegradability of poly(vinyl acetate). The presence of the pyridinium group appears to be desirable for the improvement of biodegradability of poly(vinyl acetate).

Figure 3 shows gel permeation chromatograms of the homopolymer of vinyl acetate (PVAc) recorded before and after the biological treatment. A detectable change was not observed even after 715 days of the treatment. The result appears to be consistent with the observations shown in Figures 1(A) and 2(A). In the absence of the pyridinium group, biodegradation of poly(vinyl acetate) is quite difficult.

On the other hand, gel permeation chromatograms of PVAc-*co*-VPC containing 3.9 mol % of the pyridinium group recorded before and after the biological treatment supported the degradation during the treatment (Fig. 4). However, Figure 4 indicates predominant degradation of a low molecular weight fraction. The result appears to be consistent with the observations shown in Figure 1(B) and (C), i.e., the intrinsic viscosity of polymers recovered after the biological treatment was larger than that observed before the treatment. For example, the intrinsic viscosity of PVAc-*co*-VPC containing 3.9 mol % of the pyridinium group recovered after 7 days of the treatment was 1.6 times larger than that before the treatment [Fig. 1(C)]. Degradation of the low molecular weight fraction appears to be easier than of the high molecular weight fraction.

Since there are many enzymes that catalyze hydrolysis of the ester linkage, it was anticipated that the acetoxyl group of the unit of vinyl acetate con-

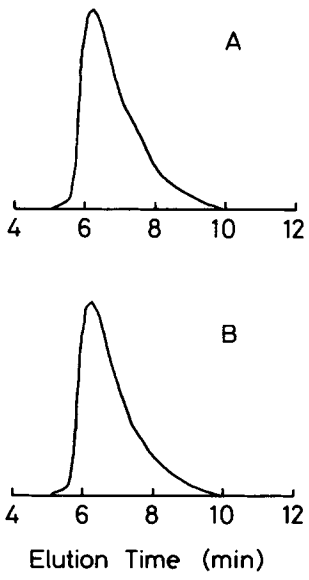

Figure 3 Gel permeation chromatogram of homopolymer of vinyl acetate: (A) before the biological treatment; (B) after placing in an aeration tank of sewage works for 715 days.

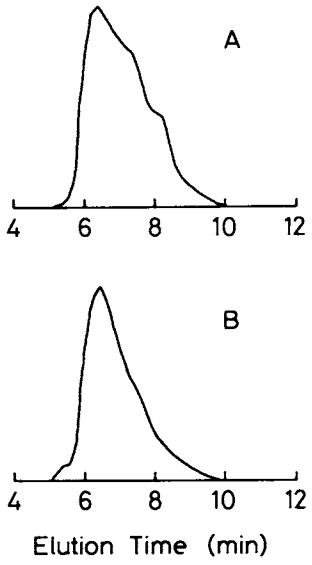

Figure 4 Gel permeation chromatogram of PVAc-*co*-VPC containing 3.9 mol % of the pyridinium group: (A) before the biological treatment; (B) after placing in an aeration tank of sewage works for 715 days.

tained in PVAc-*co*-VPC underwent the hydrolysis reaction during the biological treatment and was converted to the hydroxyl group. However, infrared spectra of the polymer recovered from the aeration tank after the biological treatment for 431 days did not exhibit the presence of the hydroxyl group in the recovered polymer sample. Hydrolysis of the ester linkage of PVAc-*co*-VPC is not plausible during the biological treatment.

Biodegradability of Poly(vinyl acetate) Containing Methyl Acrylate and a Pyridinium Group

As a trial of further improvement of the biodegradability through partial modification of the chemical structure, we attempted to incorporate an additional promoting component into the polymer chain and prepared poly(vinyl acetate) containing 16 mol % of methyl acrylate and a small amount of the pyridinium group (PVAc-*co*-MA-*co*-VPC). Methyl acrylate was employed as a promoting component for the biodegradation, because poly(methyl methacrylate) containing the pyridinium group showed significant biodegradability[22] and a similar phenomenon was anticipated for poly(methyl acrylate) containing the pyridinium group. Sample sheets of PVAc-*co*-MA-*co*-VPC were placed in an aeration tank of sewage works in a similar manner. Results are shown in Figures 5 and 6.

As can be seen in Figures 5(A) and 6(A), both

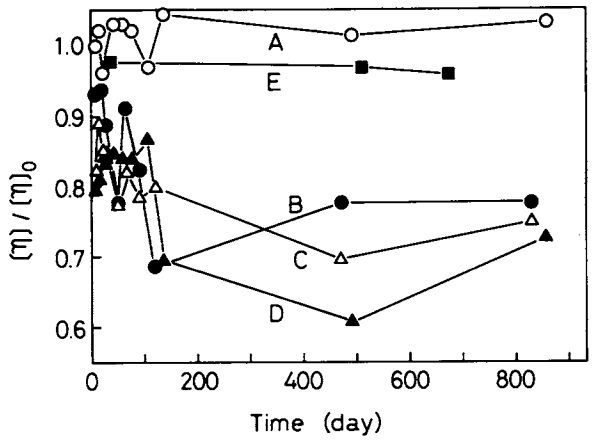

Figure 5 Ratio of intrinsic viscosity of PVAc-*co*-MA-*co*-VPC recovered after placing in an aeration tank of sewage works to that before the biological treatment. Content of the pyridinium group (mol %): (A) 0; (B) 0.9; (C) 2.8; (D) 7.9; (E) 20.4. Intrinsic viscosity of the polymer determined in a 1 : 1 (vol/vol) mixture of toluene and methanol at 30°C before the treatment (dL/g): (A) 0.229; (B) 0.315; (C) 0.340; (D) 0.264; (E) 0.210.

gravimetric weight and intrinsic viscosity of poly(vinyl acetate) containing 16 mol % of methyl acrylate free of the pyridinium group (PVAc-*co*-MA) did not show significant change during the biological treatment. In the absence of the pyridinium group, biodegradation of the copolymer of vinyl acetate with methyl acrylate was very difficult.

On the other hand, the gravimetric weight of

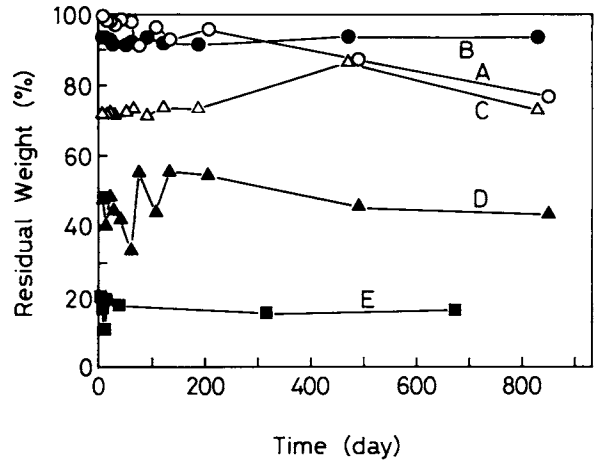

Figure 6 Weight reduction of PVAc-*co*-MA-*co*-VPC when placed in an aeration tank of sewage works. Content of the pyridinium group (mol %): (A) 0; (B) 0.9; (C) 2.8; (D) 7.9; (E) 20.4. Intrinsic viscosity of the polymer determined in a 1 : 1 (vol/vol) mixture of toluene and methanol at 30°C before the treatment (dL/g): (A) 0.229; (B) 0.315; (C) 0.340; (D) 0.264; (E) 0.210.

PVAc-*co*-MA-*co*-VPC was remarkably reduced during the biological treatment, as can be seen in Figure 6(B)–(E). After 7 days of the treatment, e.g., the rate of weight reduction was 7, 28, 52, and 84% in the case where PVAc-*co*-MA-*co*-VPC contained 0.9, 2.8, 7.9, and 20.4 mol % of the pyridinium group, respectively. The extent of the weight reduction for PVAc-*co*-MA-*co*-VPC (Fig. 6) increased with the content of the pyridinium group and was much larger than for PVAc-*co*-VPC (Fig. 2). Incorporation of methyl acrylate as an additional promoting component produced a further improvement of the biodegradability. These experimental results indicated that the weight reduction was more conspicuous when the content of the pyridinium group in the polymer chain was larger. Gel permeation chromatograms of the recovered polymer supported that the degradation was more violent when the polymer contained a greater amount of the pyridinium group. However, the weight reduction was remarkable only at the early period of the treatment and was not very significant after this. Thus, the weight reduction of PVAc-*co*-MA-*co*-VPC during the biological treatment also showed an uppermost limit.

Elementary analysis of PVAc-*co*-MA-*co*-VPC revealed that the pyridinium group was removed at the early period of the biological treatment. For example, PVAc-*co*-MA-*co*-VPC containing 7.9 mol % of the pyridinium group showed the presence of 2.84% chlorine before the biological treatment. However, chlorine was not detected after 28 and 492 days of the treatment. Disappearance of chlorine indicates the loss of the pyridinium group. The uppermost limit of weight reduction of PVAc-*co*-MA-*co*-VPC during the treatment could be attributed to the absence of the pyridinium group in the remaining polymer. PVAc-*co*-MA-*co*-VPC also showed the presence of 1.27% nitrogen before the biological treatment and the remainder of 0.27 and 1.09% nitrogen after 28 and 492 days of the treatment, respectively. The remainder of nitrogen suggests the presence of the pyridyl group in the polymer recovered from the aeration tank. The remainder of the pyridyl group appears to be not helpful for the biodegradation.

The intrinsic viscosity of PVAc-*co*-MA-*co*-VPC recovered from an aeration tank of sewage works was lower than that before the biological treatment (Fig. 5), making a sharp contrast to the case of PVAc-*co*-VPC (Fig. 1). The extent of the reduction of the intrinsic viscosity of PVAc-*co*-MA-*co*-VPC was in the following order: Figure 5(A) (0) < Figure 5(B) (0.9) < Figure 5(C) (2.8) < Figure 5(D) (7.9). Here, the content of the pyridinium group is shown in parentheses. The extent of the reduction of the intrinsic viscosity thus increased with the amount of the pyridinium group contained in the polymer. Gel permeation chromatograms of the recovered polymer indicated predominant degradation of low molecular weight fraction, as illustrated in Figure 7, where the polymer contained 7.9 mol % of the pyridinium group.

In contrast, however, PVAc-*co*-MA-*co*-VPC containing 20.4 mol % of the pyridinium group exhibited much less reduction of the intrinsic viscosity during the treatment [Fig. 5(E)]. On the other hand, the PVAc-*co*-MA-*co*-VPC showed a remarkable weight reduction during the treatment [Fig. 6(E)]. In this case, therefore, the low molecular weight fraction of the polymer was assumed to be removed severely from the sample sheet due to the vigorous degradation during the treatment and resulted in the remainder of polymer fractions of rather high molecular weight.

The unit of methyl acrylate contained in PVAc-*co*-MA-*co*-VPC was found to undergo predominant degradation over vinyl acetate during the biological treatment. For example, a sample of PVAc-*co*-MA-*co*-VPC contained 16.3 mol % methyl acrylate, 74.9 mol % vinyl acetate, and 7.9 mol % of the pyridinium group before the biological treatment. The polymer contained 0.9 mol % of the pyridyl group that did not react with benzyl chloride during the preparation procedure and remained unchanged in the polymer. After 492 days of the biological treatment, however,

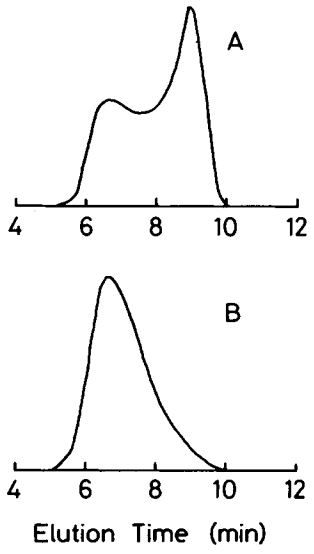

Figure 7 Gel permeation chromatogram of PVAc-*co*-MA-*co*-VPC containing 7.9 mol % of the pyridinium group: (A) before the biological treatment; (B) after placing in an aeration tank of sewage works for 208 days.

the polymer recovered from an aeration tank of sewage works contained 11.1 mol % methyl acrylate and 75.7 mol % vinyl acetate, but did not contain chlorine at all, i.e., the pyridinium group disappeared from the polymer. The content of the pyridyl group was estimated to be 13.2 mol % based on the assumption that all the nitrogen contained in the recovered polymer was involved in the pyridyl group. Based on the analytical results, the predominant degradation of methyl acrylate over vinyl acetate was concluded to have occurred during the biological treatment.

A Consideration on the Mechanism of Degradation of Poly(vinyl acetate) Containing the Pyridinium Group in the Polymer Chain

Based on the experimental observations, we considered a mechanism for the degradation of poly(vinyl acetate) containing a small amount of the pyridinium group in the polymer chain by activated sludge. The degradation is probably performed by microorganisms contained in activated sludge and must be catalyzed by some enzymes. Enzymes produced by microorganisms are classified into two categories, i.e., intracellular and extracellular enzymes. Degradation of poly(vinyl acetate) containing the pyridinium group used in this work must be catalyzed by extracellular enzymes, because the polymer is insoluble in water and cannot penetrate through the cell wall of microorganisms.

In this work, the biological treatment was performed using a polymer sheet of 0.5 mm thick. Only the surface part of the sheet would be exposed to activated sludge. The inside was perhaps not in contact with activated sludge, because microbial cells would be much larger than were the pores of polymer sheets. Determination of intrinsic viscosity, elementary analyses, and measurements of gel permeation chromatograms of the recovered polymer were performed for the whole sample and were not limited to the surface part. However, chlorine disappeared from the whole polymer sample during the early period of the biological treatment. The result indicates that the degradation is not limited to the surface part of the polymer sheet. The enzymes would have permeated the polymer sheets and catalyzed the degradation. The dramatic weight reduction illustrated in Figures 2(C) and 6(E) also suggests that the biodegradation is not limited to the surface part of the polymer sheet.

As described above, the uppermost limit of weight reduction was observed during the biological treatment of PVAc-*co*-VPC and PVAc-*co*-MA-*co*-VPC. Chlorine disappeared from these poly(vinyl acetates) containing the pyridinium group during the early period of the treatment. After this period, a further weight reduction was not significant, as can be seen in Figures 2 and 6. Therefore, the presence of the pyridinium group in poly(vinyl acetate) appeared to be necessary for the biodegradation.

Extracellular enzymes that catalyze degradation of poly(vinyl acetates) containing the pyridinium group are probably secreted by microorganisms contained in activated sludge. It is quite inconceivable that microorganisms that exist in the aeration tank of sewage works are familiar with such hydrophobic synthetic polymers as poly(vinyl acetate) containing the pyridinium group. Therefore, production of the enzymes must be induced in the cells of acclimatized microorganisms. Acclimatization of microorganisms to the hydrophobic synthetic polymers, as well as induced production of such enzymes in the acclimatized microbial cells, is probably stimulated by the polymer and would be facilitated by the capture of microbial cells by the polymer or contact of the cells with the polymer surface.

As reported in previous publications, insoluble pyridinium-type polymers capture microbial cells in a living state and are of wide application in the field of biotechnology and water purification.[24] Therefore, it is quite conceivable that incorporation of the pyridinium group improved the affinity of poly(vinyl acetate) to microbial cells and facilitated the acclimatization of microorganisms to the polymer, as well as induced production of the enzymes that catalyze the degradation. As a result, incorporation of the pyridinium group would have improved the biodegradability of the polymer.

On the other hand, the pyridinium-type polymer is strongly hydrophilic. For example, uncrosslinked poly(*N*-benzyl-4-vinylpyridinium chloride) is hygroscopic.[27] Crosslinked poly(*N*-benzyl-4-vinylpyridinium chloride) is insoluble but swells well in water.[28] Incorporation of the pyridinium group into a hydrophobic synthetic polymer enhances the hydrophilicity and would facilitate the enzymes to permeate the polymer sheet and promote the biodegradation. Therefore, it is quite conceivable that extracellular enzymes produced by microorganisms permeate the polymer sheets and catalyze the degradation. Further research is required to elucidate mechanisms of the biodegradation.

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