Notes

Synthesis of Photodegradable Polymers Having Biodegradability and Their Biodegradations and Photolysis

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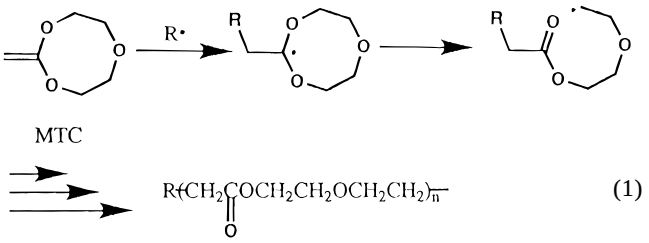
Introduction

Photodegradable polymers have been used for can carriers, multifilms for agriculture, packing materials, and so on. These photodegradable polymers are degraded to low molecular weight by light and lose their shapes, but they have little biodegradability after photolysis.[1,2] This is a major problem of photodegradable polymers.

We reported polymerization of 2-methylene-1,3,6-trioxocane (MTC) polymerized via ring-opening by a radical initiator to obtain a poly(ester−ether) (eq 1) and



(1)

found that this poly(ester−ether) was degraded by an enzyme.[3] In addition, we found that MTC copolymerized with vinyl monomers such as styrene, methyl methacrylate, and vinyl acetate to produce vinyl polymers containing the ester−ether group and that these copolymers were degraded by enzyme.[3]

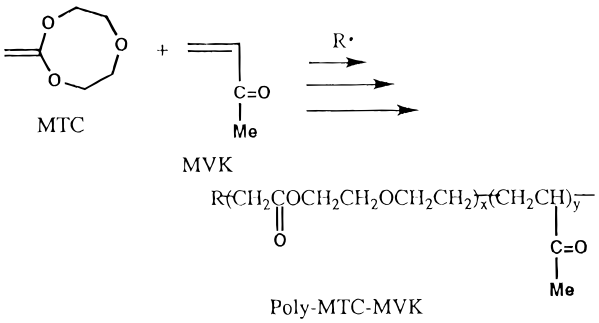
On the other hand, poly(vinyl ketones) are known as photodegradable polymers.[4,5] Photolysis of copolymers of these vinyl ketones and vinyl monomers were studied.[6−9]

We carried out radical copolymerization of MTC with methyl vinyl ketone (MVK) in order to impart biodegradability and photodegradability. We report here the copolymerization of MTC with MVK, enzymatic degradation of the copolymers before and after photolysis, and photolysis of the copolymers.

Results and Discussion

MTC was synthesized according to our previous report.[3]

Copolymerization of MTC with MVK. The radical copolymerization of MTC with MVK was carried out in benzene using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator at 60 °C. All the IR spectra of the obtained copolymers showed the absorption around 1735 cm^{-1} assigned to the ester group and the absorption around 1710 cm^{-1} assigned to the ketone group. All the ^1H NMR spectra showed a signal at 4.22 ppm, corresponding to the methylene proton ($COOCH_2$). These spectral data show that MTC undergoes a ring-opening reaction during copolymerization with MVK and that ester−ether moieties were incorporated into the backbone of poly-MVK (eq 2). The results of the copolymerizations



(2)

are summarized in Table 1. There is the tremendous difference in reactivity of MTC and MVK monomers. MVK is very active to the radicals. On the other hand, MTC is less active to radicals than MVK because MTC is a vinyl ether and the α-carbon of MTC is a quaternary carbon. Therefore, even if the feed ratio of MTC is high, much MVK is introduced into the copolymer, and when the feed ratio of MTC increases, the molecular weight of the copolymer decreases. The C=C double bond of MTC is electron sufficient because MTC is a vinyl ether, and the C=C double bond of MVK is electron deficient because the carbonyl group that is electron withdrawing bonds to the C=C double bond. Therefore, MTC and MVK may be bonded alternately in the copolymers. The copolymer with a high degree of introduction of MVK has a high possibility that MVK is next to MTC, and the copolymer that has a high degree of introduction of MTC has a high possibility that MTC is next to MVK.

Biodegradability Assay of the Copolymers. The biodegradability of the copolymers was assayed by the rate of solubilization when lipase acted on them. This enzyme assay system did not necessarily involve complete degradation into the constituent units. The biodegradability assay of the poly-MTC−MVK copolymer was also simultaneously run on polycaprolactone (PCL). The biodegradability of the poly-MTC−MVK copolymer was assayed by a total organic carbon (TOC) analyzer when lipase acted on it. Poly-MTC−MVK was hydrolyzed by *Rhyzopus arrhizus* lipase. The results are shown in Table 2.

The solubilization percentages of poly-MTC−MVK (x:y = 68:32) were calculated according to eq 3.

The value when poly-MTC−MVK (x:y = 68:32) degraded completely is

$$20000\ (\text{mg/L}) \times (12 \times 6 \times 0.68 + 12 \times 4 \times 0.32)/(130 \times 0.68 + 70 \times 0.32) = 11610\ (\text{ppm}) \quad (3a)$$

The molecular weight of MTC is 130, and the molecular weight of MVK is 70. Experimental data are

$$3545 - 119 - 41 = 3385\ (\text{ppm}) \quad (3b)$$

The solubilization percentage of poly-MTC−MVK (x:y

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Table 1. Copolymerization of MTC with MVK[a]

feed ratio MTC/MVK (mol/mol)	solv:PhH (equiv)	time (h)	yield (%)	copolymer composition[d] *x*:*y*	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$	T_m[f] (°C)
1/1	3	48	66[b]	28:72	14 000	2.5	−12
7/3	2	48	56[b]	43:57	17 000	5.2	−29
9/1	2	48	35[b]	68:32	14 000	4.3	−45
9.5/0.5	2	72	51[c]	82:18	5 200	4.7	−52

[a] Initiator: AIBN, 2 mol %. [b] Insoluble part in ether. [c] Insoluble part in *n*-hexane. [d] Estimated by ^{1}H NMR. [e] Estimated by GPC (based on PSt). [f] Measured by DSC at the heating rate of 8 °C/min.

Table 2. Hydrolysis of Poly-MTC−MVK by Lipase[a]

	TOC (ppm)				
	poly-MTC−MVK (*x*:*y*)				
	28:72	43:57	68:32	82:18	PLC
sample	645	2024	3545	10800	2025
substrate control	147	176	119	520	68

[a] Enzymatic control: 41 ppm.

Table 3. Summary of Molecular Weight Data on Degraded Poly-MTC−MVK[a]

poly-MTC−MVK *x*:*y*	GPC data					
	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n/\bar{M}_{n_0}$[c]	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n/\bar{M}_{n_0}$
28:72	1400	4.7	0.1	800	3.8	0.057
43:57	1900	4.7	0.11	1000	4.6	0.059
68:32	2500	5.7	0.18	1200	5.5	0.086
82:18	3800	3.1	0.73	1700	4.2	0.33

[a] Temp: 50 °C. [b] Irradiation time: 2 h. [c] $\bar{M}_{n_0}$: Initial number-average molecular weight. [d] Irradiation time: 6 h.

= 68:32) is

$$3385/11610 \times 100 = 29(\%) \qquad (3c)$$

The solubilization percentages of poly-MTC−MVK with copolymer composition of 28:72, 43:57, 68:32, and 82:18 were 4, 16, 29, and 92%, and that of PCL was 14%. The higher the molar ratio of *x* in the copolymer, the higher was the solubilization percentage of the copolymer. The lower the molecular weight of the copolymer produced is, the more likely is the copolymer to be apt to be attacked by enzyme because the steric hindrance decreases and the degree of the degradation of the copolymer may increase.

Photolysis of the Copolymers. The photolysis of the copolymers was assayed by the decrease in number average molecular weight ($\bar{M}_n$) of the copolymers after photoirradiation. The decrease of $\bar{M}_n$ of the copolymers was measured by gel permeation chromatography (GPC). The results are shown in Table 3. $\bar{M}_n$ decreased with the passage of irradiation time in all the copolymers. The higher the molar ratio of *y* in the copolymers, the lower $M_n/\bar{M}_{n_0}$ was at each irradiation time.

Biodegradation of the Copolymers after Photolysis. The biodegradability of the copolymers after the photolysis was assayed by the rate of solubilization when lipase acted on them.

The biodegradability of poly-MTC−MVK copolymer was assayed by a TOC analyzer when lipase acted on it. Poly-MTC−MVK was hydrolyzed by *R. arrhizus* lipase. All the reactants by lipase and all the controls had to be filtered through a filter with a pore size of 0.2 μm before analysis. However, the samples and substrate controls could not be filtered because they cause emulsification in poly-MTC−MVK (*x*:*y* = 28:72, 43:57, 68:32). Therefore, the biodegradability of only poly-MTC−MVK (*x*:*y* = 82:18) was assayed by TOC. The results are shown in Table 4. The solubilization percentage of poly-MTC−MVK (*x*:*y* = 82:18) was 82% at an irradiation time of 2 h and 59% at an irradiation time of 6 h. In other words, the solubilization percentage of poly-MTC−MVK (*x*:*y* = 82:18) was lower at an irradiation time of 6 h than at an irradiation time of 2 h. The solubilization percentage of poly-MTC−MVK (*x*:*y* = 82:18) was also lower at an irradiation time of 2 h than at an irradiation time of 0 h. This was caused by the difference in substrate control. The amount of substrate control of poly-MTC−MVK (*x*:*y* = 82:18) is higher at an irradiation time of 6 h than at an irradiation time of 2 h and is higher at an irradiation time of 2 h than at an irradiation time of 0 h. This behavior is caused by the intermolecular forces holding the copolymer molecules together at each irradiation time. Because the molecular weight of the copolymers decreases with photolysis, the intermolecular forces between the copolymers decrease. Therefore, the solubilities of the copolymers in water increase with photolysis, and substrate control increases. Consequently, it is thought that the solubilization percentages of the copolymers that were hydrolyzed by lipase decreased with photolysis.

Table 4. Hydrolysis of Poly-MTC−MVK (*x*:*y* = 82:18) by Lipase after Irradiation[a]

	TOC (ppm)	
	2 h	6 h
sample	10225	9050
substrate control	885	2327

[a] Enzymatic control: 15.1 ppm.

Experimental Section

Materials. MTC was synthesized according to the previous report.[3] PCL ($\bar{M}_n$ = 40 000) chips were purchased from Union Carbide Corp. MVK was purchased from Tokyokasei Kogyo Co., Ltd., and used after distillation. AIBN was purchased from Tokyokasei Kogyo Co., Ltd. *R. arrhizus* lipase was purchased from SIGMA Co., Ltd. This lipase is type XI, 0.09 mL, 13.8 mg of protein (Biuret), and 405 000 units/mg of protein.

Copolymerization of MTC with MVK. The copolymerization of MTC with MVK [feed ratio: MTC/MVK = 1/1 (mol/mol)] was carried out as follows: in a 15 mL sealed polymerization tube, a mixture containing MTC (2.00 g, 1.54×10^{-2} mol), MVK (1.08 g, 1.54×10^{-2} mol), and benzene (8.2 mL) was maintained at 60 °C for 48 h. The resulting product was precipitated in ethyl ether. The precipitated material was dried under reduced pressure at 40 °C to give 2.04 g (66% yield) of the copolymer (poly-MTC−MVK); IR (neat): 2950, 2865, 1735, 1711, 1355, 1165, 1130 cm^{-1}.

Biodegradability Assay of Copolymers before Photolysis. The biodegradability of the poly-MTC−MVK copolymer was assayed by a TOC analyzer when lipase acted on it. The biodegradability assay of PCL was also simultaneously run on poly-MTC−MVK. The poly-MTC−MVK and PCL were formed into a membrane inside a test tube (inside diameter, 16.5 mm; height, 165 mm). The height of the entire membrane was 19 mm. The reaction mixture in poly-MTC−MVK contained 0.2 mL of 0.2 M phosphate buffer (pH 7.0), 20 mg of poly-MTC−MVK, and 0.2 mL of bottled *R. arrhizus* lipase dissolved in 6 mL of 0.02 M phosphate buffer in a total volume

of 1 mL. Substrate control in the absence of enzyme and enzyme control in the absence of substrate were also carried out. The biodegradability assay of PCL was carried out in the same way as for poly-MTC−MVK. The reaction mixture was shaken at 30 °C for 18 h. After the shaking, the water-soluble TOC concentration in the filtrate of the reaction mixture was measured with a Shimadzu TOC-5000 analyzer.

Photolysis of Copolymers and Biodegradability Assay of Copolymers after Photolysis. The irradiation was carried out in 1.1% benzene solution (solute, 50 mg; solvent, 5 mL) using a 300 W high-pressure mercury arc. The solutions in flask were stopped under atmosphere. After the irradiation, 4 mL of the benzene solution was used for the biodegradability assay. The 4 mL of benzene solution was subdivided into 2 mL portions. One portion was used for the sample and the other for the substrate control in the TOC analyzer. The biodegradability assay was carried out in the same manner as before irradiation. The remainder of the benzene solution (1 mL) was used for measurement of molecular weight and molecular weight distribution. The molecular weight and molecular weight distribution were determined using a TOSOH HLC-8020 GPC (column: TOSOH GMH_{HR}−L+GMH_{HR}−M) calibrated with polystyrene standards in chloroform solution. Thermal analysis of the copolymer was carried out by using a Seiko DSC 220C.

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