NOTE

Synthesis and Reactions of Polycarbonate with Pendant Vinyl Groups

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The alternating copolymerization of carbon dioxide and epoxide gives an aliphatic polycarbonate with high molecular weight.[1,2] This copolymerization reaction is general for epoxide; unsubstituted, monosubstituted, and disubstituted.[1,3] However, few examples have been reported for the synthesis of carbon dioxide–epoxide copolymer with functional pendant groups. We reported that a polycarbonate having hydroxyl groups can be synthesized *via* the copolymerization of trimethylsilyl glycidyl ether and carbon dioxide.[4]

The present article describes some of the results of our study on the application of the carbon dioxide–epoxide copolymer as a degradable functional polymer. The copolymerization of carbon dioxide and epoxide having a vinyl group was carried out, and the introduction of various functional groups into the copolymer thus obtained was examined utilizing the pendant groups.

EXPERIMENTAL

Materials

Butadiene monoxide (BMO) was prepared from butadiene through the bromohydrin according to the method reported by Winstein and Lucas.[5] Epoxides were dried and distilled over calcium hydride in nitrogen atmosphere. Commercial high purity carbon dioxide gas was used without further purification.

Copolymerization

Copolymerization was carried out using a diethylzinc–water (1 : 0.9) system as the catalyst in a stainless autoclave, as reported previously for the copolymerization of propylene oxide with carbon dioxide.[6] The reaction mixture was diluted with benzene, and washed with 1 N hydrochloric acid and then with water. The benzene layer containing the copolymer was added to methanol with stirring. The precipitated white copolymer was collected by filtration and then was freeze-dried from benzene solution.

Analysis for BMO–CO$_2$ copolymer: Calcd for C$_5$H$_6$O$_3$: C, 52.63%; H, 5.30%. Found: C, 53.24%, H; 5.97%.

Bromination of BMO–CO$_2$ Copolymer

For example, butadiene monoxide–carbon dioxide copolymer (BMO–CO$_2$ copolymer) (0.5 g) was dissolved in chloroform (100 ml) in a flask fitted with a magnetic stirrer. To the solution was added bromine (0.4 g) and the mixture was stirred for 150 min at room temperature. The reaction mixture was then concentrated and poured with stirring into methanol. The white precipitate was collected and dried; yield, 0.26 g.

Reaction of BMO–CO$_2$ Copolymer and trans-Dichloro(pyridine)(ethylene)platinum (II)

About 500 mg of PtCl$_2$(C$_2$H$_4$)Py[7,8] was added to a solution (30 ml) of BMO–CO$_2$ copolymer (150 mg) in chloroform and the mixture was stirred

at room temperature. After 3 h, the precipitation of brown powder was observed. The mixture was evaporated to dryness under reduced pressure. The solid residue was washed several times with chloroform to give an insoluble product; yield, 200 mg. *Anal.* Calcd for $(C_{10}H_{11}Cl_2NO_3Pt)_x$ *i.e.*, {O–CO–O–CH$_2$CH[(CH=CH$_2$)PtCl$_2$(C$_5$H$_5$N)]}$_x$: C, 26.16%; H, 2.42%; Cl, 15.44%; N, 3.05%; Ash, 45.97%. Found: C, 25.12%; H, 2.65%; Cl, 17.38%; N, 2.87%; Ash, 45.74%.

Analyses

Gel permeation chromatogram (GPC) was registered on a Toyo Soda high speed liquid chromatograph (model HLC 802 UR) equipped with four columns of porosity ratings 7000—3000 Å (two), 3000 Å (one) and 2000 Å (one). The average molecular weight was determined from the GPC curve on the basis of the calibration curve obtained by using standard polystyrene.

RESULTS AND DISCUSSION

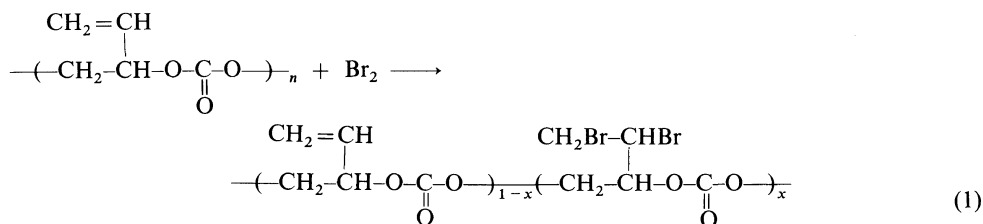### Synthesis of Polycarbonates with Pendant Vinyl Groups

Polycarbonate with pendant vinyl groups was synthesized by the copolymerization of carbon dioxide and butadiene monoxide (BMO). As shown in Table I, the copolymerization of carbon dioxide and butadiene monoxide gave the corresponding alternating copolymer in a good yield. Ternary copolymerization of carbon dioxide, propylene oxide (PO), and butadiene monoxide was conducted with equimolar amounts of the two epoxides. The product obtained was an alternating copolymer of carbon dioxide and epoxides. The reactivity of butadiene monoxide in the copolymerization with carbon dioxide was lower than that of propylene oxide. Ternary copolymerization made it possible to control the amount of pendant vinyl groups in the polycarbonate.

Bromination of Polycarbonate with Pendant Vinyl Groups

Since the haloalkyl group as a pendant group is considered to function as a precursor for the introduction of various functional groups to polycarbonate, the addition of bromine to the carbon-double bond of BMO–CO$_2$ copolymer was examined (eq 1).

$$
\begin{array}{c}
CH_2\!=\!CH \\
| \\
-\!(\!-CH_2\!-\!CH\!-\!O\!-\!\underset{\underset{O}{\|}}{C}\!-\!O\!-\!)\!-\!_n \ + \ Br_2 \ \longrightarrow
\end{array}
$$

$$
\begin{array}{cc}
CH_2\!=\!CH & CH_2Br\!-\!CHBr \\
| & | \\
-\!(\!-CH_2\!-\!CH\!-\!O\!-\!\underset{\underset{O}{\|}}{C}\!-\!O\!-\!)\!-_{1-x}(\!-CH_2\!-\!CH\!-\!O\!-\!\underset{\underset{O}{\|}}{C}\!-\!O\!-\!)\!-_x
\end{array}
\qquad (1)
$$

Table I. Copolymerization of carbon dioxide and butadiene monoxide[a]

Epoxide[b]		Time	Copolymer			
M$_1$	M$_2$	days	Yield[c]	f_{CO_2}[d, e]	M$_1$/M$_2$[e]	$[\eta]$[f]
g	g		g	mol%	mole ratio	10^2 cm^3 g^{-1}
BMO (8.8)	—	4	5.9	49	—	1.52
BMO (4.4)	PO (3.6)	5	3.7	50	0.56	1.41

[a] Catalyst, ZnEt$_2$–H$_2$O (1 : 0.9), 14 mol% with respect to epoxide; solvent, 1,4-dioxane (40 ml); CO$_2$ pressure, 40 atm (SI-unit : 1 atm = 101,325 KN·m^{-2}); temperature, 35°C.

[b] Epoxide; BMO, butadiene monoxide; PO, propylene oxide. M$_1$ and M$_2$, equimolar amount.

[c] Methanol-insoluble portion.

[d] Amount of CO$_2$ (oxycarbonyl-groups content) in the copolymer.

[e] Determined by ^{1}H NMR spectra.

[f] Measured at 30°C in benzene solution.

The ^{1}H NMR spectra of the starting copolymer and that of the reaction product (Figure 1) confirmed the successful bromination of the polycarbonate. In the ^{1}H NMR spectrum of BMO–CO$_2$ copolymer (Figure 1, A), the peaks at 3.8—4.4 ppm, 5.0—5.5 ppm, and 5.5—6.0 ppm were assigned to oxymethylene groups (a), an overlap of oxymethine (b) and methylene groups on the side chain (d), and methine groups on the side chain (c), respectively. In the spectrum of the reaction product with bromine, a new signal appeared at 3.5—4.0 ppm (h), demonstrating formation of a bromomethyl group (–CH$_2$Br) (Figure 1, B). The extent of bromination was determined by a comparison of the signal intensities of the methylene proton in bromomethyl group (h) with that of the methine proton in the unreacted vinyl group (c).

Additional confirmation of the successful bromination of the polycarbonate was provided by IR spectra, in which the band due to the stretching vibrations of the vinyl groups present in the starting copolymer at 1640 cm^{-1} was reduced in the reaction product.

The extent of bromination of BMO–CO$_2$ copolymer increased with prolonged reaction time and with an increase in the amount of bromine reacted (Table II). However, in the reaction involv-
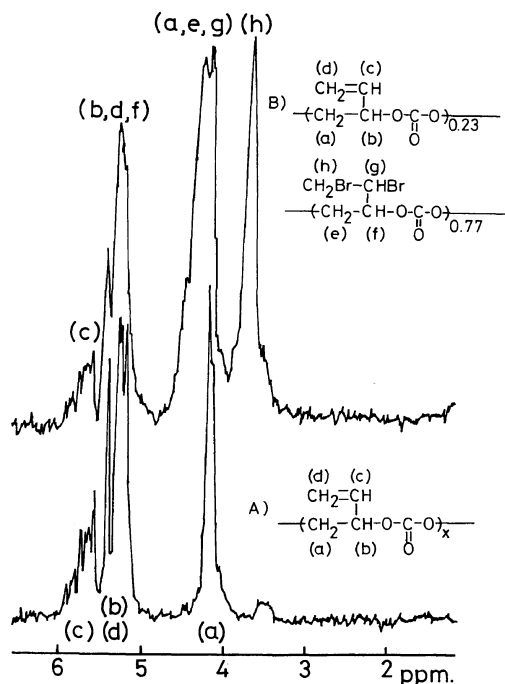
Figure 1. ^{1}H NMR spectra of A) Butadiene monoxide–carbon dioxide copolymer, and B) Brominated BMO–CO$_2$ copolymer (Table II, Run 4); in CDCl$_3$.

Table II. Addition of bromine to butadiene monoxide-carbon dioxide copolymer (BMO–CO$_2$ copolymer)[a]

Run	BMO–CO$_2$ Copolymer[b] g	Bromine g(mol%)[c]	Time h	Yield[d] g	Extent of bromination[e] ^{1}H NMR mol%	E.A. mol%	$M_{GPC} \times 10^{-4f}$
1	0.5	0.4 (50)	2.5	0.26	26	26	2.5[g]
2	0.5	0.4 (50)	12	0.40	34	40	1.1
3	1.1	1.6 (100)	60	1.10	77	56	0.55
4	1.1	1.6 (100)	260	0.85	77	56	0.45[h]
5	0.5	1.6 (200)	27	0.30	100	—	0.27

[a] In chloroform at room temperature.
[b] $M_{GPC} = 10 \times 10^4$, $[\eta] = 1.28 \times 10^2$ cm^3 g^{-1} (measured at 30°C in benzene solution).
[c] Mol% with respect to carbon-carbon double bond.
[d] Methanol insoluble portion.
[e] Determined by ^{1}H NMR spectra and elementary analyses (E.A.), respectively.
[f] On the basis of the calibration curve obtained by using standard polystyrene.
[g] $[\eta] = 0.11 \times 10^2$ cm^3 g^{-1} (measured at 30°C in benzene solution).
[h] $M_n = 0.53 \times 10^4$ (measured in benzene solution by a vapor pressure osmometer).

ing a large amount of bromine, the amount of bromine in the product from elemental analysis was not in good agreement with the calculated value from ^1H NMR spectrum, probably as a result of certain side reactions. The molecular weight of the brominated BMO–CO$_2$ copolymer, as determined by gel permeation chromatography (M_{GPC}), significantly decreased from that of BMO–CO$_2$ copolymer in the bromination. Intrinsic viscosity in benzene solution of the BMO–CO$_2$ copolymer also decreased following bromination (Table II, Run 1).

Since the copolymerization of carbon dioxide and epoxide with a substituent containing halogen, such as epichlorophydrin, has been difficult so far,[1] the procedure reported here is a good method for the introduction of a halogen to an epoxide–CO$_2$ copolymer.

In an attempt to introduce an acetyl group to the brominated copolymer, the reaction of the co-polymer in acetonitrile with potassium acetate was carried out in the presence of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) at room temperature for 24 h. This, however, resulted in the formation of cyclic carbonate. The attempted quaternization of the brominated copolymer with a large amount of triethylamine in chloroform also gave cyclic carbonate.

Synthesis of Polymer–Metal Complex

A wide variety of platinum (II) complexes has been investigated for use as antitumor drugs.[9] Taking advantage of the pendant olefinic group of the BMO–CO$_2$ copolymer, the synthesis of a poly-carbonate having a platinum complex at the side chain was carried out, to obtain a polymer–drug combination which would slowly release platinum complex by the biochemical hydrolysis of the carbonate linkage of the main chain.[10]

$$\begin{array}{c} CH=CH_2 \\ | \\ -(CH_2-CH-O-\underset{\underset{O}{\|}}{C}-O)_n- \end{array} + \ trans\text{-}[PtCl_2(C_2H_4)Py]$$

$$\xrightarrow{-C_2H_4} \quad \begin{array}{cc} CH=CH_2 & [(CH=CH_2)PtCl_2Py] \\ | & | \\ -(CH_2-CH-O-\underset{\underset{O}{\|}}{C}-O)_{1-x}(CH_2-CH-O-\underset{\underset{O}{\|}}{C}-O)_x \end{array} \qquad (2)$$

The polymer having a pendant platinum (II) complex was prepared by treating trans-dichloro-(pyridine)(ethylene)platinum (II)[7,8] with BMO–CO$_2$ copolymer in a chloroform solution at room temperature for 3 h. The product obtained was insoluble in chloroform, benzene, dichloromethane and neutral water, but was soluble in 0.01 N aqueous ammonia. In this product, platinum is considered at least to some extent to be coordinated with the pendant vinyl group, since the formation of ethylene was detected in the gaseous phase of the reaction mixture by gas liquid chromatography.

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