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COPOLYMERIZATION OF CARBON DIOXIDE AND PROPYLENE OXIDE WITH ZINC CATALYSTS SUPPORTED ON CARBOXYL-CONTAINING POLYMERS

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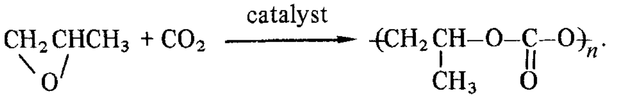
ABSTRACT

Polymer-supported zinc catalysts were prepared by the reaction of diethylzinc with polymers containing carboxyl groups. The catalysts were employed in the alternating copolymerization of carbon dioxide and propylene oxide to give poly(propylene carbonate) of high molecular weight. Copolymers of styrene and acrylic acid were shown to be better catalyst supports than poly(acrylic acid) and some other polymers. Maximum activity was achieved when the molar ratio of Zn/COOH was around unity. The yield and molecular weight of the polycarbonate rose with increasing reaction time. Higher reaction rates but lower molecular weights of the product were observed at elevated reaction temperatures.

INTRODUCTION

The utilization of carbon dioxide as a direct material for organic synthesis has received much attention in recent years. Carbon dioxide can be copolymerized with epoxides by metallic catalysts such as diethylzinc with the aid of additives, e.g., water or polyhydric alcohols to form aliphatic polycarbonates of high molecular weight [1] (Eq. 1):



$$\underset{\diagdown O \diagup}{CH_2CHCH_3} + CO_2 \xrightarrow{\text{catalyst}} (CH_2\underset{CH_3}{\underset{|}{C}}H-O-\underset{O}{\underset{\|}{C}}-O)_n . \qquad (1)$$

However, the yield of this reaction is still to be improved. One approach to more effective catalysts is to anchor the metal active center to some polymer support. The catalysts obtained in this way may have relatively high concentration of some serial structures with zinc heteroatom repeating units; this was believed to be necessary for the catalysis [2]. An attempted preparation of such catalysts and the effects of the reaction conditions on the yield and molecular weight of the polycarbonate from the copolymerization of carbon dioxide and propylene oxide in the presence of the prepared catalysts are described in this article.

EXPERIMENTAL

Materials

Commercial carbon dioxide gas was introduced into an autoclave directly from a gas cylinder without further purification. Commercial propylene oxide (PO) and dioxane (DOX) were purified by the usual procedures. Diethylzinc was prepared from the reaction of the Zn-Cu couple with ethyl iodide, then purified by vacuum distillation. The activity of $ZnEt_2$ was determined by measuring the volume of gas evolved on treating it with an excess of water.

Styrene-acrylic acid copolymers were obtained by the copolymerization of various ratios of the two monomers in toluene with benzoyl peroxide as initiator. The carboxyl content was determined by measuring the volume of ethane gas evolved on treatment of the copolymer with an excess of $ZnEt_2$.

Catalyst Preparation and CO_2/PO Copolymerization

$ZnEt_2$ was added to a dioxane solution of a styrene-acrylic acid copolymer to form a turbid slurry which was stirred until the ethane gas evolution ceased. The catalyst slurry so obtained was then transferred to a 100-mL autoclave, to which was added propylene oxide and then CO_2 to a pressure of 50-60 atm. After reaction at a given temperature for the desired period, the reaction mixture was diluted with benzene, washed with dilute HCl, then with water, and subjected to vacuum drying.

Characterization of the Polycarbonate

The IR spectra of the film samples were recorded with a PE 325 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL FX-90Q spectrometer in $CDCl_3$ solutions. Assignment of the spectral bands was done according to Ref. 3. Intrinsic viscosities were measured in benzene at 35°C by using an Ubbelohde viscometer. The average molecular weight of polycarbonate was calculated according to the following equation [4]:

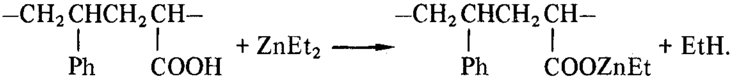
$$[\eta]\ (\mathrm{dL/g}) = 1.11 \times 10^{-4}\, \bar{M}_n^{\,0.8}. \tag{2}$$

RESULTS AND DISCUSSION

The $ZnEt_2$/PSAA or PAA systems were found to have rather high catalytic activity for the copolymerization of carbon dioxide and propylene oxide. Typical results of experiments are listed in Table 1.

Polymer Supports for the Catalysts

According to previous reports [2], effective catalytic systems for CO_2/PO copolymerization may comprise an organometallic compound, such as diethylzinc, as well as an additive possessing at least two labile hydrogen atoms in the molecule. In order to prepare such systems, several kinds of polymers containing hydroxyl or carboxyl groups, such as poly(vinyl alcohol), amylose, poly(styrene-*co*-maleic acid), poly(acrylic acid) (PAA), and poly(styrene-*co*-acrylic acid) (PSAA), were used to react with $ZnEt_2$. PSAA and PAA were found to be better supports than the other polymers because PAA and PSAA are soluble in dioxane, which facilitated their reaction with $ZnEt_2$. As the reaction proceeded, a gel-like precipitate emerged from the homogeneous polymer solution, while a quantitative amount of ethane gas was evolved:



$$-CH_2\underset{\mathrm{Ph}}{\underset{|}{CH}}CH_2\underset{\mathrm{COOH}}{\underset{|}{CH}}- + ZnEt_2 \longrightarrow -CH_2\underset{\mathrm{Ph}}{\underset{|}{CH}}CH_2\underset{\mathrm{COOZnEt}}{\underset{|}{CH}}- + EtH. \tag{3}$$

The other polymers were only soluble in such solvents as *N,N*-dimethylformamide that did not favor CO_2/PO copolymerization [2, 5].

In addition, $ZnEt_2$/PSAA systems were superior to $ZnEt_2$/PAA in that

TABLE 1. Copolymerization of CO_2 and PO[a]

	Catalyst composition		Reaction conditions		Copolymer	
Expt	St/AA, mol/mol	Zn/COOH, mol/mol	Time, h	Temperature, °C	Yield, g/mol	$\bar{M}_n \times 10^{-4}$
231′	0/1	1.0	14	60	161	5.7
230′	1/2	1.0	17	60	579[b]	
414	1/1	1.0	16	60	700	3.1
235	2/1	1.1	16	60	689[c]	8.1
248	1/1	0.65	24	60	Trace	
228	1/1	0.8	18	60	70	
228′	1/1	1.05	25	60	1 003	5.0
229′	1/1	1.55	23	60	244	4.0
233	1/1	1.2	16	60	493	2.1
243	1/1	1.0	48	60	1 333[d]	14.5
402	1/1	1.0	84	60	1 693	15.7
239′	1/1	0.95	48	40	841	20.5
408′	1/1	1.0	18	80	1 500	6.2
409	1/1	1.0	48	80	2 000	8.4

[a] The reaction was carried out in 20 mL of dioxane using 7 mL of PO and 3-4 mmol of Zn catalyst.

[b] MeOH insoluble 75.7%.

[c] MeOH insoluble 77.6%.

[d] MeOH insoluble 86.9%; analyzed C, 49.4%; H, 6.43%.

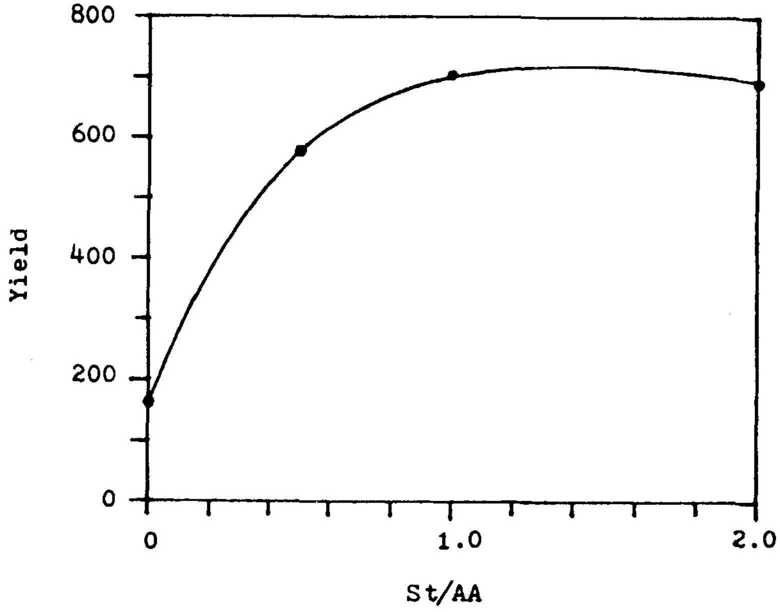


FIG. 1. Effect of support composition on the yield in grams of poly(propylene carbonate)/mol of Zn.

they gave higher yields for the CO_2/PO copolymerization (Fig. 1). Furthermore, PSAA was less hygroscopic and thus easier to handle than PAA.

Effects of Copolymerization Conditions on Catalytic Activity and Molecular Weight of the Products

Like that of the $ZnEt_2/H_2O$ system, the catalytic activity of the $ZnEt_2$/PAA or PSAA systems strongly depended upon the catalyst composition, as shown in Fig. 2. Maximum polycarbonate yield was achieved when the molar ratio of Zn/COOH was around unity. This was probably related to the dependence of the metal coordination status on the ratio, as in the case of the $ZnEt_2/H_2O$ system [3].

The $ZnEt_2$/PAA and the PSAA systems exhibited a similar pattern of reaction time dependence of the product yield and molecular weight as other systems reported. During the reaction, both the product yield and molecular

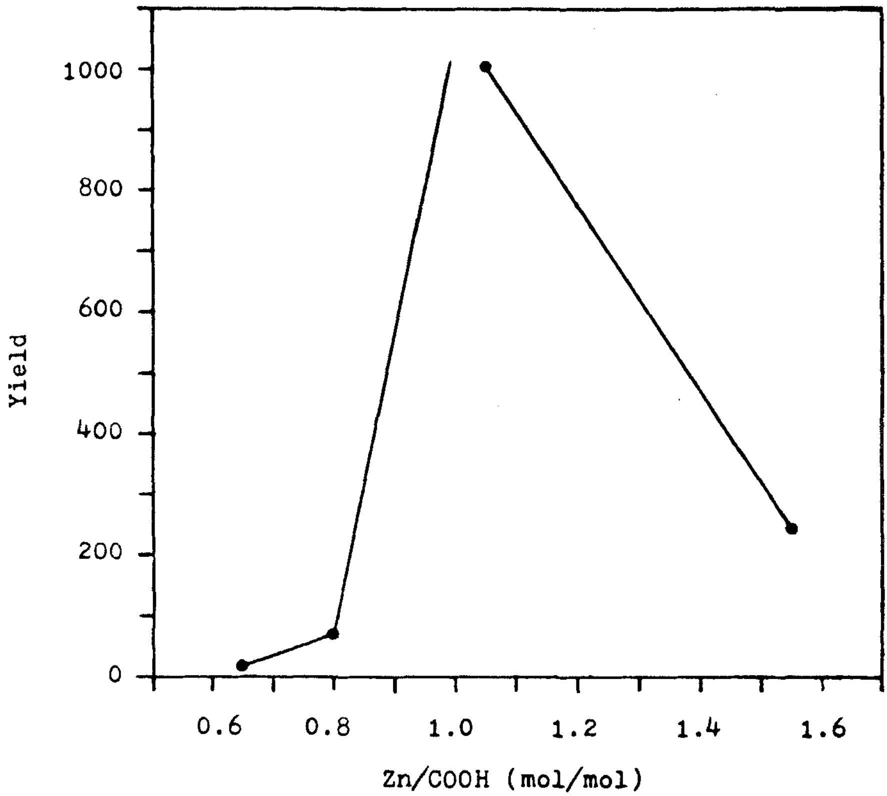


FIG. 2. Effect of Zn/COOH ratio on yield.

weight rose with increasing reaction time to a maximum (Fig. 3). This agrees with an anionic coordinate polymerization mechanism [2].

Increasing reaction temperature accelerated the copolymerization reaction, giving higher yield but lower molecular weight of the product (Fig. 4). The drop of molecular weight at elevated temperatures was probably due to the polymer degradation in the presence of the catalysts, as reported by Rokicki and Kuran [2].

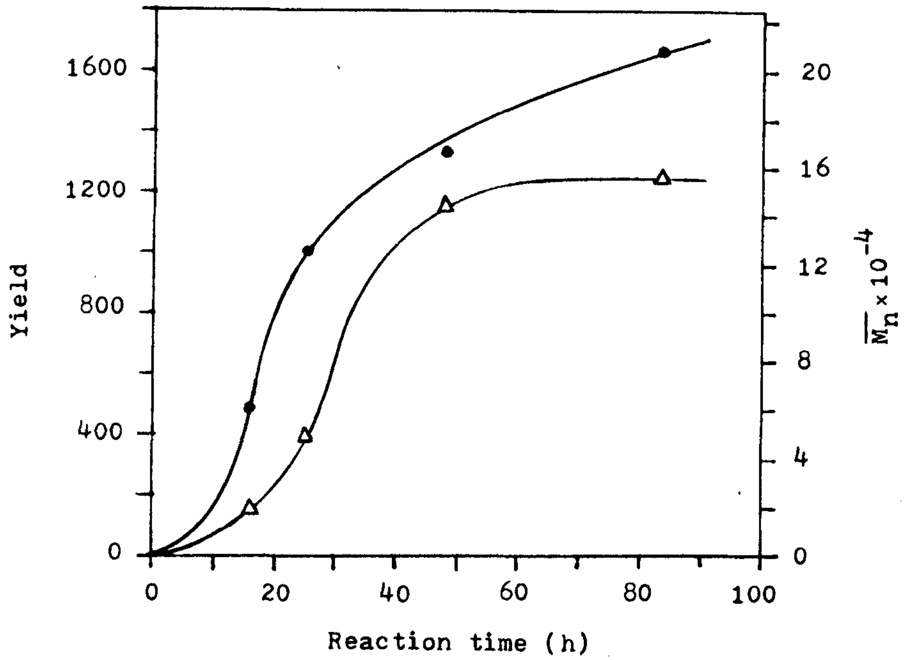


FIG. 3. Effect of reaction time on product yield (●) and molecular weight (△).

Characterization of the CO_2/PO Copolymer

The copolymer was subjected to methanol extraction to determine insoluble fraction in this solvent. Typical samples of the copolymers contained ~80% of MeOH-insoluble material, which is believed to be substantially poly(propylene carbonate). This result agrees with elemental analysis results (see Table 1).

The IR spectra of these copolymers showed strong absorptions at 1 745, 1 250, and 790 cm^{-1}, characteristic of carbonate groups. The ^1H NMR spectra of the copolymers showed chemical shifts from internal TMS at $\delta 1.30$ (d, 6 Hz, 3H) for CH_3, $\delta 4.15$ (d, 6 Hz, 2H) for CH_2, and $\delta 4.97$ (m, 1H). The ^{13}C NMR spectra showed signals at $\delta 16.2$ for CH_3, $\delta 69.0$ for CH_2, $\delta 72.4$ for CH, and $\delta 154.2$ for the carbonate carbon. The simplicity of the NMR pattern confirmed the highly alternating structure of the copolymer.

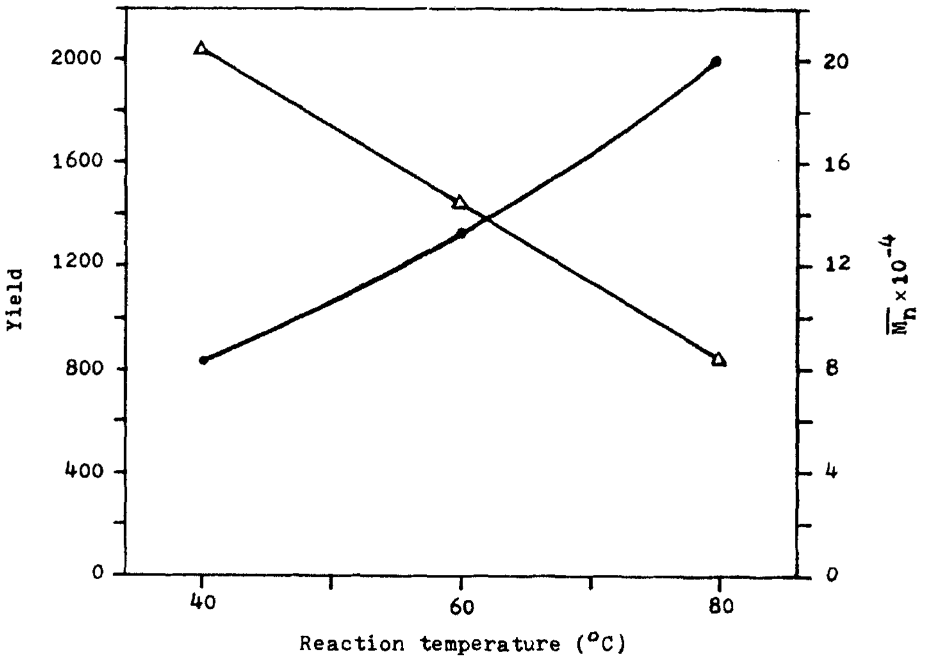


FIG. 4. Effect of reaction temperature on yield (●) and molecular weight (△) of the product.

ACKNOWLEDGMENTS

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REFERENCES

[1] S. Inoue, in *Fundamental Research in Organometallic Chemistry* (M. Tsutsui, Y. Ishii, and Y.-Z. Hwang, eds.), Van Nostrand Reinhold, New York, 1982, p. 125.

[2] A. Rokicki and W. Kuran, *J. Macromol. Sci., Rev. Macromol. Chem., C21*, 135 (1981).

[3] S. Inoue, H. Koinuma, and T. Tsuruta, *Makromol. Chem., 130*, 210 (1969).

[4] M. Kobayashi, Y.-L. Tang, T. Tsuruta, and S. Inoue, *Ibid., 155*, 61 (1972).

[5] A. Rokicki and W. Kuran, *Ibid., 180*, 2153 (1979).