NOTE

Alternating Copolymerization of CO₂ and Propylene Oxide with the Catalysts Prepared from Zn(OH)₂ and Various Dicarboxylic Acids

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Since the discovery by Inoue *et al.*¹ that carbon dioxide copolymerizes with epoxy compounds to give the corresponding polycarbonates, a number of investigations has been made to develop effective catalyst systems for this copolymerization. Most of the systems reported so far consist of a reaction mixture of diethylzinc and a compound with two active hydrogens, such as water,^{1–3} primary amines,³ dihydric phenols,^{4,5} aromatic dicarboxylic acids,⁶ and others.^{7,8} However, we have recently reported that some metal salts of acetic acid such as Zn(OAc)₂ and Co(OAc)₂ also catalyze this copolymerization.^{9,10} More recently, we found that the reaction products of zinc hydroxide and aliphatic dicarboxylic acids show very high activities for the copolymerization. This paper reports the results of the copolymerization of carbon dioxide and propylene oxide using these compounds as catalysts.

EXPERIMENTAL

Materials

Propylene oxide (PO), dioxane, acetone, and ethanol were commercially obtained from Tokyo Kasei Co. and purified by the usual procedures. Zinc hydroxide[†] (Zn(OH)₂, from Koso Chem. Co.),

dicarboxylic acids (see Table I, from Tokyo Kasei Co.) and CO₂ (from Showa Tansan Co., ultra high purity) were used without further purification. γ -Al₂O₃, MgO, and SiO₂ (from Fuji Devison Co.) were treated *in vacuo* at 300°C for 5 h immediately before use.

Preparation of Catalysts

To a 300 ml glass reactor containing 150 ml of solvent (acetone or ethanol) were added 50 mmol of a dicarboxylic acid and 50 mmol of Zn(OH)₂.

This mixture was allowed to stand at 55°C for 24 h under nitrogen. The solid product was separated, washed repeatedly with the solvent and then dried *in vacuo* at room temperature.

The metal oxides-supported Zn(OAc)₂ catalysts were prepared as follows. To an ethanol solution of 1 mmol of Zn(OAc)₂ was added 1 g of a supporting material (SiO₂, γ -Al₂O₃, or MgO). The mixture was kept standing at room temperature for 1 h with vigorous stirring; ethanol was then completely removed by evaporation *in vacuo* at 80°C to give the supported catalyst.

Polymerization Procedure

Measured amounts of a catalyst and PO were placed in a 50 ml stainless steel reactor. The mixture was cooled by liquid nitrogen and degassed *in vacuo*. CO₂ was then introduced through a wet gas meter and drying towers containing calcium chloride and phosphorus pentoxide. The reactor was kept stand-

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† Prepared by the reaction of ZnCl₂ and NaOH in H₂O, followed by washing with an ample amount of H₂O and drying. Purity, >99%.

ing at 60°C for 40 h with vigorous stirring in an oil bath equipped with a temperature regulator. The reaction mixture was diluted with methanol, washed with dilute hydrochloric acid, and the resulting

Figure 1. Infrared spectra of the product from the reaction of $\text{Zn}(\text{OH})_2$ with $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ (a) and with $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ (b).

Figure 2. Infrared spectra of the copolymers obtained over $\text{Zn}(\text{OH})_2\text{-HOOC}(\text{CH}_2)_3\text{COOH}$ (a) and over $\text{ZnEt}_2\text{-H}_2\text{O}$ (1:1) (b).

polymer was precipitated by adding much water, and dried *in vacuo* at room temperature.

Analysis of the Polymer

The nuclear magnetic resonance (NMR) spectrum of a 10 wt% solution of the polymer in deuterochloroform was measured at room temperature with a 100 MHz "JEOL" spectrometer, using tetramethylsilane (TMS) as the standard. Number-average molecular weights were measured with a Hitachi Corona 117 Vapour Pressure Osmometer, using chloroform as the solvent at 35°C.

RESULTS AND DISCUSSION

In Figure 1 are shown the infrared (IR) spectrum of the reaction product of adipic acid and Zn(OH)₂

(a), together with that of adipic acid (b). The peaks at 1702, 1280, and 930 cm⁻¹ attributed to the carbonyl and carbonyl-oxygen stretching and O-H out-of-plane deformation in adipic acid completely disappeared and a strong new peak at 1545 cm⁻¹ appeared in the spectrum (a). This strongly suggests the formation of zinc adipate (I), by the reaction of adipic acid with Zn(OH)₂ (eq 1).

Table I. Results of copolymerization of PO and CO₂ with various catalysts^a

Catalyst	Weight of catalyst		Copolymer yield		$M_n \times 10^{-4}$ ^b
	mg	mg	(g/g-Zn)		
Zn(OH) ₂ -HOOC-COOH	317	21	0.16	—	—
Zn(OH) ₂ -HOOCCH ₂ COOH	346	trace	—	—	0.8
Zn(OH) ₂ -HOOC(CH ₂) ₂ COOH	202	370	5.2	—	1.5
Zn(OH) ₂ -HOOC(CH ₂) ₃ COOH	192	4446	69.1	—	1.2 ^c
Zn(OH) ₂ -HOOC(CH ₂) ₄ COOH	209	1580	24.2	—	1.7
Zn(OH) ₂ -HOOC(CH ₂) ₅ COOH	279	778	9.6	—	—
Zn(OH) ₂ -HOOC(CH ₂) ₆ COOH	249	632	9.3	—	1.0
Zn(OH) ₂ -HOOC(CH ₂) ₈ COOH	214	609	11.5	—	—
Zn(OH) ₂ -HOOC(CH ₂) ₁₀ COOH	198	825	18.7	—	1.1
Zn(OH) ₂ -HOOCCH=CHCOOH (<i>trans</i>)	529	182	0.94	—	1.9
Zn(OH) ₂ -HOOCCH=CHCOOH (<i>cis</i>)	121	trace	—	—	—
Zn(OH) ₂ -CH ₂ =C(CH ₂ COOH)COOH	530	449	2.5	—	2.1
Zn(OH) ₂ -DL-HOCH(COOH)COOH	414	0	0	—	—
Zn(OH) ₂ -C ₆ H ₅ COOH	712	0	0	—	—
Zn(OH) ₂ - <i>o</i> -C ₆ H ₄ (COOH) ₂	230	249	3.6	—	1.8
Zn(OH) ₂ - <i>m</i> -C ₆ H ₄ (COOH) ₂	319	16	0.2	—	—
Zn(OH) ₂ - <i>p</i> -C ₆ H ₄ (COOH) ₂	276	32	0.4	—	—
Zn(OH) ₂ - <i>o</i> -C ₆ H ₄ (OH)COOH	313	45	0.4	—	—
Zn(OH) ₂ - <i>m</i> -C ₆ H ₄ (OH)COOH	638	177	0.8	—	1.4
Zn(OH) ₂ - <i>p</i> -C ₆ H ₄ (OH)COOH	425	87	0.6	—	—
[(C ₄ H ₉) ₂ NCSS] ₂ Zn	329	12	0.2	—	—
[(C ₂ H ₅) ₂ NCSS] ₂ Zn	435	10	0.1	—	—
[C ₆ H ₅ N(C ₂ H ₅)CSS] ₂ Zn	325	trace	—	—	—
Zn(CH ₃ COOH) ₂	95	50	1.5	—	—
ZnEt ₂ -H ₂ O (1:1)	247	3112	23.8	—	— ^d

^a Copolymerization was conducted without solvent at 60°C for 40 h using 31 of CO₂ and 3 ml of PO.

^b Measured by VPO.

^c Elemental analysis of the polymer: C, 45.76%; H, 6.04%.

^d Elemental analysis of the polymer: C, 46.05%; H, 6.20% (Calcd: C, 47.05%; H, 5.94%).

It may be possible that some polymeric products were also produced in addition to I. However, the degree of these side reactions could not be determined because of the insolubility of the products in ordinary solvents.

Various catalysts were prepared in a similar way, using dicarboxylic acids mainly (see Table I). The copolymerization of CO₂ and PO was conducted at 60°C for 40 h using these acids as catalysts.

In Table I are summarized the copolymerization results along with some analytical data on the copolymers. All the copolymers obtained were white solids, soluble in benzene, tetrahydrofuran, acetone, chloroform, etc., but insoluble in water, methanol, etc. They were confirmed by NMR analysis to be substantially poly(oxycarbonyloxypropylene) [poly(propylenecarbonate)], *i.e.*, an alternating copolymer of CO₂ and PO. A typical IR spectrum and elemental analysis of the copolymer are also shown in Figure 2 and Table I along with those of the copolymer obtained over the ZnEt₂-H₂O system. The data in Table I show that the catalysts prepared from aliphatic dicarboxylic acids were more effective for copolymerization, compared with the others, and that the catalyst prepared from glutaric acid the most effective. The activity of the catalyst was much greater than that of the ZnEt₂-H₂O (1:1) system, which is known to be the most effective catalyst reported so far.

Among the catalysts shown in Table I, Zn(OAc)₂ is easily soluble in polar solvents such as ethanol and water. As reported earlier,¹⁰ however, the copolymerization proceeds *via* a coordinated anionic mechanism, so it hardly takes place by soluble catalysts. Therefore, the supported catalysts with high dispersion were prepared by means of the impregnation method as described in the experimental part, for improving the activity.

The results obtained are shown in Table II. The activity was improved to a great extent as expected, and this is attributable mainly to the increase in the number of active species.

Research for bringing about a further improvement in activity is now in progress, using the

Table II. Results of copolymerization of PO and CO₂ with supported catalysts^a

Catalyst	Support	Weight of catalyst	Copolymer yield	
	m ² g ⁻¹ ^b	mg	mg	(g/g-Zn)
Zn(CH ₃ COO) ₂	—	95	50	1.5
Zn(CH ₃ COO) ₂	SiO ₂ (270)	43	396	25.5
Zn(CH ₃ COO) ₂	MgO (23)	48	238	13.8
Zn(CH ₃ COO) ₂	γ-Al ₂ O ₃ (143)	52	320	17.3

^a Copolymerization was conducted without solvent at 60°C for 40 h using 3 l of CO₂ and 3 ml of PO.

^b Measured by the Brunauer-Emmett-Teller method with nitrogen adsorption.

^c Without support.

Zn(OH)₂-glutaric acid system. The results for this will be reported in another paper.

REFERENCES

1. S. Inoue, H. Koinuma, and T. Tsuruta, *J. Polym. Sci., B*, **7**, 287 (1969).
2. S. Inoue, H. Koinuma, and T. Tsuruta, *Makromol. Chem.*, **130**, 210 (1969).
3. S. Inoue, H. Koinuma, Y. Yokoo, and T. Tsuruta, *Makromol. Chem.*, **143**, 97 (1971).
4. M. Kobayashi, S. Inoue, and T. Tsuruta, *Macromolecules*, **4**, 658 (1971).
5. M. Kobayashi, Y. L. Tang, T. Tsuruta, and S. Inoue, *Makromol. Chem.*, **169**, 69 (1973).
6. M. Kobayashi, S. Inoue, and T. Tsuruta, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2383 (1973).
7. W. Kuran, S. Pasynkiewicz, J. Skupinska, and A. Rokicki, *Makromol. Chem.*, **177**, 11 (1976).
8. W. Kuran, S. Pasynkiewicz, and J. Skupinska, *Makromol. Chem.*, **177**, 1283 (1976).
9. K. Soga, K. Uenishi, H. Hosoda, and S. Ikeda, *Makromol. Chem.*, **178**, 893 (1977).
10. K. Soga, K. Hyakkoku, and S. Ikeda, *Makromol. Chem.*, **179**, 2837 (1978).