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NOTE

Copolymerization of Epoxycyclohexane and Carbon Dioxide with Metal Amides

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As we have already reported, carbon dioxide copolymerizes with epoxide by using an organometallic system as the catalyst.[1,2] Among the catalyst systems so far examined, the most effective one found was a reaction mixture of diethylzinc and an equimolar amount of a compound having two active hydrogens, such as water and primary amines.[2] On the other hand, a reaction mixture of diethylzinc and a compound having but one active hydrogen, such as methanol and secondary amines, did not function as an effective catalyst in the copolymerization of carbon dioxide and epoxypropane.[2,3]

Certain metal dialkylamides however are known to react with carbon dioxide to give metal carbamates. For example, ethylzinc diphenylamide, formed by a reaction of diethylzinc with diphenylamine, readily reacts with carbon dioxide.[4] Tetrakis(dimethylamido)titanium is also very reactive towards carbon dioxide.[5] We found that epoxycyclohexane reacted with titanium carbamate to give quantitative yields of the carbamic esters of 1,2-diol, corresponding to the epoxide.[6]

This prompted us to examine the catalytic activity of various metal amides including zinc, aluminium, titanium and tungsten, for the copolymerization of carbon dioxide and epoxycyclohexane.

EXPERIMENTAL

Preparation of Copolymer

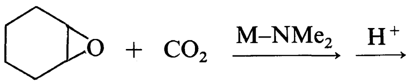
Copolymerization of carbon dioxide and epoxide by metal amide was carried out in an autoclave, as reported previously.[1,2] The reaction mixture was diluted with benzene, washed with dilute hydrochloric acid, then with water, and subjected to freeze drying, to give the product, a mixture of copolymer, cyclic carbonate and carbamic ester, depending on the reaction conditions. The copolymer was obtained as a methanol-insoluble part by pouring the benzene solution of the product into a large amount of methanol.

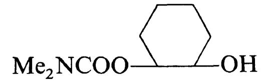
Characterization of Copolymer

The content of the oxycarbonyl unit (f_{CO_2}) of the copolymer, a poly(carbonate-ether), was determined by the ratios of the absorptions due to the methine protons adjacent to the oxycarbonyl linkage at 4.8 ppm and due to the ether linkage at 3.5 ppm in ^1H NMR of the copolymer.[7]

RESULTS AND DISCUSSION

Similar to $Ti(NMe_2)_4$, transition metal amides such as $CpTi(NMe_2)_3$,[5] $[Ti(NMe_2)_3]_2$,[8] and tungsten amide ($W_2(NMe_2)_6+W(NMe_2)_6$),[9] also reacted with carbon dioxide and epoxycyclohexane to yield 2-hydroxycyclohexyl dimethylcarbamate quantitatively, but the copolymer of carbon dioxide and epoxycyclohexane was not formed (eq 1).

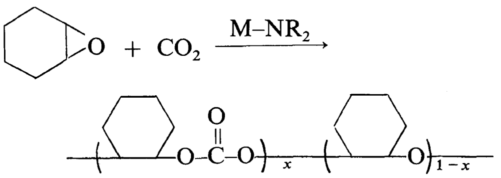




(1)

M : Ti, W

The reaction mixture of diethylzinc with an equimolar amount of diethylamine was not active for the copolymerization of carbon dioxide and epoxycyclohexane, but gave the carbamic ester in a trace amount. The reaction of carbon dioxide and epoxycyclohexane with $EtZnNPh_2$[4] however gave a copolymer having a fairly high content of oxycarbonyl unit (O–(C=O)–) ($f_{CO_2}=38\%$), though the copolymer was not completely alternating (Table I). Et_2AlNEt_2[10] afforded a copolymer having a lower content of oxycarbonyl unit ($f_{CO_2}=25\%$) and a lower molecular weight. The copolymer yield obtained with Et_2AlNEt_2 or $EtZnNPh_2$ was high for examples of carbon dioxide-epoxide copolymerization reported so far.[2]



M : Al, Zn (2)

As shown in Tabel II, the copolymerization of carbon dioxide and epoxycyclohexane with Et_2AlNEt_2 was considerably affected by the nature of solvent. In more basic solvents, the yield of copolymer was less, but the content of the oxycarbonyl unit (f_{CO_2}) of the copolymers was similar regardless of the solvent (Runs 1—4). These results indicate that the solvent competes with epoxycyclohexane or carbon dioxide to coordinate with the aluminium atom of the catalyst. When copolymerization was conducted with Et_2AlNEt_2 as the concentration of Et_2AlNEt_2 for epoxycyclohexane was increased from 1.2 mol% to 6 mol% (Runs 5, 1, and 6), the content of oxycarbonyl unit (f_{CO_2}) increased from 21% to 37%.* The copolymer obtained under higher carbon dioxide pressure had a higher content of oxycarbonyl unit, but in a lower yield (Runs 5 and 7).

Organoaluminium compounds (Et_3Al, Et_2AlNEt_2 and Et_2AlOEt) were good catalysts for carrying out the copolymerization of carbon dioxide and epoxycyclohexane giving a copolymer having a content of oxycarbonyl unit similar to each other ($f_{CO_2}=21$—27%), but aluminium isopropoxide ($Al(OCHMe_2)_3$), aluminium stearate ($(C_{17}H_{35}COO)_3Al$) and aluminium hydroxide ($Al(OH)_3$)** were not active in bringing about copolymerization. It is known that Et_3Al, Et_2AlNEt_2 and Et_2AlOEt are dimeric,[11] but

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* Although the reaction temperature of run 6 in Table II was different from those of other runs, the reaction temperature in the range from 30 to 80°C was found not to affect the content of oxycarbonyl unit of the copolymer, when the copolymerization of carbon dioxide and epoxycyclohexane was carried out with Et_2AlNEt_2.

** These aluminium compounds were commercially obtained and used without further purification.

Table I. Compolymerization of carbon dioxide and epoxycyclohexane with metal amides[a]

Run	Catalyst	mol %[b]	Time	Copolymer		
			h	Yield[c] g (%)	f_{CO_2}[d] %	$[\eta]$[e] × 10^2 $cm^3\ g^{-1}$
1	$EtZnNPh_2$	3.5	16	28.6 (57)	38	0.24
2	Et_2AlNEt_2	1.4	18	24.8 (55)	25	0.05[f]

[a] Epoxycyclohexane, 40 g; CO_2, 50 atm (SI-unit; 1 atm = 101.325 Pa); temp, 80°C.

[b] For epoxide.

[c] Methanol-insoluble part. Based on epoxycyclohexane.

[d] Content of oxycarbonyl unit in the copolymer.

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

[f] M_n, 1700 (measured by cryoscopy in benzene).

Table II. Copolymerization of carbon dioxide and epoxycyclohexane with Et_2AlNEt_2[a]

Run	Et_2AlNEt_2	Solvent	CO_2	Temp	Copolymer[c]			
	mol %[b]		atm	°C	Total	MeOH-insol		
						Yield	f_{CO_2}	M_n
1	3.0	Benzene	30	80	12.4 g	8.5 g (70%)[d]	34%	3.0×10^3
2	3.0	Dioxane	30	80	6.8	1.3 (11%)	32	2.1
3	3.0	Pyridine	30	80	4.2	0 (—)	—	—
4	3.0	Hexane	30	80	—	4.8 (41%)	32	2.0
5	1.2	Benzene	30	80	7.0	6.1 (56%)	21	3.3
6[e]	6.0	Benzene	30	30	10.2	4.7 (38%)	37	2.7
7	1.2	Benzene	105	35	1.5	0.01 (0.1%)	40	—

[a] Epoxycyclohexane, 9.7 g; time, 40 hours; solvent, 25 ml.

[b] For epoxycyclohexane.

[c] Methanol-soluble parts are the copolymers with similar f_{CO_2} to the insoluble part, as evidenced by the infrared spectra.

[d] Based on epoxycyclohexane.

[e] Time, 70 hours.

Table III. Copolymerization of CO_2 and epoxide, $R_1R_2C{-}R_3R_4C{-}O$, with Et_2AlNEt_2[a]

Run	Epoxide				Et_2AlNEt_2	Time	Products				
							Copolymer[d]			Polyether	Cyclic carbonate
	R_1	R_2	R_3	R_4(g)	mol %[c]	h	Total	Yield	f_{CO_2}		
							g	g	%	g	g
1	Me	H	H	H (17)	2.0	50	0.39	0	—	0	0.39
2[b]	Et	H	H	H (29)	0.7	240	3.6	0	—	3.6	0
3	Me	Me	H	H (7.2)	1.2	70	0	—	—	—	—
4 *cis*	Me	H	Me	H (7.2)	3.0	280	7.2	0	0	0	5.4[e]
5 *trans*	Me	H	Me	H (7.2)	3.0	520	0.07	0	—	0.07	0
6	Ph	H	H	H (24)	1.5	140	—	0.09	15	0	0
7	H	$-(CH_2)_3-$		H (8.4)	3.0	160	1.6[f]	0.03	45	0	0
8	H	$-(CH_2)_4-$		H (9.7)	1.2	70	5.0[f]	3.4	25	0	0

[a] In benzene, 40 ml; temp, 35°C; CO_2, 30 atm.

[b] Without benzene.

[c] For epoxide.

[d] Methanol-insoluble part.

[e] *Threo*-4,5-dimethyl-1,3-dioxolan-2-one. (*trans*-2,3-butylene carbonate) was isolated by the distillation (yield, 40%).

[f] Methanol-soluble parts are the copolymers with similar f_{CO_2} to the insoluble part.

$Al(OCHMe_2)_3$ is tetrameric in benzene.[12] The results of copolymerization with various aluminium compounds indicate that the catalytic activity for copolymerization is strongly dependent on the degree and strength of the association of the aluminium compounds. It is considered that this strong association of the aluminium compounds hinders the coordination of epoxide or carbon dioxide with the aluminium atom.

The copolymerization of carbon dioxide and various epoxides with Et_2AlNEt_2 was examined, as shown in Table III. Among the epoxides examined, only epoxycyclohexane gave the copolymer in good yield (Run 8). Phenylepoxyethane and epoxycyclopentane gave copolymers in low yield (Runs 6 and 7). *cis*-2,3-Epoxybutane gave *threo*-4,5-dimethyl-1,3-dioxolan-2-one (cyclic carbonate of *trans*-form) in good yield, while *trans*-2,3-epoxybutane gave neither the copolymer nor the cyclic carbonate.

CONCLUSION

It was found that transition-metal amides (Ti and W) reacted with carbon dioxide and epoxycyclohexane, to give the carbamic ester quantitatively.

Zinc and aluminium amides were found to be active catalysts for the copolymerization of carbon dioxide and epoxycyclohexane.

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