Communications to the Editor

Diethylzinc–Dihydric Phenol System as Catalyst for the Copolymerization of Carbon Dioxide with Propylene Oxide

In previous papers[1-4] has been described the copolymerization of carbon dioxide (CO_2) with epoxide to give an alternating copolymer, poly(alkylene carbonate), using some organozinc catalyst systems. In the course of further research on the copolymerization of CO_2 with propylene oxide, we have found that dialkylzinc (ZnR_2)–water and –primary amine systems are effective as catalysts, while ZnR_2–methanol and –secondary amine systems show little activity in the copolymerization.[5] We examined in detail the difference between ZnR_2–water and ZnR_2–methanol systems in relation to the mechanism of the copolymerization and pointed out that the activity of the systems in copolymerization depends on the presence or absence of the repeated Zn–O or Zn–N group.[5]

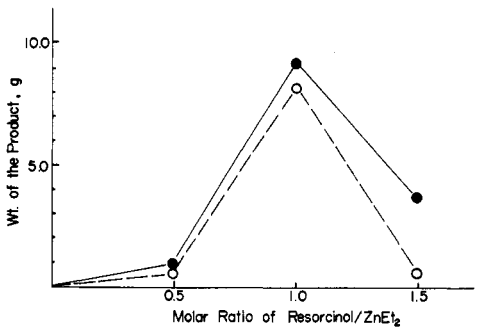


Figure 1. Copolymerization by the $ZnEt_2$–resorcinol system: ●, total product; ○, methanol-insoluble part; propylene oxide charged, 17.3 g (0.3 mol); CO_2 pressure *ca.* 30 atm; in dioxane at 35° for 48 hr.

TABLE I
COPOLYMERIZATION OF CO_2 WITH PROPYLENE OXIDE[a]

No.	Catalyst[b]	Propylene oxide, g	Time, hr	Polymer yield, g: Total	Polymer yield, g: MeOH-insol part	$[\eta]^c$ of MeOH-insol part
52	$ZnEt_2$–resorcinol (1:1)	17.3	48	9.16	8.24	0.63
45	$ZnEt_2$–resorcinol (1:1)	17.3	168	19.91	18.45	0.81
43	$ZnEt_2$–hydroquinone (1:1)	17.3	168	2.37	1.37	1.24
42	$ZnEt_2$–hydroquinone (1:1)	17.3	116	6.82	5.70	0.59
50	$ZnEt_2$–catechol (1:1)	17.3	48	2.37[d]	Trace	
49	$ZnEt_2$–water (1:1)	8.6	48	1.74	1.46	1.98
54	$ZnEt_2$–phenol (1:1.2)	8.6	48	0.47[d]	Trace	
44	$ZnEt_2$–phenol (1:2)	17.3	168	3.27[d]	Trace	
55	$ZnEt_2$–*m*-methoxyphenol (1:1)	17.3	48	1.59[d]	Trace	
56	$ZnEt_2$–methoxyphenol (1:2)	17.3	48	4.21[d]	Trace	
48	$ZnEt_2$–*p*-methoxyphenol (1:2)	8.6	48	1.48[d]	Trace	

[a] In dioxane at 35° except no. 42 (66°); CO_2 pressure *ca.* 30 atm. [b] The mixture of $ZnEt_2$ and the phenol in dioxane (10 mmol in 40 ml) was stirred for 3 hr at 25° before use, except no. 54 and 48 (5 mmol in 20 ml) and 49 (5 mmol in 20 ml, stirred for 30 min). [c] In benzene at 30° [(g/dl)$^{-1}$]. [d] Yet unidentified liquid product.

Based on the results obtained earlier, we now find that the copolymerization of CO_2 with propylene oxide takes place effectively with the system ZnR_2–dihydric phenol.

Table I presents the results obtained in the copolymerization of CO_2 with propylene oxide using diethylzinc ($ZnEt_2$)–phenol systems.

A mixture of $ZnEt_2$ and phenol in dioxane was stirred for 3 hr at 25° before use as a catalyst system. The methanol-insoluble fraction of the product is the almost alternating copolymer of CO_2 and propylene oxide, poly(propylene carbonate). *Anal.* Calcd for $+CH(CH_3)CH_2OCOO+_n$: C, 47.06; H, 5.92. Found for sample no. 43: C, 47.78; H, 6.04.

Among the systems examined, $ZnEt_2$–resorcinol and $ZnEt_2$–hydroquinone systems showed high activity in the copolymer-

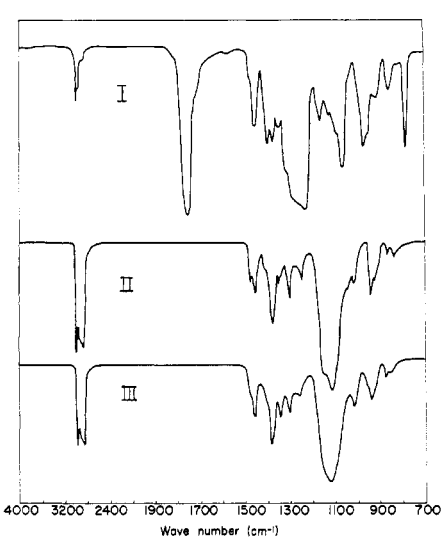


Figure 2. Ir spectra of the PO–CO_2 copolymer and poly(propylene oxide): (I) PO–CO_2 copolymer (MeOH-insoluble portion of no. 52), (II) isotactic poly(propylene oxide), (III) atactic poly(propylene oxide) (PO, propylene oxide).

(1) S. Inoue, H. Koinuma, and T. Tsuruta, *J. Polym. Sci., Part B*, 7, 287 (1969).
(2) S. Inoue, H. Koinuma, and T. Tsuruta, *Makromol. Chem.*, **130**, 210 (1969).
(3) S. Inoue, H. Koinuma, and T. Tsuruta, *Polym. J.*, **2**, 220 (1971).
(4) S. Inoue, H. Koinuma, T. Yokoo, and T. Tsuruta, *Makromol. Chem.*, **143**, 97 (1971).
(5) S. Inoue, M. Kobayashi, H. Koinuma, and T. Tsuruta, *ibid.*, in press.

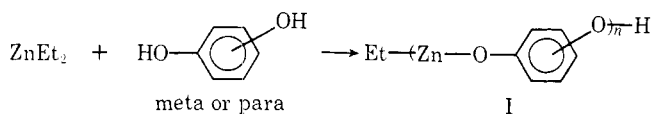
ization. In particular, the $ZnEt_2$–resorcinol (1:1) system gave a higher copolymer yield than the $ZnEt_2$–water (1:1) system, which we had found to be the most effective system among those previously examined. On the other hand, the $ZnEt_2$–monohydric phenol and –catechol systems showed almost no activity in alternating copolymerization.

Figure 1 shows the yield of the product obtained *vs.* the molar ratio of resorcinol–$ZnEt_2$. The results show the copolymer yield to be highly dependent on the resorcinol–$ZnEt_2$ ratio, with a clear optimum point at 1:1.

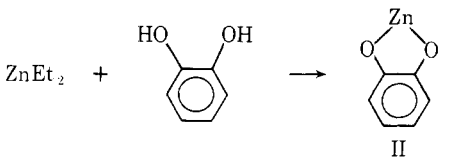
The infrared spectrum and the decomposition temperature of the copolymer obtained with the $ZnEt_2$–resorcinol or –hydroquinone systems were similar to those of the copolymer obtained with the $ZnEt_2$–water (1:1) system.[2] The ir spectrum of a solid film is shown in Figure 2 together with that of poly(propylene oxide).

The $ZnEt_2$–resorcinol (1:1) or –hydroquinone (1:1) system may give species such as I, as shown in eq 1. On the other hand, the $ZnEt_2$–catechol system would give II (eq 2) and the $ZnEt_2$–monohydric phenol system might give III and IV (eq 3 and 4).

The difference in activities toward the copolymerization among these systems may be attributed to the presence or absence of the repeated $-(-Zn-O-C_6H_4-O-)-$ group.



(1)



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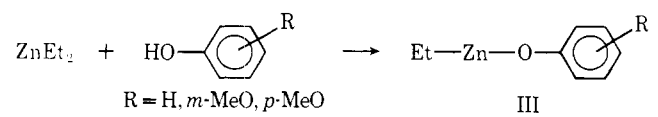
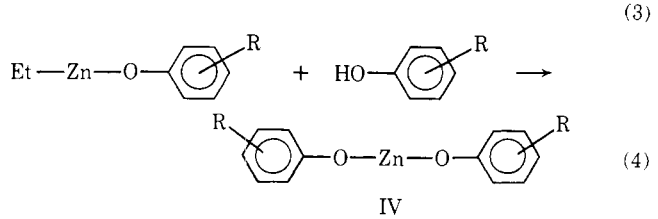


(3)



(4)

Further studies on the copolymerization and on the nature of the catalyst systems are now in progress.

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Polarized Vacuum-Ultraviolet Absorption of Poly(L-alanine)

Assignments of spectral features in the vacuum-uv region from 1300 to 1800 Å are, generally speaking, to higher energy excitons, interband transitions, or plasmons. Assignments are made within some theoretical framework and experimental data in this region can be a guide in developing the description of electronic structure in polymers. Beyond this, and in light of the increasing simplicity of instrumentation, vacuum-uv spectroscopy will most likely begin to play an increasing role in polymer conformational analysis. We have previously used it to demonstrate that poly(L-hydroxyproline) films take up a conformation strongly resembling poly(L-proline) I when prepared by evaporation to dryness in a dc electric field.[1]

We reported earlier the unpolarized transmission spectra of polypeptide films from 1300 to 2500 Å.[2] We and others[3-5] observed a band near 1650 Å in α-helical poly(L-alanine). Polyalanine spectra are not complicated by the presence of absorbing chromophores in the side chain, which indicates a peptide group origin for the band. Here we report the linear dichroism of partially oriented poly(L-alanine) films and summarize the evidence now available which is relevant to the assignment of the 1650-Å band.

High molecular weight poly(L-alanine) was obtained from Pilot Chemical Inc., Watertown, Mass. Samples were cast on 1-mm calcium fluoride (Harshaw Chemical) by repeated evaporation from trifluoroethanol (Aldrich Chemical Co.). Orientation was sought through needle shearing during evaporation. Spectra were taken with a McPherson Model 225 double-beam spectrophotometer using a biotite polarizer (McPherson Co.). The polarization ratio of the biotite was approximately 15:1 in the region of 1650 Å.

Films were selected for low scattering background as judged by the optical density in the nonabsorbing region from 2500 to 3800 Å. Polyalanine does not make well-oriented films, and the spectra reported here were obtained only after a number of trials which resulted in varying degrees of chain orientation. An estimated correction for scattering in the spectra of the best samples was made using Onari's suggestion[5] of a λ^{-1} dependence. Additional experimental details are given in ref 6.

Figure 1 shows the spectra of our most oriented low-scattering sample. The two curves are labeled according to whether the plane of polarization of the radiation was parallel ($\parallel$) or perpendicular ($\perp$) to the direction in which the needle shearing was applied. The sum of the two curves gives a spectrum identical with that of the same film using unpolarized radiation.

The spectra from 1900 to 2400 Å should be comparable to the earlier results of Gratzer, Holzwarth, and Doty.[7] The differences can be explained on the basis of our films being less oriented than the films studied by Gratzer, *et al.* Thus, their maximum in parallel polarization at 2060 Å appears as a shoulder in our spectrum, and the maximum at 1950 Å in our parallel polarization has considerable contribution from the perpendicular component of unoriented chains. The high background absorbance in our spectrum near 1800 Å is most likely due to an inadequate correction for scattering. The accepted assignments in this low-energy region attribute the 2200-Å band to an $n-\pi^*$ transition polarized perpendicular to the helix and the bands at 2060 and 1910 Å to exciton components of the $\pi-\pi^*$ monomer transition.

Figure 1 shows that the polarization of the absorption band near 1650 Å is dominantly parallel to the direction of shear-induced orientation.

(1) J. L. Bensing and E. S. Pysh, *Biopolymers*, in press.
(2) J. L. Bensing and E. S. Pysh, *Chem. Phys. Lett.*, **4**, 120 (1969).
(3) R. K. Momii and D. W. Urry, *Macromolecules*, **1**, 373 (1968).
(4) J. Brahms, J. Pilet, H. Damany, and V. Chandrasekharan, *Proc. Nat. Acad. Sci. U. S.*, **60**, 1130 (1968).
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