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Investigations on the Monomer Distribution in Maleic Anhydride-Propylene Oxide Copolymers Obtained by Ethylzinc Catalysts

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ABSTRACT

The copolymerizations of maleic anhydride (MA) and propylene oxide (PO) were carried out in toluene, dioxane, diethoxyethane, or dimethyldigol solution in the presence of ethylzinc compounds EtZnX (X = Et– or substituted phenoxy group). On the basis of the ^{1}H-NMR data of copolymers and VPC of the products of their hydrolysis, it was found that donor solvents and X substituents involving CH_3O–, Cl–, or CH_3CO– donor groups in the ortho position of the aromatic ring (e.g., X = 2-$CH_3OC_6H_4O$–, 2,6-$(CH_3O)_2C_6H_3O$–, 2-$CH_3COC_6H_4O$–, etc.) caused an increase in the number of alternating sequences in copolymers chains. In the reaction of MA and PO in tetrahydrofuran (THF) solution, the above-mentioned zinc compounds gave highly alternating MA-PO-THF terpolymers.

INTRODUCTION

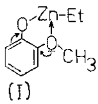
Copolymerization of cyclic anhydrides and oxiranes in the presence of organometallic catalysts has been found [1] to produce copolymers containing both ester and ether linkages. Organozinc compounds exhibit relatively high catalytic activity in these reactions. An anionic-coordinative mechanism has been proposed [2] for the copolymerization of phthalic anhydride and propylene oxide by diethylzinc ($ZnEt_2$).

Alternating copolymers of cyclic anhydrides and oxiranes, i.e., those containing only ester linkages in the copolymer chains, were obtained in the case of the copolymerization of maleic anhydride and epichlorohydrin in the presence of zinc acetylacetonate [3].

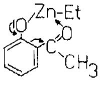
It was found [4] that the reaction of cyclic anhydrides with cyclic ethers in THF solution in the presence of organometallic compounds yields correspondent anhydride-oxirane-tetrahydrofuran alternating terpolymers.

The purpose of the present work was to examine the influence of donor solvents and catalysts structure on the tendency to alternation of the MA-PO copolymerization reaction.

The use of EtZnX homogeneous catalyst in which X was the substituent, such as 2-$CH_3OC_6H_4O$– (I), 2-$CH_3COC_6H_4O$– (II), and 3-$CH_3OC_6H_4O$– (III),* for MA-PO copolymerization reaction allowed us to observe the influence of internal complexation of zinc atoms by donor substituents, as well as inductive and conjugation effects in the catalyst molecule on the course of copolymerization.



(I)



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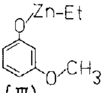

(III)

EXPERIMENTAL

$ZnEt_2$ was obtained according to the known method and purified by heating with sodium [5]. Maleic anhydride was distilled before use. Propylene oxide was dried using $LiAlH_4$. All other reactants and solvents were purified by standard methods and distilled in a nitrogen atmosphere.

Catalysts were prepared in separate flasks by introducing cocatalyst (HX) to the stirred solution of an equimolar amount of $ZnEt_2$ in a suitable solvent [6]. Then they were introduced as 1 mol solutions to 60 mL reaction vessels containing a homogenous mixture of 0.05 mol MA and 0.05 mol PO in 40 mL of corresponding solvent. One mol% on total monomer of catalyst was used. The polymerizations were carried out at 80°C within 48 h. After completion of the reaction, the reaction vessel content was dissolved in 50 mL CH_2Cl_2.

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*Catalyst association and complexation by the solvent are omitted in the formulas.

The solution obtained was washed with 5% H_2SO_4, water, and dried. Then solvents were evaporated from the solution and the remaining oils were heated at 80°C under 0.5 mmHg for some hours. Copolymers and terpolymers obtained in the above way were analyzed and then hydrolyzed according to a described method [7].

Techniques

^{1}H-NMR spectroscopy was performed on a Tesla B5487C NMR spectrometer at 80 MHz at room temperature. Solutions of 10-15% polymer in acetone-d_6 with a few percent TMS standard were employed.

^{13}C-NMR measurements were carried out at room temperature on a Varian CFT20 unit at 22.5 MHz.

VPC analyses were performed in a Varian 2868 gas chromatograph at 250°C using a column packed with Carbowax 20M.

RESULTS AND DISCUSSION

The copolymerization of MA and PO was carried out in toluene, dioxane, diethoxyethane, or dimethyldigol solution in the presence of EtZnX-type catalyst (X = C_2H_5–, C_6H_5O–, 2-$CH_3OC_6H_4O$–, 3-$CH_3OC_6H_4O$–, 2-$CH_3COC_6H_4O$–, 2,6-$(CH_3O)_2C_6H_3O$–, or 2,6-$Cl_2C_6H_3O$–). The copolymers obtained were unsaturated poly(ester-ether) resins of molecular weight in the 1000-4000 range. They contained a comparatively large amount of methanol-insoluble fraction in comparison with copolymers produced by zinc halide catalysts [8].

The monomer distribution in the copolymers was found to be dependent on solvent applied as well as the kind of catalyst (Table 1). The data presented in Table 1 show that donor solvents, e.g., dioxane, diethoxyethane, and dimethyldigol, caused a decrease of PO units in the copolymers. Assuming that the runs of MA units in the copolymer chain cannot be greater than one, the mole fraction of PO units was found to be in the 0.56-0.61 range. In the case of copolymers obtained in donor solvents, the mole fraction of PO units was in the 0.52-0.55 range.

It can be seen from Table 1 that the most advantageous catalysts for obtaining alternating copolymers were those in which the X ligand increased the electron charge on the zinc atoms as a result of the conjugation and internal complexation effect (e.g., Experiments 3 and 6, Table 1). Catalyst in which internal complexation occurred, but without the possibility of the favorable resonance effect (Experiment 5, Table 1), was less efficient. Finally, catalyst in which there were no internal complexation nor favorable conjugation effect gave the least alternating copolymer (Experiment 4, Table 1).

MA-PO copolymer composition was found to depend to a relatively

TABLE 1. Propylene Oxide Triads in ^{1}H-NMR Spectra of MA-PO Copolymers and MA-PO-THF Terpolymer Obtained in the Presence of EtZnX Catalysts[a]

Expt no	X	Yield[b]		PO triads[c]				Molar fraction of PO	
		Total	Part insoluble in methanol	ABA	ABB	AB*B	BBB	Calc[d]	Exptl[e]
			Toluene						
1	C_2H_5-	84	60	49	19	22	10	0.59	0.58
2	C_6H_5O-	79	47	47	19	21	13	0.60	0.61
3	$2\text{-}CH_3OC_6H_4O-$	69	40	53	18	19	10	0.58	0.57
4	$3\text{-}CH_3OC_6H_4O-$	51	27	41	23	24	12	0.61	0.62
5	$2\text{-}CH_3COC_6H_4O-$	66	42	51	19	21	10	0.59	0.60
6	$2,6\text{-}(CH_3O)_2C_6H_3O-$	44	18	66	13	15	6	0.56	0.53
7	$2,6\text{-}Cl_2C_6H_3O-$	72	43	61	15	15	9	0.57	0.55
			1,4-Dioxane						
8	C_2H_5-	76	40	77	11	9	3	0.54	0.52
9	C_6H_5O-	35	16	79	10	8	3	0.53	0.53
10	$2\text{-}CH_3OC_6H_4O-$	57	36	84	7	6	3	0.52	0.50
11	$2\text{-}CH_3COC_6H_4O-$	61	37	81	9	8	3	0.53	0.53
12	$2,6\text{-}(CH_3O)_2C_6H_3O-$	57	25	88	6	5	2	0.52	0.49
13	$2,6\text{-}Cl_2C_6H_3O-$	51	20	80	10	7	3	0.53	0.52

				1,2-Diethoxyethane					
14	C_2H_5	66	14	59	17	15	9	0.57	0.59
				Dimethyldigol					
15	C_2H_5-	58	10	70	15	10	5	0.56	0.55
				Tetrahydrofuran[f]					
16	C_2H_5-	90	72	27	47	24	2	-	0.36

[a] MA, 0.05 mol; PO, 0.05 mol; solvent, 40 mL; EtZnX, 1 mmol; temperature, 80°C in 48 h.

[b] In relation to both monomers.

[c] A = $-OCOCH{=}CHCO-$; B = $-OCH(CH_3)CH_2-$; B* = $-OCH_2CH(CH_3)-$.

[d] Obtained from PO triads.

[e] Obtained from ratio of methyl to vinyl region NMR signals intensities.

[f] Product terpolymer MA-PO-THF.

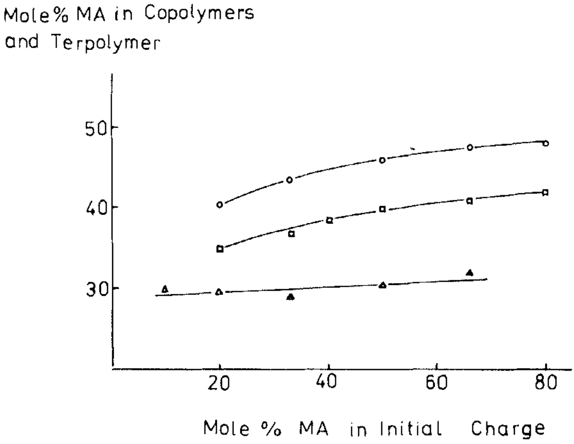

FIG. 1. Composition of MA-PO and MA-PO-THF polymers as a function of initial charge composition as produced by the catalyst $ZnEt_2$ in (□) toluene, (○) dioxane and (△) tetrahydrofuran. MA + PO = 0.1 mol; solvent, 40 mL; $ZnEt_2$, 1 mmol; temperature, 80°C in 48 h.

small extent on the monomer charge ratio (Fig. 1). This indicates the possibility of application of Markovian statistics to monomer distribution characterization [7]. Using the observable PO triads in the ^{1}H-NMR spectra of MA-PO copolymers and the relative concentrations of glycols obtained from the hydrolysis of these copolymers on VPC chromatograms, third-order Markovian statistics can be applied for characterizing monomer distribution. The results of these calculations are presented in Table 2. The ratios $M_{PO}:M_{MA}$ calculated from addition probability parameters are in good agreement with those obtained from ^{1}H-NMR signal intensities. Thus monomer distribution predicted from the third-order Markovian process fit the observed NMR and VPC data.

In the case of copolymerization carried out in solvents with strong donor properties or in the presence of a catalyst with a decreased partial positive charge on the zinc atom, the addition probabilities approach zero (Table 2). This distribution can be described by first-order Markovian statistics. Thus the structure of copolymers can be related to the Lewis acidity of the catalyst metallic center.

The MA-PO copolymers obtained were found to exhibit different signals (the difference was about 6 Hz) of vinyl protons in their ^{1}H-NMR spectra. The MA-PO copolymer characterized by the highest degree of alternation (obtained in Experiment 12, Table 1) was examined by means of ^{13}C-NMR spectroscopy (Table 3). The apparent

TABLE 2. VPC Analysis of the Products of Hydrolysis of MA-PO Copolymers and MA-PO-THF Terpolymer and Markovian Addition Probability Parameters

Expt	Mol% of runs of specific length[a]								$M_{PO}:M_{MA}$	
no.	ABA[b]	ABBA		ABBBA	ABBBBA	$P_{BAB/B}$	$P_{ABB/B}$	$P_{BBB/B}$	Calc[c]	Exptl[d]
1	69.0	16.2		13.1	1.7	0.29	0.46	0.06	1.43	1.38
6	88.8	5.8		4.9	0.5	0.18	0.45	-0.04	1.26	1.13
8	90.6	7.6		1.7	0.1	0.11	0.23	0.24	1.14	1.08
12	92.8	5.9		1.2	0.1	0.05	0.18	0.04	1.06	0.96
	ABA[b]	ABBA	ABCA	ABBCA ABCBA	ABCCA ACBCA				$M_{PO+THF}:M_{MA}$	
16	30.7	4.9	53.0	1.1	10.2	0.69	0.16	-0.02	1.80	2.28

[a] $A = -OCOCH{=}CHCO-$; $B = -OC_3H_6-$; $C = -O(CH_2)_4-$.

[b] As 100% mol% of dimers and higher oligomers in chromatograms.

[c] $1 + P_{BAB/B} + P_{BAB/B} \cdot P_{ABB/B} : (1 - P_{BBB/B})$.

[d] Obtained from ratio of methyl to vinyl region ^{1}H-NMR signal intensities. The addition probabilities for terpolymers were calculated assuming no differences between PO and THF units.

TABLE 3. ^{13}C-NMR Chemical Shifts in MA-PO Copolymer Obtained in the Presence of 2,6-$(CH_3O)_2C_6H_3OZnEt$ Catalyst[a]

Carbon atoms	Line position[b] (ppm)	Intensity (%)
$-CH_3$	16.18	76
$-CH_2-$	66.39	60
$-CH-$	69.16	80
$-CH=$	129.17	28
	129.35	56
	129.84	44
	129.95	54
	130.42	56
$-COO-$	164.42	100
	164.71	82

[a] Only signals of intensity above 10% are listed.
[b] In ppm downfield from TMS. $CDCl_3$ was the solvent.

distinction of vinyl carbon atoms in the ^{13}C-NMR spectrum seems to be caused by partial isomerization of MA unsaturated double bonds to the trans isomer.

It was found that MA-PO polymerizations carried out in THF solution by the EtZnX catalysts produced MA-PO-THF terpolymers. Third-order Markovian statistics were applied for these terpolymers, assuming no difference between PO and THF units as components of the corresponding glycols obtained from the terpolymers hydrolysis. The results obtained, presented in Table 2, show that in this case the addition parameters $P_{ABB/B}$ and $P_{BBB/B}$ are close to zero. Thus this distribution can be described by second-order Markovian statistics.

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