Epoxide Copolymerization with the Dialkylaluminum Acetylacetonate–Dialkylzinc–Water Catalyst System

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ABSTRACT: The diisobutylaluminum acetylacetonate–water–diethylzinc catalyst system has been used to terpolymerize epichlorohydrin (**1**), propylene oxide (**2**), and allyl glycidyl ether (**3**) in benzene at 50°. Reactivity ratios for the various monomer pairs have been determined by the Fineman–Ross, and by a nonlinear regression technique. The latter clearly gives values which more accurately predict copolymer compositions. The reactivity ratios for the different monomer pairs are **1**/**2**, 0.55/1.76; **2**/**3**, 1.89/0.64; **1**/**3**, 0.62/0.25. The significance of these values is discussed and used to test terpolymerization relationships described in the literature. The variation of terpolymer composition with conversion in batch polymerizations has been studied; analyses of actual terpolymers agreed with calculated values using the determined reactivity ratios. The terpolymers synthesized have been characterized by several techniques.

In a previous publication Kuntz and Kroll described the development of catalyst systems derived from pure, separately synthesized, dialkylaluminum acetylacetonates (R_2Alacac) for the polymerization of epichlorohydrin (ECH), propylene oxide (PO), and allyl glycidyl ether (1-(allyloxy)-2,3-epoxypropane, AGE).[1] The chemistry involved in the formation of the active catalyst species from a mixture of R_2Alacac–water–dialkylzinc (R_2Zn) was studied.[1]

This article describes in detail the terpolymerization of ECH–PO–AGE using the *i*-Bu_2Alacac–0.5 water–Et_2Zn catalyst system. The reactivity ratios for the various monomer pairs have been determined by the Fineman–Ross procedure and by a nonlinear regression technique; a comparison of the precision of the two procedures is made. The significance of these values is discussed and used to test terpolymerization relationships described in the literature. We discuss the variation of terpolymer composition as a function of conversion in batch polymerizations and compare calculated and observed polymer composition. The terpolymers synthesized have been characterized by several techniques.

Results and Discussion

Table I shows typical data for the batch terpolymerization of ECH–PO–AGE. Polymerizations were carried out in benzene solvent at 50°, and gave 50–60% conversion in 20 hr. The products were isolated by precipitation into methanol or boiling water.

We were aware that the batch polymerization technique would not afford a compositionally unique polymer, but that the isolated material would be the composite of all the macromolecules prepared during the synthesis period. Therefore, we studied the reactivity ratios in the ECH–PO–AGE monomer system, in an attempt to learn how terpolymer composition varied with conversion.

Various feed compositions for each of the comonomer pairs were prepared and polymerized to less than 10% conversion. Copolymers were carefully deashed with methanol and HCl and analyzed; no ash was found in microcombustion analyses of these samples. For the ECH–PO system microchlorine analyses using an oxygen combustion procedure and infrared analyses were used to determine copolymer composition. For the ECH–AGE pair chlorine analyses and infrared spectroscopy were used for copolymer analysis. The PO–AGE copolymers were analyzed by an infrared technique, as were terpolymers.

Table II shows the reactivity ratios obtained from these experiments by both the Fineman and Ross[2] treatment and by nonlinear regression procedures related to those described in the literature.[3,4] The Fineman and Ross procedure has been used a great deal in copolymerization research but has been the subject of some criticism because its use involves subjective decisions and a means of obtaining meaningful estimates of errors is not straightforward.[3,4] Fineman and Ross transformed the copolymer composition equation to a linear equation with one reactivity ratio as the slope and the other as the intercept. (For simplicity of notation in this discussion we will deal with the single monomer pair M_1, M_2.) These parameters could then be determined by linear least squares analysis. However, the values of r_1 and r_2 that give the best fit to the transformed linear equation do not give the best fit to the original copolymerization equation as will be shown below. Also, the Fineman–Ross analysis is usually performed twice since the transformation can be applied to give r_1 as the slope and r_2 as the intercept or *vice versa.* Thus, four values are obtained from the calculations, two for r_1 and two for r_2. Which values should be chosen? Usually, the slope of the linear equation can be obtained with more precision than its intercept and many workers report the values for r_1 and r_2 obtained in this way rejecting the reactivity ratio values obtained from the intercept. The values calculated using the Fineman and Ross method shown in Table II were chosen this way. The confidence interval is derived from the 95% confidence level for the slope

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(1) I. Kuntz and W. R. Kroll, *J. Polym. Sci., Part A-1*, **8**, 1601 (1970).

(2) M. Fineman and S. D. Ross, *ibid.*, **5**, 259 (1950).

(3) D. W. Behnken, *ibid., Part A*, **2**, 645 (1964).

(4) P. W. Tidwell and G. A. Mortimer, *ibid., Part A*, **3**, 369 (1965).

TABLE I
ECH–PO–AGE BATCH TERPOLYMERIZATIONS

	Experiment no.					
	1	2	3	4	5	6
ECH, mol %	66	66.5	65	65	64	63
grams	138	138	736	138	138	736
PO, mol %	33	33.5	33	33	32	32
grams	43	43	232	43	43	232
AGE, mol %	1	0.5	2	2	4	5
grams	2.6	1.3	27.4	5.2	10.7	82
Benzene, ml	281	281	1500	281	281	1500
i-Bu$_2$Alacac, mol[a]	0.027	0.027	0.144	0.027	0.027	0.144
Et$_2$Zn, mol	0.027	0.027	0.144	0.027	0.027	0.144
Water, mol	0.0135	0.0135	0.072	0.0135	0.0135	0.072
Polymerization time, hr (50°)	22	22	20	20	20	20
Yield of polymer, g[b]	97	85	437	122	113	353
Wt % conversion	53	47	44	66	59	33
Inherent viscosity[c]	5.12	3.32	4.98	3.74	1.91	2.69
Acetone solubles, %[d]			19			15
Crystallinity index[e]			9	8	6	3

[a] Diisobutylaluminum acetylacetonate. [b] Obtained by precipitation into methanol. [c] Determined in 1-chloronaphthalene, at 135°, 0.1 g dl^{-1}. [d] Determined on a 2-g sample at the boiling point of acetone in a Kumagawa apparatus for 24 hr. [e] See Experimental Section for procedure.

TABLE II
REACTIVITY RATIOS FOR THE VARIOUS MONOMER PAIRS

Monomer pair M$_i$/M$_j$	ECH (M$_1$)–PO(M$_2$)–AGE(M$_3$)					
	ECH/PO		PO/AGE		ECH/AGE	
Reactivity ratio	r_{12}	r_{21}	r_{23}	r_{32}	r_{13}	r_{31}
Fineman and Ross procedure	0.49	1.45	2.01	0.59	0.53	0.29
Confidence interval	0.43–0.54	1.37–1.53	1.89–2.23	0.57–0.61	0.51–0.55	0.27–0.31
Sum of squares[a]	0.00367		0.00235		0.00590	
Nonlinear regression procedure	0.55	1.76	1.89	0.64	0.62	0.25
Confidence interval	0.52–0.60	1.67–1.89	1.84–1.98	0.62–0.67	0.58–0.66	0.23–0.27
Sum of squares[a]	0.00190		0.000545		0.001705	
$r_{ij}r_{ji}$	0.97		1.21		0.16	
Approximate 95% confidence interval for $r_{ij}r_{ji}$	0.86–1.08		1.13–1.29		0.14–0.18	

[a] The sum of squares of the deviations between the experimental and calculated values is a measure of how well the reactivity ratio values fit the experimentally observed data. The smaller the sum of squares the better the agreement with experimental results.

in the two separate equations. It is not the simultaneous confidence interval for r_1 and r_2 considered as a pair. The statistical terms in the table are defined in most statistics texts.[5]

The nonlinear regression technique used is similar to that described by Behnken[3] and Tidwell and Mortimer.[4] By means of a computer program, reactivity ratios are determined that minimize the sum of the squares of the differences between experimental values of the copolymer composition and those calculated from the copolymerization equation which for mathematical convenience is put in the form shown in eq 1

$$F_1 = \frac{r_1f_1^2 + f_1f_2}{r_1f_1^2 + 2f_1f_2 + r_2f_2^2} \tag{1}$$

where F_1 is the mole fraction of monomer 1 in the copolymer and f refers to the mole fraction of monomer in the feed. It should be noted that since

$$f_2 = 1 - f_1$$

there is only one independent variable in eq 1. The computer program expands eq 1 in a Taylor's series about r_1 and r_2, retaining only the linear terms, and using initial estimates of the reactivity ratios provided in the computer input, and improved values are calculated by stepwise multiple regression and a modified steepest descent technique.[6] These estimates are used to generate still better estimates, and the iteration process is repeated until the sum of squares is minimized. Finally, the best estimates of the reactivity ratios are shown in the computer output, along with their confidence interval and the sum of squares deviations. The computer program was written by Booth and Peterson under the direction of Box.[7] A general discussion of the problem of nonlinear estimation may be found in Draper and Smith.[8]

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(5) See, for example, W. J. Dixon and F. J. Massey, Jr., "Introduction to Statistical Analysis," 3rd ed, McGraw-Hill, New York, N. Y., 1969.

(6) O. L. Davies, "Design and Analysis of Industrial Experiments," 2nd ed, Oliver and Boyd, Edinburgh, 1956.

(7) G. W. Booth and T. L. Peterson, "Non-Linear Estimation," IBM Share Program, Paper No. 687, WLNL1, 1958.

(8) N. R. Draper and H. Smith, "Applied Regression Analysis," Wiley, New York, N. Y., 1966, Chapter 10.

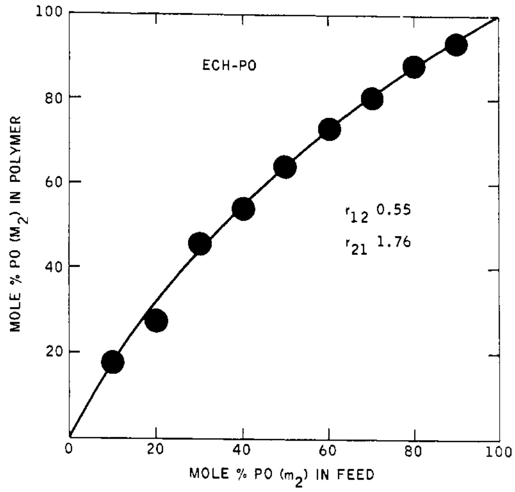

Figure 1. Copolymerization of ECH-PO. Data points are experimental, curve is from nonlinear regression analysis.

As shown in Table II the reactivity ratios obtained by the nonlinear regression approach give more desirable smaller sums of squares than those obtained by the Fineman and Ross procedure. Figure 1 shows the quality of the agreement between experimental and calculated data obtained using the nonlinear regression approach. Figure 2 is a plot indicating how the residual sum of squares varies with the estimated values of r_{13} and r_{31} for the ECH-AGE comonomer pair. The figure shows contour lines of equal sum of squares that define a response surface whose minimum contains the best values for r_{13} and r_{31}.

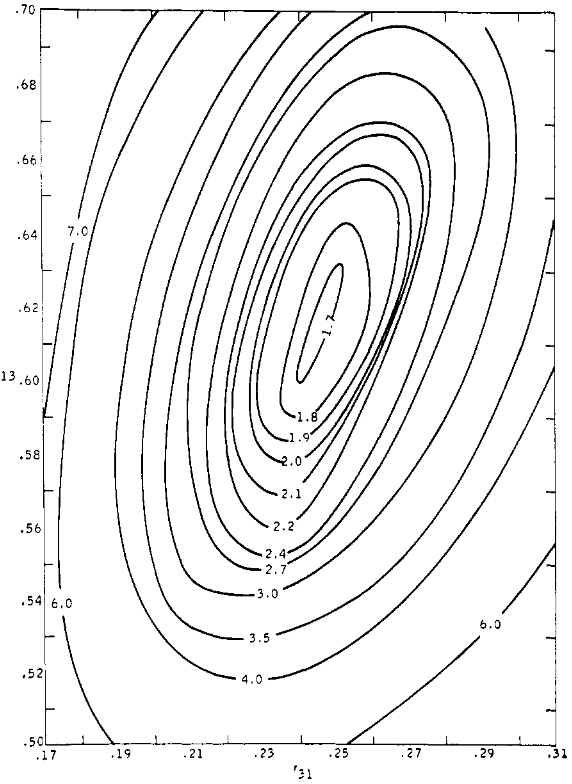

Figure 2. Response surface for the reactivity ratios for the ECH-AGE system. The contour lines are the sum of squares of the deviations ($\times 10^3$) of the compositions calculated using the specified reactivity ratios and the experimentally observed results. The smaller the number, the better the agreement. Note that the contour lines are not drawn at constant intervals.

This comparison clearly shows that the nonlinear regression procedure is superior to that of Fineman and Ross. In all cases the values for the reactivity ratios obtained by the regression technique minimize the deviations between the experimental and calculated results. A current review considers the advantages of the nonlinear regression procedure and other problems in the determination of reactivity ratios.[9]

Some comments on the reactivity ratios shown in Table II can be made. The monomer reactivity in this system decreases in the sequence PO > ECH > AGE with all propagating chain ends. The relative reactivity for PO and ECH, which follows the expected electron donor nature of the two substituents, is the same as that observed in the Et_3Al–water initiated copolymerizations with phenyl glycidyl ether.[10] This is also the relative basicity of the monomers toward BF_3–Et_2O.[11] It may also be noted that the reactivity ratio products for the PO/AGE and ECH/AGE systems are 1.2 and 0.16, respectively. Reactivity ratio products greater than unity are not usual in polymer chemistry but are sometimes observed;[12] reactivity ratios greater than unity were reported for some of the monomer pairs polymerized by Price and Brecker with related catalyst systems.[10] In the PO/AGE system AGE tends to add to either growing chain end with close to equal facility, while with ECH/AGE, AGE tends to add to ECH ended chains. This indicates that AGE residues will not form long sequences in the terpolymer; this behavior is desirable for the effective use of AGE to introduce sites for subsequent cross-linking on vulcanization.

Several theoretical analyses of terpolymerizations have been described in the literature and a discussion of how our results compare with these predictions is warranted. Ham has derived the relationship shown in eq 2 for free-radical terpolymerizations.[13] Other equations he describes permit the calculation of two reactivity ratios when the other four are known.[13] Valvassori and Sartori have shown that eq 2 is not restricted to free-radical systems but applies to any terpolymerization in which the steady-state condition given in eq 3 is true.[14] We have tested eq 2 with our data for the

$$r_{13}r_{21}r_{32} = r_{12}r_{31}r_{23} \tag{2}$$

$$k_{ij}(\mathrm{M}_i^*)(\mathrm{M}_j) = k_{ji}(\mathrm{M}_j^*)(\mathrm{M}_i) \tag{3}$$

ECH-PO-AGE system and find the result shown in eq 4, where the limits shown are based on standard deviation

$$0.70 \pm 0.07 \neq 0.26 \pm 0.03 \tag{4}$$

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(9) P. W. Tidwell and C. A. Mortimer, *J. Macromol. Sci., Rev. Macromol. Chem.*, in press.

(10) C. C. Price and L. R. Brecker, *J. Polym. Sci., Part A-1*, 7, 575 (1969).

(11) Y. Yamashita, T. Tsuda, M. Okada, and S. Iwatsuki, *ibid., Part A-1*, 4, 2121 (1966).

(12) K. F. O'Driscoll, T. Higashimura, and S. Okimura, *Makromol. Chem.*, **85**, 178 (1965).

(13) G. Ham, Ed., "Copolymerization," Interscience, New York, N. Y., 1964, p 40.

(14) A. Valvassori and G. Sartori, *Advan. Polym. Sci.*, **5**, 28 (1967).

TABLE III
PREDICTEDAND EXPERIMENTAL REACTIVITY RATIOS
MONOMERS: ECH-1, PO-2, AGE-3

				r_{ik}		r_{jk}	
i	j	k	$r_{ij}r_{ji}$	Calcd[a]	Exptl[b]	Calcd[c]	Exptl[b]
1	2	3	0.97	1.04	0.62	1.13	1.89
2	3	1	1.21	0.47	1.76	0.93	0.25

[a] From eq 5. [b] From Table II. [c] From $r_{jk} = r_{ik}/r_{ij}$, a rearrangement of eq 5, using r_{ik} and r_{ij} values from Table II.

tions estimated from the larger of the two unsymmetrical confidence intervals for each reactivity ratio. The validity of eq 2 for certain free-radical and ionic polymerization systems has been reviewed by Valvassori and Sartori.[14] Clearly, for the monomers ECH–PO–AGE polymerized with the R_2Alacac-water-R_2Zn catalyst system the relationship does not hold.

O'Driscoll has also postulated that in ionic terpolymerizations eq 5 may hold if the reactivity ratio product

$$r_{ik} = r_{ij}r_{jk} \qquad (5)$$

for the monomer pair i,j is equal to 1;[15] a similar equation was developed by Crespi, Valvassori, and Sartori.[16] We have tested eq 5 with our reactivity ratios and obtain the results shown in Table III. It is apparent from these results that eq 5 does not apply in our system, even in the case where $r_{ij}r_{ji}$ is unity. It appears that the simplified terpolymerization equations do not apply, even in an approximate fashion, unless *all* the reactivity ratio pair products are essentially unity, a situation that does not exist for the system discussed in this paper.

Having values for the reactivity ratios we could use the terpolymer composition equation developed by Kahn and Horowitz.[17] The computer program they describe uses the reactivity ratios for the three possible copolymer pairs and the initial monomer concentrations to calculate the average composition of the terpolymer made as a function of monomer conversion in a batch polymerization. It prints out the instantaneous concentrations of the monomers, the cumulative average terpolymer composition and the *instantaneous* terpolymer composition being made from the remaining concentrations of the three monomers.

Figure 3 shows the average terpolymer composition when the feed is 63 mol % ECH, 31% PO, and 6% AGE as a function of conversion. Figure 4 shows the instantaneous terpolymer composition for the same system. The independent variable in the computer program is mole per cent conversion of PO. In our polymer syntheses we measure total weight per cent conversion of monomers; several indicative values in weight per cent conversion units are shown in the figures. Figures 3 and 4 confirm that PO is the most active monomer present. The initial terpolymer made contains about 43 mol % PO and 52 mol % ECH compared to 31 and 63 mol % concentrations, respectively, in the feed. The figures also show that the amount of AGE in the terpolymer is close to that present in the feed and essentially constant during the entire course of the terpolymerization. With increasing conversion, the relative amount of ECH increases. Computations made with other feed compositions gave similar agreement with analytical data.

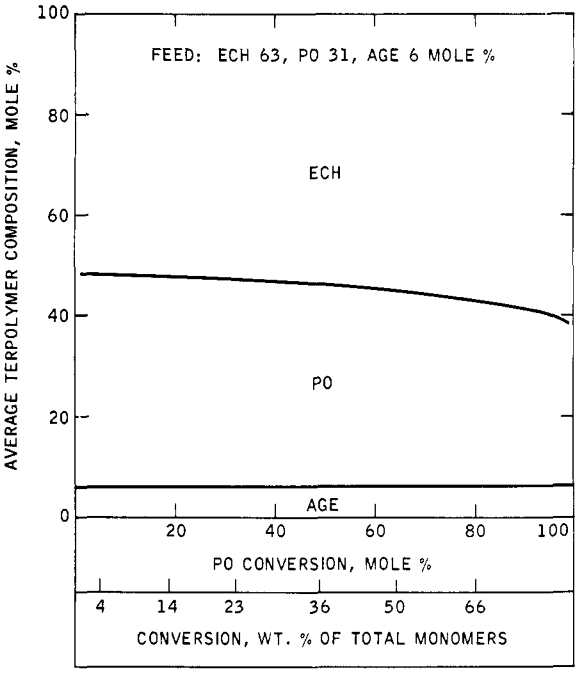

Figure 3. Average terpolymer composition. Feed composition in mole per cent, ECH-63, PO-31, AGE-6. Abscissa is shown in terms of mole per cent conversion of PO monomer to polymer, and weight per cent conversion of total monomers to polymer.

The purpose of these studies was to determine for our system how terpolymer composition varied with conversion level in preparative batch polymerizations. These batch polymerizations were typically carried out

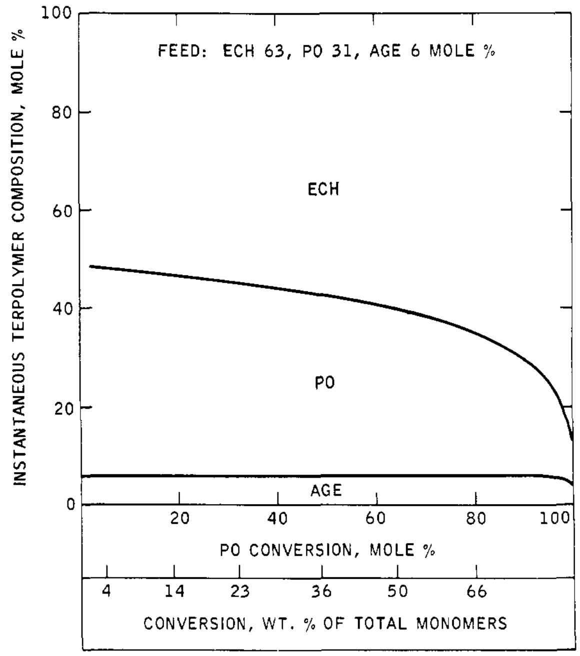

Figure 4. Instantaneous terpolymer composition, for the same system described in Figure 3.

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(15) K. F. O'Driscoll, *J. Polym. Sci., Part A*, **2**, 4201 (1964).
(16) C. Crespi, A. Valvassori, and G. Sartori, in ref 12, p 275.
(17) D. J. Kahn and H. H. Horowitz, *J. Polym. Sci.*, **54**, 363 (1961).

TABLE IV
ACTUAL AND CALCULATED TERPOLYMER ANALYSES

Wt % conversion	Found, %			Found − Calcd		
	C	H	Cl	C	H	Cl
36[a]	47.38	7.15	25.23	−0.14	+0.01	+1.00
50[b]	46.13	6.85	25.58	−0.27	−0.21	+0.31
67[a]	47.38	7.08	26.00	+0.39	+0.05	+0.88
72[b]	45.21	6.99	26.46	−1.23	+0.03	+0.49
95% confidence interval for the difference (found − calcd[c])				±0.41	±0.22	±1.17

[a] Feed: ECH 63, PO 31, AGE 6, mol %. [b] Feed: ECH 64, PO 32, AGE 4, mol %. [c] Calculated from the standard deviation for the respective elemental analysis.

to 40–60 wt % conversion levels. From our studies we conclude that the terpolymers have varying proportions of ECH and PO, and essentially constant levels of AGE.

It is interesting to compare actual terpolymer compositions with those calculated by the computer program. Table IV shows the analytical results from terpolymers made from two feed compositions at various conversion levels. These polymers were carefully deashed and no residue was observed in the microcombustion analyses whose results are shown in the table. From the computer printout we took similar conversion levels and calculated the corresponding elemental analysis values for the average terpolymer composition; the difference between observed and calculated values is shown. Using independent estimates of the standard deviations for the various elemental analyses, we calculated the 95% confidence intervals for the differences between found and calculated values. These confidence intervals are also given in Table IV. The agreement between the theoretical and experimental values is acceptable in every case but one carbon analysis and lends support to the reliability of the reactivity ratios we have calculated.

Characterization Studies. Characterization of the ECH–PO–AGE terpolymers was carried out using several techniques. That terpolymers were truly formed was indicated by simple fractionation experiments. When we took terpolymer samples and fractionated them, for example, into acetone-soluble and acetone-insoluble portions, both fractions gave indistinguishable elemental analyses. DTA procedures on these products gave glass transition temperature values for the terpolymers which generally fell between those for poly(ECH) and poly(PO). X-Ray data and particularly pyrolysis gas chromatography all indicate that terpolymers were formed.

As indicated in Table I the terpolymers were high molecular weight products as indicated by inherent viscosities from 2 to 5 dl/g. These viscosity measurements were carried out in 1-chloronaphthalene at 135° usually at concentrations of 0.05–0.10 g/dl. Under these conditions the polymers were completely soluble and showed no gel. These solutions showed no change in solution viscosity when they were maintained at 135° for several hours. When the polymers were extracted continuously in a Kumagawa apparatus at 56° with boiling acetone they were *not* completely soluble. Typically, they were 80% insoluble in this test.

TABLE V
X-RAY EXAMINATION OF ECH–PO–AGE
TERPOLYMER AND RELATED HOMOPOLYMERS

$ECH_{0.60}PO_{0.35}AGE_{0.05}$[c]		Poly(PO)[b]		Poly(ECH)[a]	
d spacings, Å	Relative intensity *I*	*d* spacings, Å	Relative intensity *I*	*d* spacings, Å	Relative intensity *I*
9.3	100				
7.1	5	5.24	Strong		
4.67	11				
4.54	16	4.28	Very strong	4.57	100
3.113	69	3.38	Very weak	3.86	25
				3.13	26
				3.05	21
2.818	9	2.80	Weak		
2.6	8	2.62	Weak		
Crystallinity index	8.7		80		36

[a] Isida[19] has reported 4.56 Å strong, 3.83 Å medium, and 3.09 Å weak. [b] Prepared with the Pruitt and Bagget catalyst.[18] [c] Subscripts indicate stoichiometric composition; they do not imply block copolymer structure.

Clearly, these results indicated the polymers were partially crystalline materials.

The X-ray results shown in Table I and those shown in more detail in Table V confirm this hypothesis. In Table V, the terpolymer has a crystallinity index of 9. For comparison we show results with a highly crystalline poly(PO) prepared by the $FeCl_3$–PO catalyst[18] and fractionated from acetone at −20°; and a poly(ECH) with an inherent viscosity of 4.3 made with our three component catalyst system. Comparing the "*d*" spacings and relative intensities for the terpolymer with those for the homopolymers shows that the diffraction patterns of the terpolymers do not contain the lines of the homopolymer patterns. It can be inferred that the structure of the terpolymer is entirely distinct from those of the homopolymers.

When we examined a sample of poly(ECH) by DTA it showed a first-order transition of 105–110°, and a glass transition of about −35°. The literature describes the synthesis of a crystalline poly(ECH) with a

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(18) M. E. Pruitt and J. M. Baggett, U. S. Patent 2,706,181 (April 12, 1955).

TABLE VI
DTA RESULTS WITH ECH–PO–AGE POLYMERS

Terpolymer composition mol %			Transitions	
ECH	PO	AGE	First order Temp, °C	Glass Temp, °C
100			105–110	−34 to −40
	100		70	−65 to −75
60	30	5		−52
80	10	10	45, 65, 85	−50
50	40	10	145	−60

melting point of 119°.[19] The crystalline poly(PO) prepared by Pruitt and Baggett was reported to melt at 70°.[18] Some of our results are shown in Table VI. The samples were examined in a routine way with no particular annealing procedures. Literature studies have shown that first-order transitions can be made to vary widely depending on the details of sample thermal history. Therefore, we do not draw any conclusions from the melting behavior results shown in the table. The glass transition values may have more significance. The samples shown in Table VI show a glass temperature between those for the pure homopolymers, and indicate that copolymers have been produced.

Pyrolysis–gas chromatography was used to study the polymers we synthesized. To simplify the interpretation of results ECH–PO copolymers were used. In the procedure polymer samples were pyrolyzed for 30 sec, reaching a maximum temperature of approximately 900°. The volatile products were transported by the carrier gas directly into the gas chromatograph for separation. For comparison, homopolymers of ECH and PO were also examined by this technique.

The results of these experiments with a 50 mol % ECH–PO copolymer are shown in Figure 5. The abscissa is a scale chosen to rank the peak positions in the gc traces according to their order of occurrence; the peak position is determined by the retention time of the volatile fragments resulting from polymer pyrolysis. The identity of these fragments was not determined. The ordinate is a scale which represents peak height normalized to 100% for each chromatogram.

From the figure we can compare the relative amounts of the various degradation products. Poly(PO) gives, primarily, only two, low-order fragments. Poly(ECH) and the ECH–PO copolymer, on the other hand, yield a larger number of fragments and more uniform intensity distributions. The ECH–PO copolymer, however, is seen to have a relative intensity pattern different from that of either homopolymer, although certain of the peak positions are closely related to those in the homopolymers. These results confirm that the ECH–PO polymer product is, indeed, a copolymer and not a mixture of homopolymers. We believe that it is reasonable to assume that this conclusion is also valid in the terpolymerization case and that there, too, terpolymers are produced, not mixtures of homopolymers.

Conclusions

The reactivity ratios for the various comonomer pairs have been determined for the ECH–PO–AGE monomer system using the R_2Alacac–0.5 water–R_2Zn initiator. The reactivity ratio product for the monomer pairs ECH–PO and PO–AGE is close to unity, while that of ECH–AGE is significantly less than unity. The first two monomer pairs tend to form random copolymers while ECH–AGE tends to form alternating copolymers. The reactivity ratio values indicate that for ECH–PO–AGE terpolymers, containing small amounts of AGE, the distribution of monomer residues is essentially random, and block terpolymers are not produced.

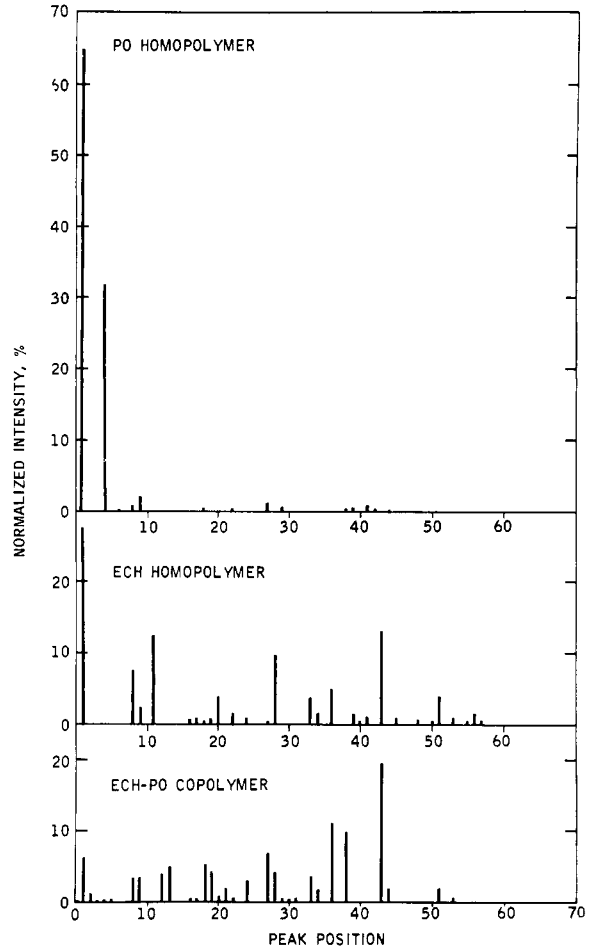

Figure 5. Pyrolysis gas chromatography results. See text for discussion.

The comparison of the classical Fineman and Ross procedure, with a nonlinear regression technique for determining reactivity ratios, clearly shows the latter to have definite advantages. These observations support the views in the literature which encourage the use of the nonlinear regression procedure for determining reactivity ratios.[3,4,9] Actual terpolymer analyses agreed with calculated values obtained using the determined reactivity ratios.

Experimental Section

Polymerization procedures, R_2Alacac synthesis, and starting material purification have been described previously.[1] DTA measurements were made on a modified Leeds and Northrup differential thermal analyzer.

Copolymerization Procedure. A typical low conversion experiment used in determining reactivity ratios used the following procedure. In a glove box, under nitrogen, 7.38 ml of PO, 5.28 ml of AGE, 25 ml of benzene, 1.8 mmol of *i*-Bu_2Alacac, 0.9 mmol of water, and 1.8 mmol of Et_2Zn

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(19) S. Ishida, *Bull. Chem. Soc. Jap.*, 33, 727 (1960).

TABLE VII
CO- AND TERPOLYMER INFRARED PROCEDURE

Component	Peak, cm^{-1}	Base line	Adjusted absorbance coefficient
ECH	740	Minimum absorbance between 700 and 780 cm^{-1}	0.863
AGE	915	Line drawn from 950 cm^{-1} tangent to the curve in the 850–870-cm^{-1} region	0.877[a]
PO	1370	1390 cm^{-1}	0.590

[a] The absorbance at 915 cm^{-1} is corrected by adding $(0.047A_{740} - 0.249A_{1370})$, where A_n is the absorbance at n cm^{-1}.

were charged to a screw-capped ampoule. The monomers were distilled immediately before use, and the reagents were added in the sequence enumerated. The ampoule was transferred to a tumbling water bath at 50° for 2 hr. The reaction was then terminated by the addition of 50 ml of methanol; the reaction mixture was transferred to a Waring Blendor. Then, 150 ml of 5% HCl containing an equal volume of ice was added and blended for 5 min at high speed. The organic phase was separated, the solvent evaporated, and the copolymer dried in the vacuum oven at 40°. The yield of polymer was 0.40 g (3.6% conversion to polymer). Infrared analysis of this copolymer gave its composition as 92.6% PO, 7.4% AGE.

Infrared Procedures. Co- and terpolymer compositions were determined by infrared reflectance measurements with a Beckman IR-8 instrument on films cast from CCl_4 solutions onto aluminum foil substrates. Insoluble samples were solubilized by heating in tetrahydrofuran containing concentrated HCl. The degraded polymer was extracted into CCl_4, the solution washed three times with water, dried with K_2CO_3, centrifuged, and then used for film preparation. Experiments showed this treatment did not affect the composition determination. Absorbance coefficients were evaluated from homopolymer spectra. Since films were not of identical thickness, the path length was normalized by using the area under the 1100-cm^{-1} ether band; the sum of eight absorbances measured at 20-cm^{-1} intervals from 1170 to 1030 cm^{-1}, from a base line drawn from 1200 to 850 cm^{-1}, was taken. We standardized on the value of 8.00 for this sum; dividing the absorbance sum for a particular sample into this value gave a path length correction factor which was used to multiply the observed absorbance at the frequencies used to determine the terpolymer composition. The monomer unit concentrations were measured at the frequencies shown in Table VII.

Crystallinity Measurements. Crystallinity values were estimated from X-ray diffractometer traces obtained by transmission diffraction with Cu Kα radiation. A LiF crystals monochromator was used in the diffracted beam and the monochromated radiation was received by a Geiger counter.

The monochromator crystal was bent and ground according to well-known principles, to reflect the divergent diffracted beam with high intensity and good resolution. Diffractometer traces within the limits of 7–32° in 2θ were resolved into areas A_c and A_a due, respectively, to the crystalline and amorphous phases of the polymers. The crystallinity index, X_c, was defined by the simple relationship shown in eq 6.[20] A more sophisticated analysis in which the areas

$$X_c = \frac{A_c}{A_c + A_a}(100) \tag{6}$$

are corrected by experimentally determined factors[21] was not feasible within the scope of this investigation.

Polymer Pyrolysis. Experiments were conducted with an Aminco pyrolyzer attached to the "A" channel of a Wilkens Aerograph, Model 1520, dual-column, dual-flame detector gas chromatograph, equipped for temperature programming. Polymer samples, approximately 1 mg in size, were introduced into the pyrolyzer unit in quartz capillary tubing. Pyrolysis was carried out for 30 sec under an applied heater voltage which produced a maximum sample temperature of approximately 900°. The characteristics of this pyrolyzer have been described.[22]

The volatile products resulting from pyrolysis of the polymer were separated on a 10-ft column packed with 20% Carbowax 20M on Chromosorb P (60–80 mesh). Helium was used as the carried gas. The temperature programming schedule used in all experiments was as follows: (1) isothermal for 10 min at 50°, (2) 6°/min to 220°, (3) isothermal for 35 min at 220°.

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