above that where the intensity of the ion is 1%, which was assigned the appearance potential value[16] of 13.8 v. Data for the substituted phenyl ions were obtained at the voltage at which the intensity of Ar^+ is 10% of its value at 48 v on this instrument. As explained in the preceding paper,[4] this potential is assigned a value of 19 v.[17]

(16) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p 280.

(17) Laurence Dusold assisted with several spectra.

Catalyst-Controlled Monomer Distributions in Copolymers. Copolymerization of Propylene Oxide and Maleic Anhydride

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Abstract: The monomer distribution in the copolymer propylene oxide–maleic anhydride, prepared by seven different homogeneous catalysts, has been obtained by high-resolution nuclear magnetic resonance spectroscopy of the copolymer and by vapor phase chromatography of the hydrolyzed copolymer. The nmr analysis yields the relative concentrations of triads in the completed chain, and the vpc analysis yields the relative concentrations of runs of propylene oxide up to a length of four. Greatly differing monomer distributions are observed depending on which catalyst is used in the copolymerization. However, in all cases, the monomer distributions can be described by Markoffian statistics of order either one, two, or three.

Monomer distributions in copolymers formed by free-radical propagation can be characterized by the statistics of Markoffian processes.[1] From the order of such statistics one knows to what extent monomers previously added to the chain affect further additions. Normally, this effect is short range. In fact, for ethylene–vinyl chloride[2] and ethylene–vinyl acetate[2] the growing chain has no (instantaneous) memory and the monomer distribution is described by zeroth-order Markoffian statistics. The monomer distribution for completely alternating copolymers[3] can be described by first-order Markoffian statistics. This implies a mechanism in which the terminal free-radical unit is involved in determining the chain propagation.

Some catalytic homopolymerizations of methyl methacrylate[4] and of propylene[5] produce diastereosequence distributions for which the parameters of Markoffian descriptions cannot be evaluated or reliably confirmed, so that the applicability of Markoffian statistics is not clear. Coleman and Fox proposed an alternative to explain such distributions.[6] Their general mechanism assumes that the end of the growing chain has two reactive states in equilibrium, both capable of adding monomer, each with its own stereospecificity. When the rates involved in the equilibrium step are comparable with the rates of chain propagation, the diastereosequence distribution is non-Markoffian and strongly depends explicitly on monomer concentration. When

the equilibrium rates are very fast or slow compared to the propagation, the mechanism predicts a distribution which is indistinguishable from that arising from a Markoffian process. The Coleman–Fox mechanism can also be applied to catalytic copolymerizations with analogous predictions.

Maleic anhydride and propylene oxide can be copolymerized[7] to yield an unsaturated poly(ester-ether) (*i.e.*, [-C(=O)CH=CHC(=O)OCHCH$_3$CH$_2$O-]) with a number of different catalysts. The monomer distributions for these copolymers have been obtained using a combination of high-resolution proton magnetic resonance spectroscopy on the copolymers and vapor phase chromatography on the glycol ethers produced by hydrolyzing the copolymers. The nmr analysis yields the relative concentrations of triads in the completed chain (A*A*A, A*A*B and B*A*A, A*B*A, B*B*B, B*B*A and A*B*B, and B*A*B, where A is propylene oxide and B is maleic anhydride). Vpc analysis yields the relative concentrations of runs of A (BAB, BAAB, BAAAB, BAAAAB, BAAAA...AB) up to a length of four.

From the experimental monomer distributions it can be shown that any plausible mechanism of chain propagation in this particular copolymerization does not involve a non-Markoffian process with dynamic equilibrium between two or more states. The monomer distributions produced by the various catalysts differ greatly but still can be described by Markoffian statistics of order either one, two, or three. Factors are

(1) F. P. Price, *J. Chem. Phys.*, **36**, 209 (1962).

(2) J. Schaefer, *J. Phys. Chem.*, **70**, 1975 (1966).

(3) L. M. Minsk, G. P. Waugh, and W. O. Kenyon, *J. Am. Chem. Soc.*, **72**, 2646 (1950).

(4) F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).

(5) J. C. Woodbrey and Q. A. Trementozzi, *ibid.*, **C8**, 113 (1965).

(6) B. D. Coleman and T. G. Fox, *J. Chem. Phys.*, **38**, 1065 (1963). See also L. Peller, *ibid.*, **43**, 2355 (1965).

(7) R. F. Fischer, *J. Polymer Sci.*, **44**, 155 (1960); E. Schwenk, K. Gulbins, M. Roth, and K. Hamann, *Makromol. Chem.*, **51**, 53 (1962); T. Tsuruta, K. Matsuura, and S. Inoue, *ibid.*, **75**, 212 (1964); H. G. Wodill, J. G. Milligan, and W. J. Peppel, *Ind. Eng. Chem. Prod. Res. Develop.*, **3**, 53 (1964); R. M. Hedrick, U. S. Patent 3257477 (June 21, 1966).

Table I. Propylene Oxide–Maleic Anhydride Monomer Distribution from Vapor Phase Chromatographic Analysis

Catalyst	Charge ratio	Conversion	Wt % of A appearing in runs of specific length[a,b]				
			BAB	BAAB	BAAAB	BAAAAB	BAAAA...B
$SbCl_5$	12:1	0.41	0.00	0.09	0.14	0.11	0.66
	6:1	0.68	0.00	0.16	0.22	0.13	0.49
	3:1	0.73	0.01	0.15	0.23	0.13	0.48
	1:1	0.43	0.04	0.18	0.21	0.12	0.45
LiBr	3:1	0.49	0.93	0.07	0.00	0.00	0.00
$Al(OR)_3$	1:1	0.79	0.29	0.53	0.18	0.00	0.00
BF_3	3:1	0.24	0.01	0.04	0.21	0.20	0.54
	1:3		0.04	0.12	0.24	0.12	0.48
$ZnCl_2$	3:1	0.80	0.03	0.05	0.57	0.30	0.05
$SnCl_4$	3:1	0.88	0.01	0.12	0.63	0.12	0.13
	1:3	0.26	0.05	0.33	0.53	0.09	0.00
$CdCl_2$	10:1	0.39	0.05	0.16	0.46	0.16	0.16
	3:1	0.75	0.13	0.22	0.35	0.19	0.11

[a] To obtain the relative numbers of BAB, BAAB, etc., the weight per cent of A in the run is divided by the number of A units in the run. [b] Error is estimated at ±0.02 for runs of one to three and ±0.05 for runs of four and sum of all higher runs. This estimate was obtained from reproducibility of a given hydrolysis and from hydrolysis to hydrolysis. Error estimate is also consistent with nmr data (see Table IV). The larger error for four and longer runs reflects the difficulty in obtaining the vpc of tetramers (see text). These estimates are not necessarily upper or lower limits.

discussed which currently prevent formulating an exact mechanism relating monomer distribution and catalyst.

Experimental Section

1. Copolymerization Procedure. A 300-ml, three-necked, round-bottomed flask was fitted with a mechanical agitator, reflux condenser, and heating mantle. After addition of 39.2 g (for example) of maleic anhydride the apparatus was evacuated and the vacuum released with nitrogen. Propylene oxide sufficient to give the desired monomer charge ratio was then added and the mixture stirred to give complete solution. (Propylene oxide was distilled from CaH_2 before use. Maleic anhydride pellets (Monsanto Co.) were used as received if a test portion gave a clear solution when completely dissolved in dry benzene.) Catalyst was then added sufficient to give 10–40 mmoles/l. $CdCl_2$, $ZnCl_2$, and (i-$C_3H_7O)_3Al$ were added as solids and $SnCl_4$ and $SbCl_5$ as 1 M solutions in CCl_4. BF_3 was added dropwise as $BF_3 \cdot Et_2O$.

The polymerization was carried out from 20 to 40° (with LiBr and BF_3 catalysts at 80°) for periods of 4 to 16 hr. After the reaction period, excess monomer was stripped from the mixture in a rotating evaporator by raising the temperature and lowering the pressure in stages until 100° (1 mm) was achieved. The presence of unreacted maleic anhydride was determined by its characteristic 5.4-μ band. Product copolymers were straw-colored resins which flowed very slowly at room temperature.

Copolymerizations employing LiBr were conducted in sealed glass tubes under nitrogen. The sealed tube with the monomers and catalyst was agitated until complete solution was attained and then was placed in a protective metal container and heated to 75° for 24 to 36 hr. The polymer work-up was essentially as described above. The LiBr-catalyzed copolymers contrasted with all others in that they were always chocolate brown in color.

2. Hydrolysis. Copolymers were quantitatively analyzed by total hydrolysis of the component ester groups using excess NaOH in aqueous ethanol followed by back-titration with standard HCl solution.

Larger copolymer samples were hydrolyzed to obtain the resulting glycol ethers for analysis by vapor phase chromatography. The copolymer (10–30 g) was mixed gradually with a sufficient amount of 7 M aqueous KOH to provide about a 5% excess. After standing at 30–35° overnight, the still strongly alkaline mixture was extracted with three 30-ml portions of anhydrous diethyl ether which were combined and set aside. The aqueous residue was neutralized with concentrated hydrochloric acid and cooled to 0° for 30 min; the resulting maleic acid was removed by centrifugation. The filtrate was treated with 3 M $BaCl_2$ until no more barium fumarate precipitated. An equal volume of methanol was added, the mixture was centrifuged, and the liquors were fractionally distilled to isolate the propylene glycol present.

The ether extract was stripped of diethyl ether and distilled at about 1 mm. The distillate was collected up to 165° (1 mm), which includes glycols through at least tetrapropylene glycol. Higher glycol ethers are retained in the pot residue. Nmr and infrared
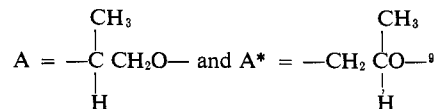
spectra of the distillate and residue were almost identical except for the magnitude of the 3.0-μ hydroxyl band.

3. Vapor Phase Chromatography. The distilled glycol ethers were analyzed with an Aerograph Model 350-B instrument using a 3 ft × 0.25 in. column of 5% SE-52 (General Electric silicon fluid) on Chromosorb W, a white diatomaceous earth. The temperature was programmed at 4°/min from 130 to 200°.

4. Nuclear Magnetic Resonance Spectroscopy. Nmr samples were prepared from a 25% by weight copolymer in deuterated chloroform solution containing 1% by volume of hexamethyldisiloxane (τ 9.94) as internal reference. Spectra were obtained from a Varian HR-100 spectrometer with an operating probe temperature of 80°. Double-resonance field-sweep spectra were obtained by the technique described by Johnson.[8] Each spectrum was calibrated by side-band modulation.

Results

1. Vapor Phase Chromatography. The relative amounts of runs of propylene oxide units in propylene oxide–maleic anhydride (PO–MA) copolymers are presented in Table I. Relative area response factors on known sample sizes were determined on known mono-, di-, tri- and tetrapropylene glycols. The area response was linear with sample size over the range employed for all four compounds. The dipropylene glycol response appeared as four peaks corresponding to the glycols of the configurations AA*, AA (and A*A1), and to each of the two stereo pairs of A*A, where

$$A = \underset{H}{\overset{CH_3}{-\overset{|}{\underset{|}{C}}\ CH_2O-}} \quad \text{and} \quad A^* = \underset{H}{\overset{CH_3}{-CH_2\ \overset{|}{\underset{|}{C}O}-}}$$[9]

The tri- and tetrapropylene glycol responses appeared in clusters of peaks resulting from partial resolution of configurational isomers. Ten samples of a given mixture reproduced each other in the relative area response for the various peaks ±5%. The error in the determination of the tetra peak was greater than the others, because the signal amplitude-to-width ratio was much lower. Samples of the pot residue were injected in an attempt to determine the small amounts of the tetraglycol remaining. Errors up to ±25% are possible for this peak.

(8) L. F. Johnson, Technical Information Bulletin, Vol. III, No. 3, Varian Associates, Palo Alto, Calif., 1962, p 5.
(9) A. J. Havlik, D. E. Udlock, and D. D. Lawson, Jet Propulsion Laboratory Technical Report No. 32-581, 1964.
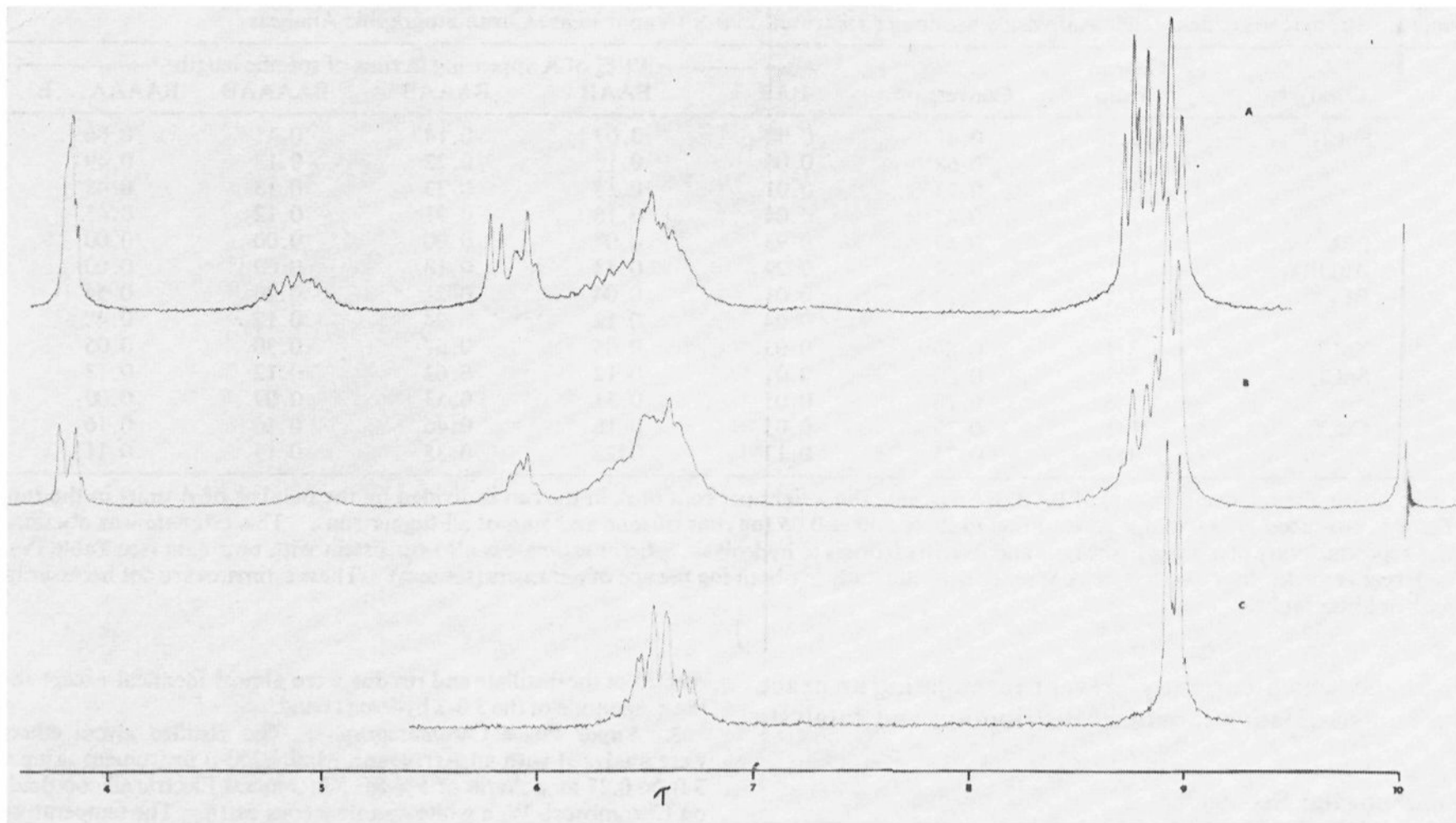
Figure 1. 100-Mc/sec spectra of PO–MA copolymers from catalyst system (A) CdCl₂, 3:1, and (B) SbCl₅, 1:1. The ratio following the catalyst is the initial charge ratio of PO to MA. The lower trace (C) is polypropylene oxide. Hexamethyldisiloxane is the internal reference and CDCl₃ the solvent. Spectra were recorded at 80°. The methyl region of A at τ 8.9 shows seven lines arising from four distinct types of methyl doublets in the copolymer chain.
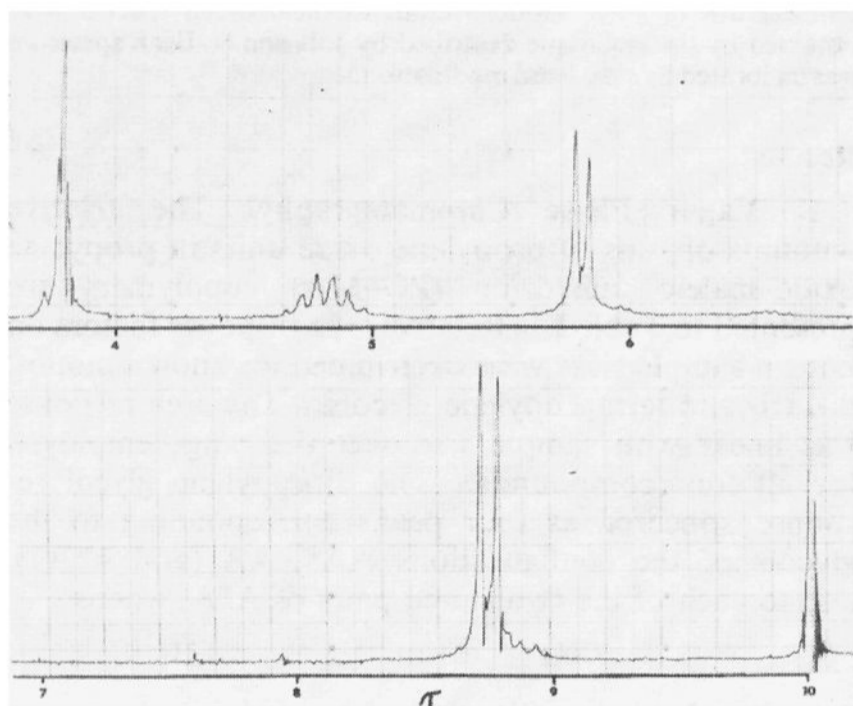

Figure 2. 100-Mc/sec spectrum of PO–MA copolymer formed from LiBr catalyzing a 3:1 PO:MA charge ratio. The simple appearance of the spectrum is due to the almost complete alternating character of the copolymer. The vinyl region (τ 3.8) is expanded in Figure 5a.

2. Nmr Line Assignments and Measurement of Signal Intensities. The nmr spectra of three PO–MA copolymers and pure polypropylene oxide appear in Figures 1 and 2. The copolymer spectra show resonances at about τ 3.8 due to the vinyl *cis* protons in MA units in the chain. The absence of any vinyl signals to substantially lower values eliminates the possibility of consecutive MA units in the chain as well as any vinyl *trans* protons. The resonances at about τ 8.75 arise from methyl groups in PO units which have PO or MA neighbors on either side. (For simplicity PO will always be

designated as A and MA as B.) The eight lines in the methyl region, listed in Tables II and III, arise from four unique methyl group doublets in the three possible nmr distinguishable triads AAA, AAB (and BAA), and BAB. The doublet from AAA triads can be assigned to the highest field doublet by comparison with the polypropylene oxide spectrum in Figure 1C. The doublet from BAB triads can be assigned to the lowest field doublet by comparison with the PO–MA copolymer spectrum in Figure 2. This particular copolymer has a MA content of 50% with no consecutive MA units, so that the entire chain is necessarily alternating. The remaining two doublets belong to AAB and BAA sequences. (The reason for two dou-

Table II. Propylene Oxide–Maleic Anhydride Nmr Methyl-Region Line Positions in CDCl₃ as Solvent at 80°

Line	Cps from HMDS at 100 Mc/sec	Doublet no.ᵃ
1	129	1
2	125	2
3	123	1
4	119	2
5	114	3
6, 7	108	3, 4
8	103	4

ᵃ Assignment made in Table III.

blets will be discussed in the next paragraph.) The validity of these assignments can be checked by comparison of the observed intensities with those predicted from the relative concentrations of runs of PO for a co-

polymer with no runs longer than four as determined by the vpc analysis. The results of this calculation are presented in Table IV. Observed and predicted concentrations are in excellent agreement, thereby confirming the assignments.

Table III. Propylene Oxide–Maleic Anhydride Nmr Line Assignments

Proton	Sequence[a]	Order with increasing magnetic field	Line position, τ
–C*H*:C*H*–	ABA[T]		3.7–3.8
	AB[T]		
–C*H*:C*H*–	A*BA	1	
	ABA	2	3.8
	A*BA*		
	ABA*	3	
–C*H*–	B*A*B		
	B*A**B		
	B*A*A		5.0
	B*A*A*		
	A*A**B		
	A*A**B		
–C*H₂*–	B*A*B		5.9
	B*A**B		
All other PO –C*H₂*– and –C*H*– protons			6.0–7.0
–C*H₃*	B*A*B	1	
	B*A**B		
	B*A*A		
	B*A*A*	2	8.9
	A*A**B		
	A**A**B		
	A*A*B		
	A**A*B	3	
	B*A**A		
	B*A**A*		
	(A)(A)(A)[b]	4	

[a] T = terminal, A = –CH(CH₃)CH₂O–, A* = –CH₂CH(CH₃)O–, B = –C(CO)CH=CHCOO–. [b] All eight combinations of A and A* appear here.

Table IV. Predicted Propylene Oxide–Maleic Anhydride Nmr Spectrum from Observed Vpc Runs of Propylene Oxide[a]

| Runs of A units	Rel run concn by vpc	BAB	AAB	AAA
		—Rel concn of predicted nmr— sequences of three BAA,		
BAB	0.05	0.05	0.00	0.00
BAAB	0.16	0.00	0.32	0.00
BAAAB	0.18	0.00	0.36	0.18
BAAAAB	0.02	0.00	0.04	0.04
BAAAA...AB	0.00	0.00	0.00	0.00
		0.05	0.72	0.22 Predicted
		0.07	0.73	0.20 Observed

[a] For sample SnCl₄, 1:3. Similar agreement exists for other samples.

Since the vpc analysis of dipropylene glycol obtained from the hydrolysis of the copolymer indicated the presence of all three types of dimer configurations, the PO monomer can be considered to add to the chain in either a forward or backward fashion. That is, if the chain is considered to grow from left to right and oxygen linkages are considered to be always on the right-hand side of a monomer unit (oxygen–oxygen linkages are not allowed so this method of counting is

complete), then the eight possible ways of forming AAB,BAA units are listed in Table III. It becomes clear then that the lower field of the two AAB,BAA doublets is due to those methyls immediately adjacent to a B unit, while the higher field is due to methyls separated from a B unit by –CH₂–. Similarly, there are eight ways of forming A and A* units to make AAA triads. The differences in the chemical shifts of the various AAA triads do not allow them to be distinguished, if indeed all eight are present. No stereochemical conformational effects are observed. Examples of the spectra are given in Figures 3 and 4.
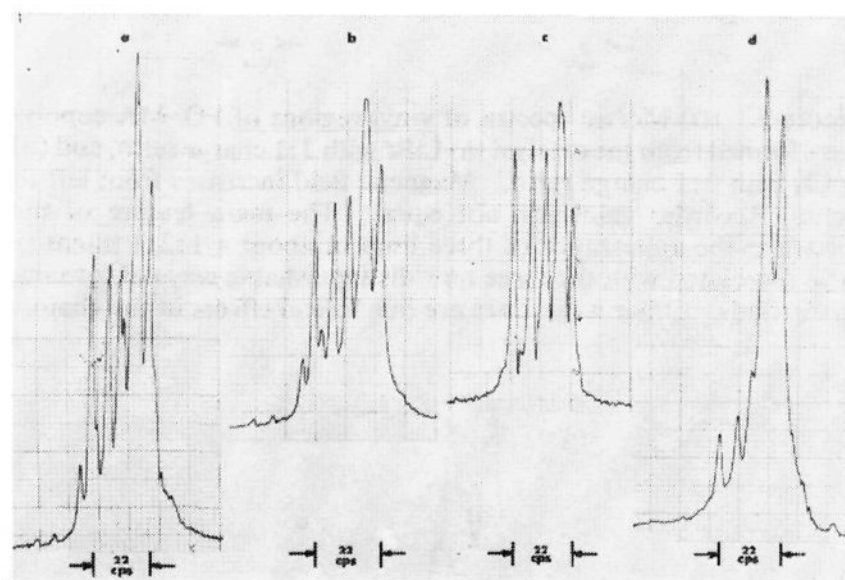
Figure 3. 100-Mc/sec spectra of methyl regions of PO–MA copolymers formed from an initial 3:1 PO:MA charge ratio using the catalyst (a) ZnCl₂ (d₆-dimethyl sulfoxide as nmr solvent), (b) ZnCl₂, (c) SnCl₄, and (d) BF₃ (all with deuteriochloroform as solvent). Magnetic field increases left to right. Left-hand marker is centered under methyl region line number 2. The solvent shift observed between a and b reveals the multiplicity of the third doublet (see Table III). The very weak doublets to lowest field in Figures 3a and 3b are probably due to methyl protons in terminal PO units in the chain.
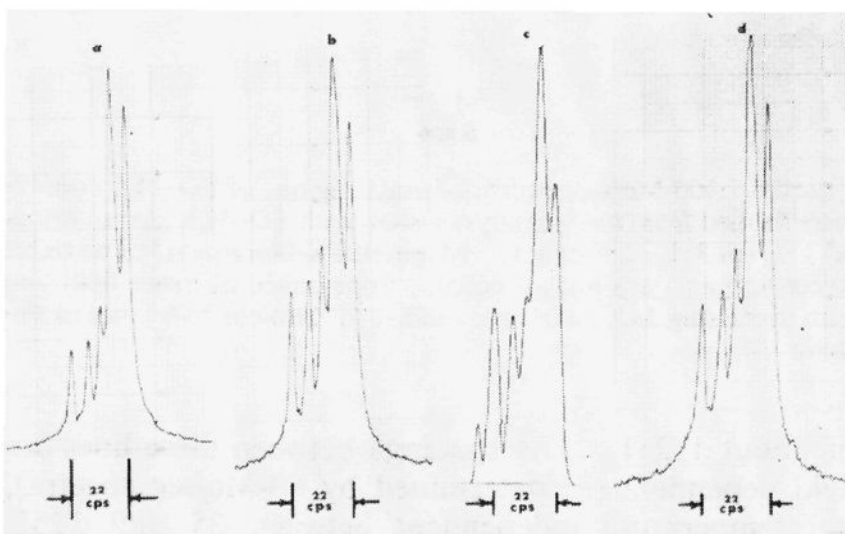
Figure 4. 100-Mc/sec spectra of methyl regions of PO–MA copolymers formed from the SbCl₅ catalyst system with initial PO:MA charge ratios of (a) 12:1, (b) 6:1, (c) 1:1, and (d) 3:1. The conversions are about the same for all copolymers; c is actually the least-squares calculated fit of the spectrum shown in Figure 1B. Magnetic field increases from left to right. The left-hand marker is centered under methyl region line number 2.

The presence of all combinations of A, A*, and B in ABA triads can be confirmed from the vinyl region. Figures 5, 6c, and 7d show the vinyl regions of various copolymers as essentially three lines spread over about 5 cps at 100 Mc/sec and usually with an intensity ratio
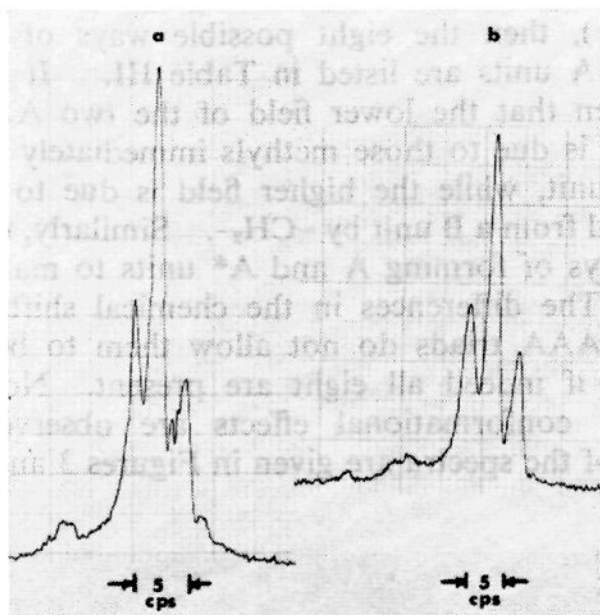
Figure 5. 100-Mc/sec spectra of vinyl regions of PO–MA copolymers formed from the catalyst (a) LiBr with 3:1 charge ratio, and (b) SnCl₄ with 3:1 charge ratio. Magnetic field increases from left to right. Recorder gains are not equal. The main feature of the spectra is the appearance of three lines in about a 1:2:1 intensity ratio associated with the three nmr distinguishable ways of forming ABA triads. Other weak lines are due to end effects in the chain.
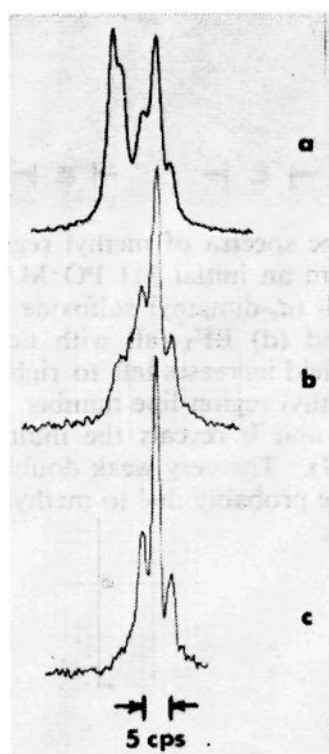

Figure 6. 100-Mc/sec spectra of vinyl regions of PO–MA copolymers formed from Sbcl₅ catalyst system with PO–MA charge ratios (a) 1:1, (b) 3:1, and (c) 6:1. Magnetic field increases left to right. Recorder gains are not all equal. Appearance of lower field line with increasing MA content is related to terminal MA units in the chain.

of about 1:2:1. The spacings between these lines are field dependent (as determined by 60-Mc/sec spectra), but temperature independent between 35 and 125°. The three lines are assigned to the three nmr distinguishable ways of forming ABA:A*BA, ABA (and A*BA*), and ABA*₁triads.[10] Apparently the ratio of

(10) Assignment of the three main lines in the vinyl region to three stereochemical isomers of ABA is very unlikely in view of the greater chemical shift differences which would be expected from the configurational isomers, known to be present in the chain from the vpc analysis. Analyzing a different type of spectrum J. D. Ingham, D. D. Lawson, S. L. Manatt, N. S. Rapp, and J. P. Hardy (*J. Macromol. Chem.*, **1**, 75 (1966)) have concluded that the observed two ¹⁹F nmr lines in the monotrifluoroacetate of poly(propylene oxide) of molecular weight about 900 are due to conformational differences in end groups rather than A and A* configurational differences. While this interpretation is consistent with respect to their measurements on both poly(propylene oxide) and optically active poly(propylene oxide), it is not
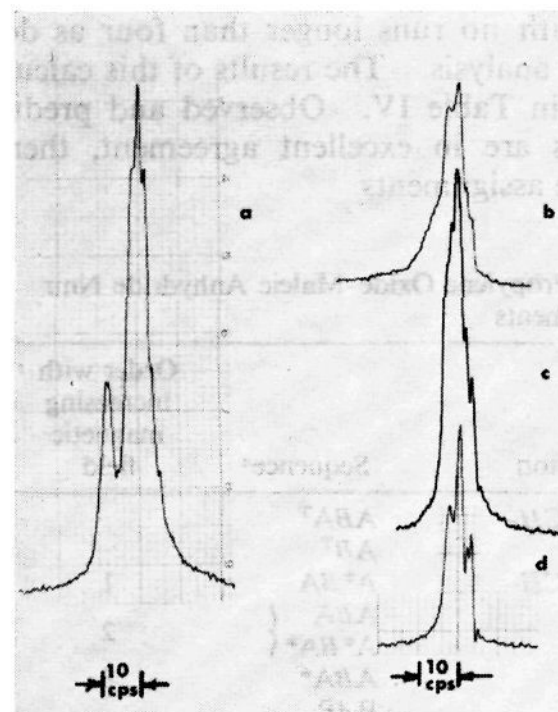

Figure 7. 100-Mc/sec spectra of vinyl regions of PO–MA copolymers formed from CdCl₂ catalyst system with PO–MA charge ratios (a) 1:3, (b) 1:1, (c) 3:1, and (d) 10:1. Magnetic field increases left to right. Recorder gains are not all equal. Appearance of lower field line with increasing MA content is related to terminal MA units in the chain.

chemical shift to coupling constant is much less than one for the two nonequivalent vinyl protons in the ABA and A*BA* triads resulting in only a single line. Since the additional lines observed in the vinyl region (Figures 6b,c and 7a,b,c), and in particular the lines to the low-field side of the triplet, increase in intensity as the monomer charge ratio is changed in the direction of making shorter chains, these lines are assigned to B units associated with terminal units of the chain either in the form ABA^T or AB^T where the superscript indicates a terminal unit. Vapor phase osmometry placed the molecular weights of these copolymers in the 1500–2500 range, which for an 80% PO copolymer corresponds to DP values of about 20–40. Since in at least some of the catalyst systems the growing chains apparently tend to end with or near B units, a substantial number of B units can be involved with the ends. (This point will be discussed later in the section.)

The remainder of the PO–MA spectra is due to –CH₂– and >CH– protons in PO units. The assignments are straightforward and are given in Table III. Confirmation of these and further confirmation of the methyl-region assignments were obtained by double-resonance experiments in which the regions at τ 5.0, 5.9, and 6.0–7.0, were selectively irradiated and the collapse of the various methyl doublets at τ 8.9 observed. The observed ratio of intensity of methyl to nonmethyl PO signals was 1.00 ± 0.03.

With DP values as low as 20, the absence of pronounced end effects must be established before the monomer distribution can be interpreted meaningfully. If $P_n(X_1X_2...X_n)$ is the probability of finding a particular sequence $X_1X_2...X_n$ among all sequences with length n, where X is A or B, and if end effects can be neglected then any sequence must have a successor and a predecessor unit which is either A or B independent of

the only interpretation. Their results can be explained in terms of A and A* configurational differences for end groups in view of the recent work of C. C. Price and R. Spector (*J. Am. Chem. Soc.*, **87**, 2069 (1965)) on head-to-head polymerization of PO. Price and Spector conclude that optical and structural inversion occur with a 1:1 correspondence.

Table V. Propylene Oxide–Maleic Anhydride Monomer Distribution from Nmr Analysis[a]

Catalyst	Initial charge ratio	BAB[b] (1)	BAA, AAB		AAA (4)	MA		
			(2)	(3)		Calcd[c]	Exptl[d]	Exptl[e]
SbCl₅	12:1	0.00	0.14	0.13	0.74	0.89	0.90	0.87
	6:1	0.00	0.23	0.23	0.54	0.81	0.85	0.83
	3:1	0.00	0.21	0.17	0.61	0.83	0.84	0.79
	1:1	0.05	0.22	0.21	0.52	0.79	0.80	0.76
LiBr	3:1	0.96	0.03	0.01	0.00	0.51	0.49	0.50
BF₃	3:1	0.00	0.14	0.09	0.76	0.89	0.92	0.89
	1:3	0.04	0.29	0.20	0.47	0.78	0.71	0.67
ZnCl₂	3:1	0.03	0.30	0.29	0.37	0.75	0.79	0.75
SnCl₄	3:1	0.02	0.31	0.40	0.27	0.73	0.76	0.73
	1:3	0.07	0.33	0.40	0.20	0.70	0.75	0.73
CdCl₂	10.1	0.04	0.38	0.32	0.26	0.72	0.77	0.75
	3:1	0.15	0.35	0.34	0.16	0.67	0.74	0.70

[a] Relative triad concentrations obtained from computed least-squares fit of methyl region. Error estimated at ±0.02 for each triad. [b] Line assignments for methyl doublets given in Tables II and III. [c] Obtained from eq 2 as check on end effects. [d] Obtained from ratio of methyl to vinyl region nmr signal intensities. [e] Obtained from chemical analysis. The small systematic difference between chemical and nmr values for M_A may be due to some effect of the catalyst complex system during hydrolysis and titration.

the initiation and regardless of the mechanism.[11] In particular

$$P_1(A) = P_2(AA) + P_2(AB) \qquad (1)$$

$$= \frac{1}{2}\left[1 + P_2(AA) - P_2(BB)\right]$$

For PO–MA copolymers with no runs of B greater than one, eq 1 reduces to

$$M_A = 1 \Big/ \left(2 - \left[AAA + \frac{1}{2}\Big\{BAA, AAB\Big\}\right]\right) \qquad (2)$$

Observed and calculated values of M_A from composition data and nmr data, respectively, are given in Table V and satisfactorily indicate that end effects do not interfere with the evaluation of chain parameters. However, deviations from the monomer distribution of an infinitely long chain can be large for a short chain when the probabilities in the initial step are far different from those in the propagation step and when there is a strong tendency to produce long runs of one monomer. (Otherwise, effects of an asymmetric induction vanish by DP 10 to 15.[12]) Neither of these two factors operate in this copolymerization.[13]

Signal intensities were measured by copying, cutting, and weighing the spectra and are accurate to about ±2%. The intensities of the overlapping doublets of the methyl region were measured by computer fitting of the observed spectra with the Gaussian model of eq 3, using a nonlinear regression technique.[14]

$$y_i = \sum_{j=1,8} c_j \exp\{-T_j(x_i - x_j^0)^2\} \qquad (3)$$

y_i equals the ith observed value of the resonance signal. x_i is the ith value of the magnetic field. $c_1 = c_3$, $c_2 = c_4$, $c_5 = c_7$, $c_6 = c_8$, and $c_j^2 = T_j$. x_j^0, the observed center of the peaks, and about ten y_i values for each peak were input to the program. Thus, the entire region was fitted with four independent parameters, thereby avoiding the difficulties of a many-parameter fit.[2] Areas under each of the j curves were obtained by

(11) B. D. Coleman and T. G. Fox, *J. Polymer Sci.*, **A1**, 3183 (1963); K. Ito and Y. Yamashita, *ibid.*, **A3**, 2165 (1965).
(12) T. Fueno and J. Furukawa, *ibid.*, **A2**, 3681 (1964).
(13) See Results. Tables I and V indicate the absence of long runs. Table VI indicates consistent results obtained from symmetrical Markoffian statistics.
(14) H. O. Hartley, *Technometrics*, **3**, 269 (1961).

numerical integration. One standard deviation was about 0.02 in absolute magnitude for the entire methyl region normalized. An example of the fit is shown in Figure 4c.

Conversion and compositional data are given in Figures 8–10 and discussed in their captions.
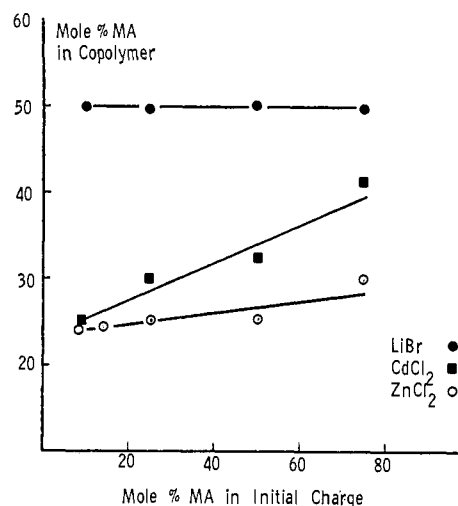

Figure 8. Final composition of PO–MA copolymers as a function of initial charge composition as produced by the catalyst systems (a) ZnCl₂, (b) CdCl₂, and (c) LiBr. The effect of a change in charge ratio is slight, making unlikely an equilibrium step with rates comparable to the rates of propagation in the copolymerization.

Analysis and Discussion of Monomer Distribution

The data in Tables I and V permit two striking observations to be made: first, the pronounced tendency for some catalysts (ZnCl₂, CdCl₂, SnCl₄) to produce runs of three PO units preferentially while other catalysts (SbCl₅) show no such tendency and, second, the insensitivity of the monomer distribution in copolymers produced by both kinds of catalysts to change in the bulk monomer charge ratio. In the SbCl₅ and SnCl₄ systems, for example, a change in the average charge ratio during copolymerization of more than an order of magnitude[15] has only a minor effect on the

(15) With SnCl₄ as catalyst, initial and final charge ratios of PO–MA were 3.0 and 1.5, respectively, in one copolymerization and 0.3 and 0.07
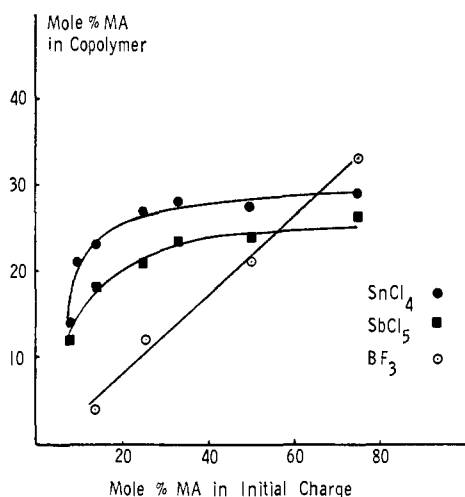
Figure 9. Final composition of PO–MA copolymers as a function of initial charge composition as produced by the catalyst systems (a) BF_3, (b) $SbCl_5$, and (c) $SnCl_4$. $SbCl_5$ and $SnCl_4$ systems produce copolymers whose compositions have only a small dependence on charge ratio. Yet the monomer distributions produced by $SbCl_5$ and $SnCl_4$ are totally different.

Figure 10. Total conversion of PO–MA copolymers as a function of initial charge composition as produced by the catalyst systems (a) $SbCl_5$, (b) $ZnCl_2$, and (c) $SnCl_4$. The fact that these curves pass through maxima indicates the existence of a critical charge composition comonomer in excess of which acts as diluent. This is true for catalysts which both do and do not homopolymerize PO, but not for all catalysts (*e.g.*, LiBr).

monomer distribution. The possibility of a non-Markoffian, Coleman and Fox type mechanism mentioned earlier describing the copolymerization is unlikely because of this insensitivity of the observed monomer distribution to the bulk monomer charge ratio. (A Markoffian Coleman–Fox mechanism is still, of course, possible.) BF_3 is a possible exception and will be mentioned later.

In order, then, to describe the preference some catalyst systems have to form runs of three PO units in terms of a Markoffian process, at least a third-order Markoffian process must be considered.

Normally the number of parameters needed to describe a third-order Markoffian process prohibits a reliable experimental verification. However, the PO–MA system is unusually well suited to analysis because of the simplification of no runs of B greater than one and because both nmr and vpc data can be collected on the same sample.

In the copolymerzation of A and B as a third-order Markoffian process with runs of B greater than one not allowed, five states are defined.[16]

$$\langle 1 \rangle = AAA$$
$$\langle 2 \rangle = AAB$$
$$\langle 3 \rangle = ABA \qquad (4)$$
$$\langle 4 \rangle = BAA$$
$$\langle 5 \rangle = BAB$$

Propagation consists of the chain, growing left to right, adding monomer units thereby making transitions between the five states of eq 4. The addition probabilities x, y, and z are defined in the following way.

$$x = P_{AAA/A}$$
$$y = P_{ABA/A} \qquad (5)$$
$$z = P_{BAA/A}$$

in another. With $SbCl_5$ as catalyst, initial and final charge ratios were 12.0 and 14.4 in one copolymerization and 3.0 and 1.2 in another. The monomer distributions for these copolymerizations are in Tables I and V and are only slightly dependent on charge ratio.

(16) A and A* are considered equivalent with respect to the monomer distribution. A description of the isomer distribution in PO–MA copolymers will be given in a later work.
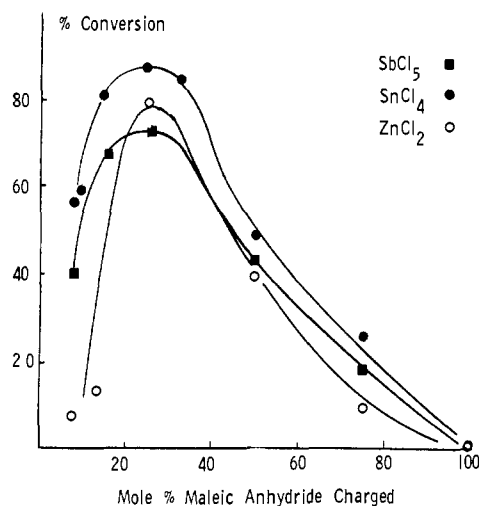
where P is the probability of the monomer written to the right of the line adding to an infinitely long chain ending with the units written to the left on the line. The transition probability matrix $\mathbf{P}$ is defined by eq 6 and connects the five states.

$$\mathbf{P} = \begin{pmatrix} x & 0 & 0 & z & 0 \\ 1-x & 0 & 0 & 1-z & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & y & 0 & 0 \\ 0 & 0 & 1-y & 0 & 0 \end{pmatrix} \qquad (6)$$

Following Price,[1] $\mathbf{P}$ is a stochastic matrix allowing a simple solution of the eigenvalue equation

$$\mathbf{P}V = \lambda V \qquad (7)$$

where V is a five-element column vector whose components represent the relative concentrations of triads in the steady-state distribution of states $\langle 1 \rangle$ to $\langle 5 \rangle$ and λ is equal to one.[17] The results of the solution of eq 7 are given below.

$$\eta_{AAA} = cyz$$
$$\eta_{AAB} = cy(1 - x)$$
$$\eta_{ABA} = c(1 - x) \qquad (8)$$
$$\eta_{BAA} = cy(1 - x)$$
$$\eta_{BAB} = c(1 - y)(1 - x)$$

$$M_A/M_B = 1 + y + yz/(1 - x)$$

where the η's are relative concentrations of triads and c is a constant. $M_A = 1 - M_B$ is the mole fraction of A in the total copolymer.

The formulas for longer runs are a simple extension of eq 8.

$$\eta_{BAAB} = \eta_{BAA}(1 - z)$$
$$\eta_{BAAAB} = \eta_{BAA}z(1 - x) \qquad (9)$$
$$\eta_{BAAAAB} = \eta_{BAA}xz(1 - x)$$

(17) Since the charge ratio is not a constant, the observed process is resolved into a sum of steady-state Markoff-like processes. See L. Peller in ref 6.

Table VI. Propylene Oxide–Maleic Anhydride Addition Probability Parameters

Catalyst	Charge ratio	y	x	z	M_A/M_B Calcd[a]	M_A/M_B Exptl[b]
SbCl$_5$	12:1	1.00 ± 0.10	0.84 ± 0.02	0.87 ± 0.03	7.7	9.0
	6:1	1.00 ± 0.09	0.69 ± 0.02	0.74 ± 0.03	4.6	5.7
	3:1	1.00 ± 0.09	0.75 ± 0.02	0.80 ± 0.03	5.3	5.2
	1:1	0.81 ± 0.06	0.70 ± 0.02	0.72 ± 0.03	3.8	4.0
LiBr	3:1	0.02 ± 0.01	0.00	0.00	1.02	0.96
Al(OR)$_3$[c]	1:1	0.53 ± 0.02	0.01 ± 0.20	0.18 ± 0.05	1.6	1.4
BF$_3$	3:1	1.00 ± 0.10	0.86 ± 0.02	0.96 ± 0.02	8.9	11.5
	1:3	0.86 ± 0.06	0.60 ± 0.04	0.77 ± 0.03	3.5	2.4
ZnCl$_2$	3:1	0.91 ± 0.05	0.28 ± 0.08	0.91 ± 0.02	3.1	3.8
SnCl$_4$	3:1	0.95 ± 0.05	-0.01 ± 0.20	0.77 ± 0.03	2.9	3.1
	1:3	0.84 ± 0.05	0.03 ± 0.20	0.53 ± 0.05	2.3	3.0
CdCl$_2$	10:1	0.90 ± 0.04	0.09 ± 0.10	0.68 ± 0.04	2.6	3.3
	3:1	0.69 ± 0.04	-0.08 ± 0.30	0.50 ± 0.05	2.4	2.8

[a] Obtained from eq 8 and the results following eq 11. [b] Obtained from ratio of methyl to vinyl region nmr signal intensities. If M_A/M_B (exptl) is obtained from chemical analysis, agreement between experimental and observed values of M_A/M_B is about the same. [c] Nmr analysis assumed known from vpc analysis.

Defining the ratios R_1, R_2, and R_3

$$R_1 = \eta_{BAB}/2\eta_{BAA}$$
$$R_2 = \eta_{BAAAB}/\eta_{BAAB} \quad (10)$$
$$R_3 = 2\eta_{BAA}/\eta_{AAA}$$

the addition probabilities x, y, and z can be obtained from

$$y = 1/(1 + 2R_1)$$
$$z = [-R_2 + (R_2{}^2 + 2R_2R_3)^{1/2}]/R_3 \quad (11)$$
$$x = 1 - zR_{3/2}$$

Values for x, y, and z obtained from PO–MA nmr and vpc data are presented in Table VI. As an internal check, the value of M_A/M_B, given by eq 8 can be calculated from x, y, and z and compared to experiment. The two values are in agreement well within experimental error (see Table VI). Thus, monomer distributions predicted from third-order Markoffian statistics fit the observed nmr, vpc, and composition data for all seven catalyst systems. The fact that $x \neq z$ for the BF$_3$-, ZnCl$_2$-, SnCl$_4$-, and CdCl$_2$-catalyzed systems indicates that these monomer distributions cannot be described by second order or lower Markoffian statistics. This result is further illustrated in Table VII. However, for the SbCl$_5$ catalyst system $x = z$ so that this simpler distribution can be described by second-order Markoffian statistics. For the LiBr catalyst system $x = z = y$, and this distribution, essentially that of a completely alternating copolymer, can be described by first-order Markoffian statistics. (Conceivably Al(OR)$_3$ could be second order. The BF$_3$-catalyzed copolymers might be considered inadequately described because of the general uncertainty about any Markoffian description. That is, the copolymer composition depends fairly strongly on charge ratio so a non-Markoffian description cannot be ruled out, and the third-order Markoffian description is not definitive.)

Predicting runs of A of four and higher from the value of x in Table VI produces fair agreement with experiment. Discrepancies are probably due mostly to experimental difficulties in accurately determining runs of four or more. The possibility also exists that some of the monomer distributions might be better described by higher order Markoffian statistics.

Table VII. Failure of Second-Order Markoffian Statistics to Describe Certain Propylene Oxide–Maleic Anhydride Monomer Distributions

Catalyst	Charge ratio	Assumed order of Markoffian statistics describing monomer distribution	η_{BAAAB}/η_{BAAB} Calcd[a]	η_{BAAAB}/η_{BAAB} Exptl[b]
BF$_3$	3:1	2	0.87 ± 0.02	3.5 ± 1.5
ZnCl$_2$	3:1	2	0.56 ± 0.03	7.6 ± 2
SnCl$_4$	3:1	2	0.43 ± 0.03	3.5 ± 0.6
CdCl$_2$	3:1	2	0.43 ± 0.03	1.9 ± 0.4

[a] Obtained from eq 9 and 11 with $x = z \neq y$ using only nmr data. [b] Obtained from vpc data in Table I.

There is no pronounced dependence of monomer distribution on monomer charge ratio since the observed Markoffian addition probabilities, x, y, and z, are usually either close to zero or one for a charge ratio on the order of one. These probabilities have the form $1/(1 + g)$,[1] where g is the charge ratio multiplied by various rate constants and is either large or small to give a probability close to zero or one. Therefore, $1/(1 + g)$ is rather insensitive to changes in g.

Clearly, the catalyst is associated with the reactive site in the PO–MA copolymerization because of the vastly different monomer distributions observed. Also, it seems very possible that, in some catalyst systems, monomer units in the coordination sphere and not yet a reacted part of the completed chain share in control of propagation of the chain. However, specifying a mechanism which relates final monomer distribution to the catalyst used is not possible because so many factors in the copolymerization are unknown: (1) the geometry of the mono- or polynuclear coordination center under the reaction conditions; (2) the number of monomer units coordinated by the catalytic center (or centers if more than one type is present); (3) the geometrical equivalence or nonequivalence of these coordinated monomers with respect to the growing chain, whether none, some, or all of them can add to the chain from the coordination sphere, and how this addition is affected by other monomers in the coordination sphere; (4) the extent to which monomer units one, two, and three positions back in the completed chain, away

from the reaction site, can control future propagation; (5) the degree to which addition from the coordination sphere to the growing chain is by single units or by runs of units (in other words, the integrity of the coordination number during propagation); (6) the initiation and termination reactions.

Mechanisms relating the structure of the various catalysts to the observed monomer distributions can be written for the copolymerization which are described by P of eq 6 (or a very similar matrix) where only the last unit in the completed chain can affect growth, if suitable assumptions are made about the remaining unknown factors above (for example, assumptions about the con-

trol of propagation by monomers in the coordination sphere). Under different assumptions mechanisms can be written, described by P, where either the last two or the last three units in the completed chain can affect growth. At this time what can be said unambiguously is that any mechanism that is adopted is under the restriction that the monomer distributions it predicts be indistinguishable from the experimentally observed Markoffian distributions.

Inclusion Compounds. XIX.[1a] The Formation of Inclusion Compounds of α-Cyclodextrin in Aqueous Solutions. Thermodynamics and Kinetics

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Contribution from the Max-Planck-Institut für Experimentelle Medizin and the Max-Planck-Institut für Physikalische Chemie, Goettingen, Germany. Received July 5, 1966

Abstract: From spectrophotometric measurements it is concluded that α-cyclodextrin forms a 1:1 adduct with nitrophenol at acidic and alkaline pH. The rate of recombination of the bimolecular reaction is about $10^8 \, M^{-1} \, \text{sec}^{-1}$ and, therefore, almost diffusion controlled. The binding of a series of azo dyes with α-cyclodextrin is highly stereospecific. In contrast to methyl orange, dyes of the type 4'-dimethylaminophenylazo-1-naphthalene-4-sulfonate form 1:1 complexes with cyclodextrin. The substitution of the dyes in the 4' and 3' positions has little influence on the equilibrium constant, while the rate of the reaction is changed by seven orders of magnitude. This behavior suggests a mechanism in which the dyes are enclosed in the cyclodextrin ring. The rate-determining step of the reaction is probably a partial melting of the water structure around the dye when it enters the cyclodextrin ring. This bond formation is compared with the enzyme substrate binding.

W hen starch is degraded by an amylase of *Bacillus macerans*, cyclodextrins[2,3] are formed by transglucosidation. Depending on the number of glucose residues in the molecule, the rings of these dextrins have different internal diameters (Table I). Figures

Table I

	Name	Internal diameter, A
6 glucose	α-Cyclodextrin	6
7 glucose	β-Cyclodextrin	7.5
8 glucose	γ-Cyclodextrin	9–10

1a and 1b show space-filling models of α-cyclodextrin. The cyclodextrins form a number of crystalline adducts with aromatic compounds, paraffins, and carboxylic acids, as well as nobel gases.[4,5] The crystalline iodine-cyclodextrin complex was studied by X-ray diffraction

and found to be a molecular inclusion compound.[6] Also potassium acetate is accommodated in the void space of the crystalline adduct.[7]

Cyclodextrins form complexes in aqueous solution with azo dyes, nitrophenol, and other substances.[4] Although there is no direct proof for a fixation of the guest molecules within the void space of the cyclodextrin, the complexes are usually regarded as inclusion compounds in which hydrogen bonding,[8] van der Waals forces,[9] and hydrophobic interactions[10,11] are the main binding forces.

This explains the interest cyclodextrins have found as models for studying the primary step of enzyme[12] or antigen–antibody reactions.[4]

It is the aim of this work (a) to show that cyclodextrins can indeed form inclusion compounds with various

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