(1.5 g) was dissolved in 15 ml of HMPA. 4,6-Diaminoisophthalaldehyde (1 g) and an equimolar amount of diacetyl compound were then added. To the solution, 0.5 ml of a 10% aqueous lithium hydroxide mixture was added. The mixture was heated for 1 hr at 80°, 2 hr at 100°, 2 hr at 120°, and 2 hr at 140°. The materials were isolated as under A: yields V 94%, VI 93%, VII 95%.

Anal. Calcd for $C_{18}H_{10}N_2$ (V, prepared in HMPA + 10% LiCl): C, 85.02; H, 3.6; N, 11.02. Found: C, 82.83; H, 4.71; N, 9.25.

Anal. Calcd for $C_{17}H_9N_3$ (VI, prepared in HMPA + 10% LiCl): C, 79.99; H, 3.55; N, 16.46. Found: C, 77.64; H, 4.87; N, 15.04.

Anal. Calcd for $C_{24}H_{14}N_2O$ (VII, prepared in HMPA): C, 83.22; H, 4.07; N, 8.09. Found: C, 82.98; H, 4.09; N, 7.79.

Thermogravimetric analyses were run with a 10°/min temperature increase.

Acknowledgment. In conclusion, I wish to thank Dr. J. K. Stille and Loren Gotter of the University of Iowa for performing the thermogravimetric analyses of our samples. The financial support of this investigation by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

Non-Markoffian Monomer Distributions in Copolymers. The Copolymerization of Ethylene Oxide and Maleic Anhydride

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ABSTRACT: The monomer distribution in ethylene oxide–maleic anhydride copolymers catalyzed by $SnCl_4$ has been determined by a proton nmr analysis of the whole chains and a glpc analysis of the glycol ethers obtained upon hydrolysis of the chains. The analyses have established that while the monomer distribution is probably homogeneous from chain to chain, it has a directly observable, long-range nonrandomness which is non-Markoffian. This result is interpreted in terms of a copolymerization model in which the catalyst can either coordinate different combinations of monomers prior to their addition to the chain or can add them directly to the chain. The model also accounts for the $SnCl_4$-generated monomer distributions in copolymers made from related cyclic ethers and anhydrides.

If the relative probabilities of addition of monomers to a growing copolymer chain can be predicted by the knowledge of a finite number of preceding additions, the resulting monomer distribution can be described by Markoffian statistics. This is the situation for most copolymers generated by free radicals. However, the monomer distributions in some copolymers generated by Freidel–Crafts catalysts have irregularities which cannot be described by Markoffian statistics.[1,2] More information about these copolymerizations is required than just a history of the past few events in order to predict the relative addition probabilities.

The monomer distribution in ethylene oxide–maleic anhydride (EO–MA) copolymers, polymerized using $SnCl_4$ as a homogeneous catalyst, is an example of a distribution which cannot be described by Markoffian statistics. The distribution has been determined by nmr analysis of the whole chains and by glpc analysis of the glycol ethers obtained upon hydrolysis of the chains. It appears to be homogeneous from chain to chain but has a directly observable long-range nonrandomness which is distinctly non-Markoffian. (Thus the nonrandomness is different from that of an alternating copolymer or that of a block copolymer.) Such a distribution is consistent with a propagation model in which one chemically unique type of catalyst can either coordinate different combinations of monomers prior to their addition to the chain or can simply add them directly to the chain. The competition between these two kinds of processes produces the non-Markoffian character of the distribution. Simpler models fail to describe all the details of the observed monomer distribution. The model is sufficiently general to describe the $SnCl_4$-generated monomer distributions in copolymers made from related cyclic ethers and anhydrides.

Experimental Section

1. Copolymerizations of Ethylene Oxide and Maleic Anhydride. Ethylene oxide and maleic anhydride were copolymerized in a 100-ml round-bottomed flask fitted with a magnetic stirrer and a 6-in. neck, the latter to allow for immersion in a constant-temperature bath maintained at 33°. The reactants were added in various molar ratios but with the sum of reactants always equal to 0.4 mol. After the addition of reactants, the flask was sealed with a rubber serum cap. Catalyst solution (100 μl containing 0.83 mmol/ml of $SnCl_4$ in cyclohexane) was injected into the reaction mixture by a syringe gun with a micrometer dial. Reaction times were varied from 1.5 to 48 hr to produce low (2–4%) and high (60–80%) conversion copolymers. The extent of reaction was determined by a combination of nmr and gravimetric techniques.

2. Nuclear Magnetic Resonance Spectroscopic Analysis. Proton nmr spectra at 60 and 100 MHz of 15% (by weight) solutions of the copolymers in $CDCl_3$ were obtained using Varian A-60 and HA-100 spectrometers, respectively, with operating probe temperatures of about 35°. The relative

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(1) J. Schaefer, R. J. Kern, and R. J. Katnik, *Macromolecules*, **1**, 107 (1968).

(2) J. Schaefer, *ibid.*, **1**, 111 (1968).

intensities of overlapping lines in the spectra were determined by computer simulation using a Du Pont 310 curve resolver.

3. Hydrolysis of the Chains. The copolymer (1 or 2 g) was hydrolyzed overnight with an excess of concentrated NaOH. Concentrated HCl was then added dropwise until the solution was slightly acidic. The mixture was cooled for several hours to precipitate the bulk of the maleic acid. After precipitation, the mixture was filtered and the filtrate collected in a round-bottomed flask to which about 150 ml of methyl ethyl ketone was added for every 10 ml of water present. The resulting mixture formed a water-rich azeotrope boiling at 73°. After the bulk of the water had been removed, the temperature increased to 79° where the methyl ethyl ketone distilled. The azeotrope allowed the complete separation of water from the glycols with virtually no loss of glycol. The glycols left in the flask were extracted with about 5 ml of benzene and derivatized with an excess of bis(trimethylsilyl)acetamide.

4. Gas-Liquid Partition Chromatographic Analysis. Analysis by glpc was performed using a F & M Model 5750 chromatograph operated with an injection port temperature of 300°, detector block temperature of 300°, flow rate of 170 ml/min, and bridge current of 150 mA. Molar response factors for the trimethylsilyl ether derivatives of the monomer, dimer, and trimer of ethylene glycol were obtained as follows. Mixtures of the glycols of varying compositions were made and 20 mg of tripropylene glycol, an internal standard, was added to 100 mg of each mixture. Volatile trimethylsilyl ether derivatives were formed by adding 100 μl of bis(trimethylsilyl)acetamide to 30 μl of each mixture. Chloroform was added as a solvent to prevent any precipitation of the derivatives. The mixtures were allowed to react at least 4 hr at room temperature to ensure quantitative conversions. The ether derivatives were then analyzed on a 0.25-in. × 6 ft, 5% SE-33 on 60-80 mesh Diatoport S column, holding for 7 min isothermally at the initial temperature, 75°, and then programming at the rate of 6.0°/min to 150°. The upper temperature limit was held until the derivative of tripropylene glycol eluted. A calibration curve for each glycol was made by plotting the ratio of glycol peak area to internal standard peak area against mole per cent glycol. The slope of the line (extrapolated through zero) gave the relative molar response factors for monomer, dimer, and trimer as 1.61, 1.18, and 1.00, respectively, with an error of less than ±5%.

Ether derivatives of the glycols resulting from hydrolysis of the copolymers were analyzed similarly except the temperature was programmed to 350° instead of 150° to permit elution of the derivatives of the higher glycols. Molar response factors for trimethylsilyl ether derivatives of the higher glycols are the same as that for the trimer,[3,4] within experimental error. (As the glycols increase in length they become similar and their molar response factors approach the same value.)

Results

The ethylene oxide–maleic anhydride chains are poly(esterethers), $-C(=O)CH=CHC(=O)-O(CH_2CH_2O)_N-$, in which consecutive maleic anhydride units do not occur. The molecular weights of the copolymers are on the order of 5000 as determined by vapor phase osmometry.

The 60-MHz proton nmr spectra of the ethylene oxide units in high-conversion EO–MA chains of two compositions are shown in Figure 1 along with the spectrum of poly(ethylene oxide). The copolymer spectra can be interpreted in terms of triads of monomers in the chain and the assignments are given in Table I. The highest field copolymer line is assigned to the central protons in A*A*A sequences (where A is $-CH_2CH_2O-$ and B is $-C(=O)CH=CHC(=O)O-$) by comparison to the poly(ethylene oxide) spectrum, and the lowest field line, in part, to the central protons in B*A*B sequences since this line most markedly decreases with decreasing maleic anhydride content. Although the two copolymers differ in composition by only 6%, they were prepared from reaction mixtures in which the charge ratio (the ratio of reactants) differed by a factor of 2. The B*A*B concentrations (relative to other

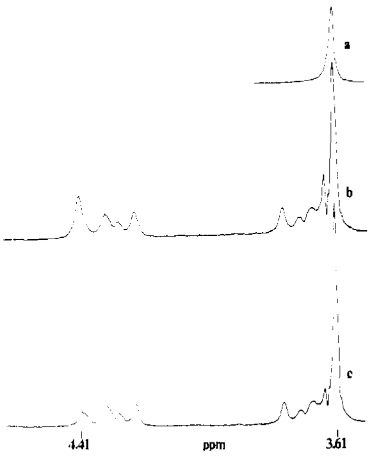

Figure 1. The 60-MHz nmr spectra of $CDCl_3$ solutions of (a) poly(ethylene oxide), and the ethylene oxide units of ethylene oxide–maleic anhydride copolymers containing (b) 0.74 mol fraction ethylene oxide and (c) 0.80 mol fraction ethylene oxide. The magnetic field increases from left to right. The spectra can be interpreted in terms of triads of monomers in the chain.

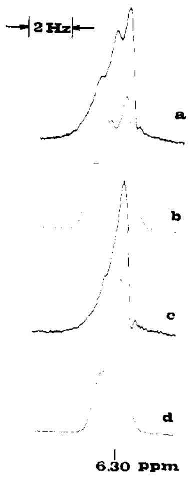

Figure 2. The 60-MHz nmr spectra of $CDCl_3$ solutions of the maleic anhydride units of the two ethylene oxide–maleic anhydride copolymers of Figure 1. The maleic anhydride content of the copolymers decreases from a to c. Computer simulations of the spectra are shown in b and d. The spectra are not complicated by structural or stereoisomerism and can be interpreted in terms of pentads of monomers in the chain.

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(3) J. P. Fletcher and H. E. Persinger, *J. Polym. Sci., Part A-2*, **6**, 1025 (1968).

(4) J. Schaefer, R. J. Katnik, and R. J. Kern, *J. Amer. Chem. Soc.*, **90**, 2476 (1968).

TABLE I

LINE ASSIGNMENTS FOR ^{1}H NMR SPECTRA OF ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS

Sequence	Line position (δ)
$-\mathrm{CH_2CH_2O}\quad \mathrm{C}H_2\mathrm{C}H_2\mathrm{O}\quad \mathrm{CH_2CH_2O}-$	3.61
$-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2C}H_2\mathrm{O}\quad \mathrm{CH_2CH_2O}-$	3.70 (multiplet center)
$-\mathrm{CH_2CH_2O}\quad \mathrm{C}H_2\mathrm{CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$	
$-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{C}H_2\mathrm{CH_2O}\quad \mathrm{CH_2CH_2O}-$	4.32 (multiplet center)
$-\mathrm{CH_2CH_2O}\quad \mathrm{CH_2C}H_2\mathrm{O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$	
$-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{C}H_2\mathrm{C}H_2\mathrm{O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$	4.41
$-\mathrm{CH_2CH_2O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{C}H{=}\mathrm{C}H\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \mathrm{CH_2CH_2O}-$	6.30
$-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}C}H\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \mathrm{CH_2CH_2O}-$	6.31
$-\mathrm{CH_2CH_2O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{C}H{=}\mathrm{CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$	
$-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{C}H{=}\mathrm{CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \mathrm{CH_2CH_2O}-$	
$-\mathrm{CH_2CH_2O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}C}H\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$	
$-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{C}H{=}\mathrm{C}H\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\quad \mathrm{CH_2CH_2O}\quad \overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{CH{=}CH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$	6.32

TABLE II

RELATIVE CONCENTRATIONS OF SOME SEQUENCES OF FIVE UNITS IN ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS AS DETERMINED BY ^{1}H NMR ANALYSIS

Mole fraction of EO in copolymer	BA*B*AB	BA*B*AA,AA*B*AB	AA*B*AA
0.80	0.00	0.20	0.80
0.74	0.14	0.28	0.58
0.73	0.16	0.30	0.54

possible triads) of any two $\mathrm{SnCl_4}$-generated copolymers of this type are very different when the charge ratios employed are different.[5] The sharp peak at δ 3.65 is due to the presence of *p*-dioxane formed in small amounts during the copolymerization. The remaining lines of the copolymer spectrum and part of the lowest field line form a typical X_2Y_2 spin multiplet arising from the central protons in B*A*A,A*A*B sequences.

The 60-MHz proton nmr spectra of the maleic anhydride units in the chains are shown in Figure 2, along with their computer simulations. Only single lines are expected from nonequivalent vinyl protons in the same maleic anhydride units because of the small ratio of chemical shift to *cis* spin–spin coupling constant. The spectra can be interpreted in terms of pentads of monomers in the chain and the assignments, made on the basis of how the intensities of the lines vary with the maleic anhydride content of the chain, are also given in Table I. The relative concentrations of the pentads are given in Table II.

The 100-MHz proton nmr spectrum shown in Figure 3a confirms the interpretation of the maleic anhydride signal as due to chemical shift differences of three different resonances while that in Figure 3c shows the low-field ethylene oxide signal in B*A*B sequences completely resolved from those in B*A*A,A*A*B sequences. Computer simulations of these spectra are given in Figures 3b and 3d which allow the line intensities to be determined with less than about ±10 and ±5% error, respectively.

Hydrolysis of the chains produces glycol ethers which can be derivatized and analyzed chromatographically

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(5) R. J. Kern and J. Schaefer, *J. Amer. Chem. Soc.*, **89**, 6 (1967).

TABLE III

THE RELATIVE MOLAR RUN CONCENTRATIONS, [B(A)$_N$B], IN HIGH-CONVERSION, SnCl$_4$-CATALYZED ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS AS DETERMINED BY GLPC ANALYSIS[a]

	Relative concentration		
N	I	II	III
1	0.090	0.252	0.215
2	0.118	0.098	0.065
3	0.459	0.480	0.542
4	0.108	0.089	0.080
5	0.049	0.029	0.047
6	0.076	0.030	0.029
7	0.039	0.012	0.011
8	0.021	0.005	0.006
9	0.018	0.003	0.003
10	0.011	0.001	0.001
11	0.007		
12	0.003		

[a] The initial EO:MA charge ratios are 6:1, 3:1, and 1:1, respectively, for columns I, II, and III. The mole fractions of EO in copolymer are 0.80, 0.74, and 0.73, respectively, for columns I, II, and III.

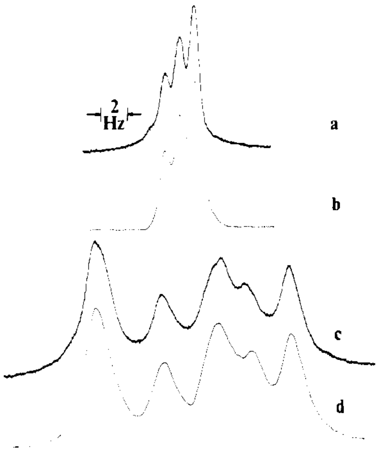

Figure 3. (a) The 100-MHz version of the spectrum of Figure 2a; (b) a computer simulation of this spectrum; (c) the 100-MHz version of the low-field part of Figure 1b, and (d) its computer simulation.

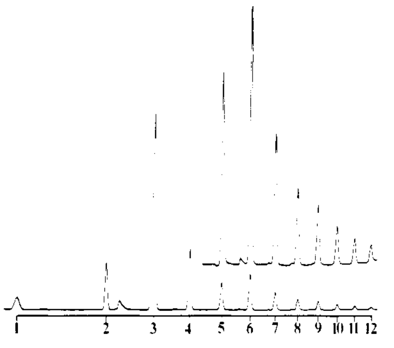

Figure 4. The chromatograms of the trimethylsilyl ether derivatives of the glycols obtained from hydrolysis of a high-conversion EO–MA copolymer made from a charge ratio of 6:1 using SnCl$_4$ as catalyst. The numbers along the horizontal axis indicate the number of ethylene oxide units in the glycol. The insert was taken at higher gain.

TABLE IV

THE RELATIVE MOLAR RUN CONCENTRATIONS, [B(A)$_N$B], IN LOW-CONVERSION, SnCl$_4$-CATALYZED ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS AS DETERMINED BY GLPC ANALYSIS[a]

	Relative concentration	
N	I	II
1	0.080	0.223
2	0.095	0.089
3	0.477	0.488
4	0.107	0.079
5	0.057	0.035
6	0.082	0.037
7	0.037	0.020
8	0.021	0.012
9	0.018	0.007
10	0.011	0.005
11	0.007	0.002
12	0.005	0.001
13	0.002	

[a] The EO:MA charge ratios are 6:1 and 3:1, respectively, for columns I and II. The mole fractions of EO in copolymer are 0.79 and 0.75, respectively, for columns I and II.

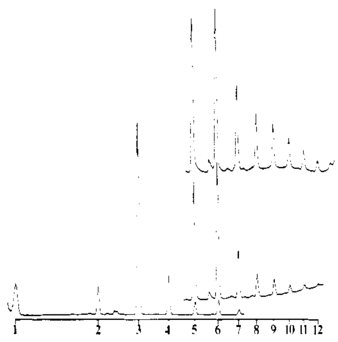

Figure 5. The chromatograms of the trimethylsilyl ether derivatives of the glycols obtained from hydrolysis of EO–MA copolymers made from a charge ratio of 3:1 using SnCl$_4$ as catalyst. The lower and middle chromatograms are of derivatives of glycols from a high-conversion copolymer and the upper chromatogram from a low-conversion copolymer. The upper two chromatograms were taken at higher gain.

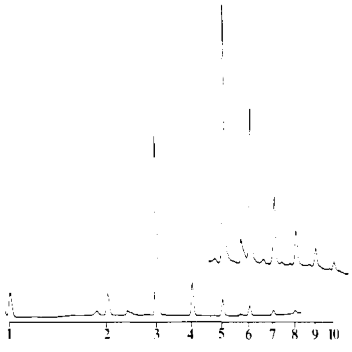

Figure 6. The chromatograms of the trimethylsilyl ether derivatives of the glycols obtained from hydrolysis of a high-conversion EO–MA copolymer made from a charge ratio of 1:1 using SnCl$_4$ as catalyst. The insert was taken at higher gain.

TABLE V
RELATIVE CONCENTRATIONS OF SEQUENCES OF THREE UNITS IN ETHYLENE OXIDE–MALEIC ANHYDRIDE COPOLYMERS (HIGH CONVERSION)

Mole fraction of EO in copolymer	Exptl technique	B*A*B	B*A*A,A*A*B	A*A*A
0.80	Glpc	0.02	0.49	0.48
	EO ^{1}H nmr	0.01	0.49	0.50
	MA ^{1}H nmr	0.02	0.48	0.50
	EO ^{13}C nmr	0.00	0.50	0.50
	MA ^{13}C nmr	0.02	0.48	0.50
0.74	Glpc	0.09	0.54	0.37
	EO ^{1}H nmr	0.09	0.52	0.39
	MA ^{1}H nmr	0.10	0.51	0.39
	EO ^{13}C nmr	0.10	0.52	0.38
	MA ^{13}C nmr	0.12	0.50	0.38
0.73	Glpc	0.08	0.54	0.38
	EO ^{1}H nmr	0.10	0.52	0.38
	MA ^{1}H nmr	0.11	0.51	0.38

as shown in Figures 4–6. The relative molar concentrations of the glycols (and hence of the runs of various lengths in the chain) are given by the areas of the peaks, multiplied by the suitable molar response factors. Run concentrations for copolymers made under a variety of conditions are presented in Tables III and IV and are accurate to about ±5%.

Analysis of the Monomer Distribution. 1. Internal Consistency of the Data. The run concentrations, $[\mathrm{B(A)}_N\mathrm{B}]$, presented in Table III can be used to predict the normalized relative concentrations of the nmr observed triads.[5] Since consecutive B units do not occur

$$[\mathrm{A}\mathit{A}\mathrm{A}] = \sum_{M=3}^{\infty} (M-2)[\mathrm{B(A)}_M\mathrm{B}] \Big/ \sum_{M=1}^{\infty} M[\mathrm{B(A)}_M\mathrm{B}]$$

$$[\mathrm{B}\mathit{A}\mathrm{A,A}\mathit{A}\mathrm{B}] = \sum_{M=2}^{\infty} 2[\mathrm{B(A)}_M\mathrm{B}] \Big/ \sum_{M=1}^{\infty} M[\mathrm{B(A)}_M\mathrm{B}]$$

$$[\mathrm{B}\mathit{A}\mathrm{B}] = [\mathrm{BAB}] \Big/ \sum_{M=1}^{\infty} M[\mathrm{B(A)}_M\mathrm{B}]$$

Values for these triads predicted from glpc data are presented in Table V and are in good agreement with the experimental nmr values.

Another indication of the reliability of the experiments and correctness of the nmr line assignments is available from a prediction of the nmr triad concentrations from the observed pentad concentrations. Thus

$$[\mathrm{B}\mathit{A}\mathrm{B}]/[\mathrm{B}\mathit{A}\mathrm{A,A}\mathit{A}\mathrm{B}] = ([\mathrm{BA}\mathit{B}\mathrm{AB}] + {}^1\!/_2[\mathrm{BA}\mathit{B}\mathrm{AA,AA}\mathit{B}\mathrm{AB}])/(2[\mathrm{AA}\mathit{B}\mathrm{AA}] + [\mathrm{BA}\mathit{B}\mathrm{AA,AA}\mathit{B}\mathrm{AB}])$$

The ratio $[\mathrm{B}\mathit{A}\mathrm{B}]/[\mathrm{A}\mathit{A}\mathrm{A}]$ can be determined from the total composition and the fact that consecutive B units do not occur. These triad predictions are presented in Table V and are in good agreement with the observed values.

Finally, ^{13}C nmr spectra of these same copolymers have been obtained earlier and interpreted in terms of triads and pentads in the chain.[6] The relative concentrations of sequences found from these experiments are presented in Table V. All five experimentally independent ways of determining sequences of three units in EO–MA chains are in agreement, within experimental error.

2. Comparisons of the Relative Concentrations of Runs of Ethylene Oxide. Comparisons of the run concentrations establish three essential features of the monomer distribution. First, the relative run concentrations in low-conversion EO–MA chains are virtually the same as in the high-conversion material made from the same charge ratio. This is shown in Figure 5 and Tables III and IV. Because the polymerization is never carried to very high conversions creating large changes in the charge ratio, both low- and high-conversion chains can therefore be described by the same mechanism generating the same statistical monomer distribution.[4]

Second, there is no repeating pattern in ethylene oxide run concentration, $[\mathrm{B(A)}_N\mathrm{B}]$, with increasing length, N, for copolymers made from a charge ratio of three or more as shown in Figures 4 and 5. Runs of lengths three and six are each (to a different degree) more probable than runs one unit longer and shorter while those of length nine are much more probable than those one unit longer but somewhat less probable than those one unit shorter. The run probabilities are thus *non*-random and irregular. The irregularity eliminates the possibility of any reasonably finite Markoffian description of the monomer distribution, one of whose prominent characteristics is a prediction of regularity in the probabilities for generating the longer runs.[1,4]

Third, the runs themselves are nonrandomly distributed in the whole chain. For example, if the distribution of closed runs of ethylene oxide in the chain were random, the probability of finding two consecutive runs of length one would be $^1/_{16}$ for the EO–MA copolymer made from the 3:1 charge ratio, while the probability of finding a run of length one adjacent to a run of some other length would be $^6/_{16}$ and the probability of finding two adjacent runs each longer than one would be $^9/_{16}$. (The probabilities are determined directly from the run concentrations given in Table

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(6) J. Schaefer, *Macromolecules*, 2, 210 (1969).

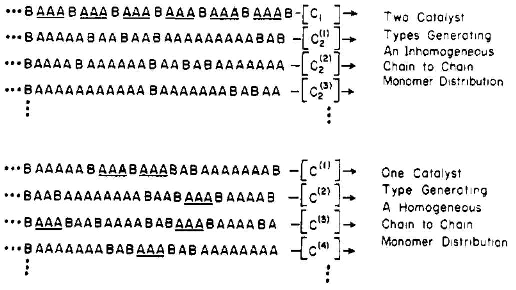

Figure 7. Two schemes for generating EO–MA copolymers.

III.) This random distribution of closed runs in the chain would produce relative values for the concentrations of the pentads [BA*B*AB], [BA*B*AA,AA*B*AB], and [AA*B*AA] equal to 1:6:9. The experimental ratios are 1:2:4, and are clearly nonrandom.

3. Chain-to-Chain Homogeneity of the Monomer Distribution. For catalyst systems such as $SnCl_4$ generating chains from cyclic ethers and anhydrides, there is a possibility that two or more chemically unique catalytic types are formed, each producing chains significantly different from the other.[4] Figure 7 illustrates the point. The upper half of the figure shows an inhomogeneous chain-to-chain distribution generated by two catalytic types (designated by the subscripts; ignore the superscripts for the moment). One catalytic type generates ethylene oxide runs of length three *exclusively*. (This kind of inhomogeneity is the most important because of the large concentration of runs of length three and the possibility that they are generated by an independent catalytic site.) If the chains are hydrolyzed this distribution cannot be distinguished from the chain-to-chain homogeneous distribution produced by the scheme illustrated in the bottom half of Figure 7.

However, the possibility of such an inhomogeneity in EO–MA chains is small. The observed monomer distribution cannot be described as a simple sum of Markoffian distributions, one of which contains only runs of length three. The irregularities in the observed distribution involve more than just the relative concentration of the runs of length three. They extend to the relative concentrations of runs of length four, five, six, and seven. (Compare, for example, the ratio of concentrations of runs of length five to length four with the far different ratio of concentrations of runs of length eight to length seven.)

Of course, the observed distribution can always be assumed to be very complicated. That is, it can be assumed to be a sum of a Markoffian distribution (of runs of length three) and a non-Markoffian distribution, with the latter adjusted in such a way to just compensate for the discrepancies of the former with the observed distribution. There is no evidence that this occurs and seems rather unlikely since the most obvious irregularities in the relative concentrations of runs occur at intervals of three suggesting they are related. Finally, the observed distribution can be assumed to be a sum of two or more non-Markoffian distributions. Since the problem of describing a chemical system which can produce a non-Markoffian monomer distribution in a copolymer still remains, the possibility of a complicated sum of such distributions will be ignored. No qualitative, chemically interesting conclusions will be affected by doing this.

4. A Non-Markoffian Description of the Monomer Distribution. In order to explain how a single catalytic type can generate a nonrandom, non-Markoffian monomer distribution in a copolymer chain, the catalyst is assumed to coordinate different combinations of monomers prior to their addition to the chain and to add these monomers to the chain in two different ways.[2,7] Consider the following states of the catalyst

$$\{1\} = \mathrm{AM}$$
$$\{2\} = \mathrm{AMA}$$
$$\{3\} = \mathrm{AMAA}$$
$$\{4\} = \mathrm{AMAAA}$$
$$\{5\} = \mathrm{BM}$$
$$\{6\} = \mathrm{BMA}$$
$$\{7\} = \mathrm{BMAA}$$
$$\{8\} = \mathrm{BMAAA}$$

where M represents the inorganic metal(s), perhaps permanently combined with some organic species but unchanged throughout the copolymerization. The catalyst must be considered an integral part of the growing chain end since its changing (from, say, $SnCl_4$ to $SbCl_5$) drastically alters the resulting monomer distribution.[5] The monomer, either A or B, written to the left of M is the last unit in the completed chain while those written to the right are coordinated by the catalyst, considered part of the chain but not yet completely reacted. Since experimental details of exactly how such a catalyst coordinates or associates monomers in a reaction sphere are not known, no attempt is made to specify them here.

The homogeneity of the chain-to-chain monomer distribution generated by the mechanism is represented schematically in the lower half of Figure 7, where the superscripts represent the various catalytic states $\{1\}$, $\{2\}$, $\{3\}$, $\{4\}$, ... As the chain grows the end may change from one catalytic state to another, then to another, and so on. Monomers enter the chain either by a nonpropagating process such as $\{8\} \rightarrow \{1\}$ or by a process which increases the length of the chain such as $\{8\} + \mathrm{A} \rightarrow \{1\}$. The competition between these two kinds of processes (coordination prior to addition *vs.* direct addition) complicates the propagation, makes it non-Markoffian, and ensures the irregularity and nonrandomness of the relative run concentrations with increasing run length and with respect to their distribution in the chain.[2]

The high probabilities for observing runs of length three and six (compared to two and five, for example) can be attributed to the favorability of cycles, such as

$$\{5\} + \mathrm{A} \rightarrow \{6\}$$
$$\{6\} + \mathrm{A} \rightarrow \{7\}$$
$$\{7\} + \mathrm{A} \rightarrow \{8\}$$
$$\{8\} + \mathrm{B} \rightarrow \{5\}$$

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(7) B. D. Coleman and T. G Fox, *J. Chem. Phys.*, **38**, 1065 (1963).

which completes a cycle producing $B(A)_3B$ in the chain and

$$\begin{aligned}
\{5\} + A &\rightarrow \{6\}\\
\{6\} + A &\rightarrow \{7\}\\
\{7\} + A &\rightarrow \{8\}\\
\{8\} \quad &\rightarrow \{1\}\\
\{1\} + A &\rightarrow \{2\}\\
\{2\} + A &\rightarrow \{3\}\\
\{3\} + A &\rightarrow \{4\}\\
\{4\} + B &\rightarrow \{5\}
\end{aligned}$$

which completes another cycle producing $B(A)_6B$ in the chain. (Note that all eight states are required to produce the latter cycle.) The rate constants for the various steps in any cycle may, of course, be very different. In this model as the charge ratio is lowered, the concentration of B monomer increases and the process $\{8\} + B \rightarrow \{5\}$ becomes highly favored over the process $\{8\} \rightarrow \{1\}$, thereby disrupting the cycle producing exclusively $B(A)_6B$ and removing the irregularity of the longer relative run concentrations with increasing run length. This is, in fact, observed for the EO–MA chain made from a 1:1 charge ratio. The probabilities for many of the other processes are also dependent on the charge ratio but not necessarily in a simple fashion. So, for example, the probability for the formation of BAB units in the chain at first increases with increasing concentration of maleic anhydride in the charge and then appears to pass through a maximum.

A mathematical procedure which can be used to describe this mechanism quantitatively has been presented before.[2] It is avoided here since no new qualitative insights can be gained.

Discussion

The mechanism presented to explain the key features of the EO–MA monomer distribution can be made considerably *more* complicated. Thus depolymerization processes can be added to explain the formation of *p*-dioxane during the copolymerization, additional states can be added in which maleic anhydride units are coordinated before entering the chain, and all the states can be connected by nonpropagating processes as illustrated above for states 1 and 8. However, it does not appear likely that the mechanism can be made considerably *less* complicated and still describe the rather involved, nonrandom non-Markoffian, homogeneous EO–MA monomer distribution which is actually observed. For example, it is difficult to see how, in the absence of some sort of coordination sphere, a maleic anhydride unit about to enter the chain can be informed when there are six rather than five preceding ethylene oxide units in the chain so that addition can be made more favorable; or how, in the absence of a competition at the growing chain end between different *kinds* of transition processes, a homogeneous but non-Markoffian distribution can result for both low- and high-conversion copolymers.

The mechanism may be considered a general description of the way in which $SnCl_4$ catalyzes the copolymerization of cyclic ethers with anhydrides. For example, substituting propylene oxide for ethylene oxide and sulfur dioxide for maleic anhydride and using $SnCl_4$ as catalyst produces a copolymer having a non-Markoffian monomer distribution.[1,2] This distribution has nonrandom (although far less obviously nonrandom) run concentrations of lengths two, four, six, etc., instead of three, six, nine, etc., observed for the EO–MA distribution. The propylene oxide–sulfur dioxide distribution can be described by events connecting only $\{1\}$, $\{2\}$, $\{5\}$, and $\{6\}$ by assuming that the presence of SO_2 alters the catalyst in such a way that fewer monomers are coordinated. Furthermore, substituting propylene oxide for ethylene oxide, keeping maleic anhydride as the comonomer, and using $SnCl_4$ as a catalyst produces a copolymer having very close to a Markoffian monomer distribution[4,5] (neglecting some complications in the early stages of the polymerization). The propylene oxide–maleic anhydride distribution greatly favors runs of propylene oxide of length three and involves the coordination and arrangement of the propylene oxide units (with respect to their head and tail sense of direction) prior to addition to the final chain.[8] This distribution can be described by states 1 through 8 by assuming that the rate constants for the nonpropagating processes are small.

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(8) J. Schaefer, R. J. Katnik, and R. J. Kern, *Macromolecules*, 1, 101 (1968).