The Monomer Distributions of Propylene Oxide–Sulfur Dioxide Copolymers[1]

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ABSTRACT: The monomer distributions in low-conversion propylene oxide–sulfur dioxide copolymers, poly(sulfite ethers), prepared from three different, homogeneous catalysts, have been obtained from an nmr analysis of the copolymers and a chromatographic analysis of the glycol ethers resulting from hydrolysis of the copolymers. Both Markoffian and non-Markoffian chain statistics are observed depending on the catalyst. These chains are compared to propylene oxide–maleic anhydride chains generated by the same catalysts.

Sulfur dioxide has long been recognized to copolymerize with olefins to form polysulfones, $-S(=O)_2-(CHRCH_2)_N-$.[2] Using a variety of homogeneous catalysts, SO_2 can also be copolymerized with propylene oxide (PO) to form a poly(sulfite ether), $-S(=O)O-(CHCH_3CH_2O)_N-$. The monomer distributions in low-conversion poly(sulfite ether) PO–SO_2 copolymers have been obtained from an nmr analysis of the copolymers and a glpc analysis of the glycol ethers resulting from hydrolysis of the copolymers. The monomer distributions depend on the particular catalyst employed. Those generated by $SnCl_4$ and $SbCl_5$ show a long-range order over runs of PO as long as twelve. From the dependence of the long-range order on the comonomer charge ratio (the ratio of reactants), these distributions can be characterized as non-Markoffian. The catalyst Et_2Zn produces a monomer distribution which shows no long-range order and can be characterized as Markoffian.

The PO–SO_2 monomer distributions are distinctly different from those in propylene oxide–maleic anhydride (PO–MA) copolymers made from the same catalysts.[3] These differences are noted in terms of the way combinations of monomers may be associated with the growing chain end by the catalyst.

Experimental Section

1. Copolymerization. Propylene oxide and sulfur dioxide at 0° were placed in a 100-ml stainless steel bomb followed by small amounts of a solution of catalyst in dry benzene. The bomb, two-thirds full, was capped and heated to room temperature for about 24 hr for high conversion and shorter periods for low-conversion copolymers. The viscous product was stripped *in vacuo* to leave a clear straw-yellow product. (Small amounts of propylene sulfite were found in the cold trap.) The catalyst residue was removed by dissolving the product in wet benzene, or acetone containing 2% (v/v) water, filtering or centrifuging the insoluble hydrous oxides, and then removing the benzene or acetone *in vacuo*. The catalyst Et_2Zn, $SnCl_4$, and $SbCl_5$ were employed in a monomer to catalyst molar ratio of approximately 1000:1. constant Propylene oxide and SO_2 treated as above but without catalyst present produced no polymer.

2. Hydrolysis of Copolymers. Copolymer (25 g) was treated at room temperature in a 250-ml centrifuge bottle with 3–5-ml portions of a solution of 50 g of NaOH pellets in 100 ml of water. Small increments of NaOH solution were added until the reaction mixture tested strongly basic after 12 hr at 40–50° under nitrogen. About 50 ml of methanol was added. After centrifuging the mixture, supernatant liquors were removed and two more methanol extractions were made. The residual white solids were dried and weighed. *Anal.* Calcd for Na_2SO_3: S, 25.4; equiv wt (against standardized $KMnO_4$ solution), 63.0. Found: S, 24.9; equiv wt, 62.5. The combined liquors were neutralized to form polypropylene glycol ethers. The hydrolysis was performed within 1 day of the polymerization.

3. Glpc Analysis. Glpc analysis was performed on an F & M Model 720 chromatograph with an injection port temperature of 300°, detector block temperature of 300°, flow rate of 185 ml/min, and bridge current of 150 mA. Volatile trimethylsilyl ether derivatives of the propylene glycol ethers were formed from bis(trimethylsilyl)acetamide. The ether derivatives were analyzed on a 0.25 in. × 5 ft 5% SE-33 on 60/80 mesh Diatoport-S column programmed from 75 to 300° at a rate of 7.5°/min. The glpc relative molar response factors of the trimethylsilyl ether derivatives of the monomer through hexamer of propylene glycol ethers were obtained from blends of these derivatives and tetraethylene glycol dimethyl ether, used as an internal standard.[3b] A calibration curve of each glycol was made by plotting the ratio of glycol peak area to internal standard peak area against mole per cent glycol. For the monomer through hexamer, the relative molar response factors are 2.01 ± 0.14, 1.42 ± 0.07, 1.13 ± 0.05, 0.95 ± 0.05, 1.02 ± 0.03, and 1.01 ± 0.03, respectively. As the glycols become longer (and so more similar), the glpc molar response factors become equal. Thus, when N, the number of PO units in a run, is greater than 3, the relative number or molar concentrations of runs of PO are equal to the relative areas of the corresponding peaks. When N is equal to 1, 2, and 3, the observed peak areas must be multiplied by 2.0, 1.4, and 1.1, respectively, to give the relative molar run concentrations.

4. Nmr Analysis. The 60-MHz nmr spectra of the copolymers were obtained from a 15% by weight solution of copolymer in $CDCl_3$ using a Varian A-60 spectrometer with a probe temperature of 35°.

Results and Analysis

1. Glpc Analysis of the Monomer Distribution. Hydrolysis of PO–SO_2 copolymers with NaOH produces polypropylene glycol ethers and Na_2SO_3 in 90–95% yields. This is proof that the primary structure of the chain consists of sulfite linkages connecting the

(1) Parts of this paper were read at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) E. M. Fettes and F. O. Davis review the field in "High Polymers," Vol. XIII, Part III, N. G. Gaylor, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

(3) (a) R. J. Kern and J. Schaefer, *J. Amer. Chem. Soc.*, **89**, 6 (1967); (b) J. Schaefer, R. J. Katnik, and R. J. Kern, *ibid.*, in press.

TABLE I

PROPYLENE OXIDE–SULFUR DIOXIDE MONOMER DISTRIBUTION FROM GLPC ANALYSIS. RELATIVE MOLAR RUN CONCENTRATIONS,[a] $[B(A)_NB]$

	Catalyst			
	Et_2Zn	$SnCl_4$	$SbCl_5$	$SbCl_5$
	Initial and final $PO-SO_2$ charge ratios			
N	10:1	7:1	7:1	1:1
1	0.071	0.019	0.007	0.006
2	0.413	0.348	0.179	0.342
3	0.263	0.169	0.209	0.266
4	0.153	0.169	0.109	0.095
5	0.058	0.076	0.113	0.095
6	0.024	0.073	0.114	0.083
7	0.013	0.041	0.072	0.040
8	0.005	0.042	0.061	0.027
9	...	0.022	0.047	0.020
10	...	0.020	0.036	0.011
11	...	0.010	0.030	0.008
12	...	0.010	0.025	0.006

[a] Estimated error for run concentrations is on the order of ±5% (see text).

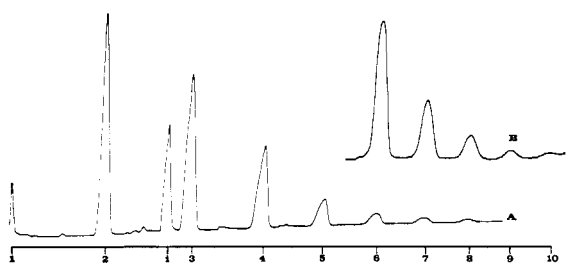

Figure 1. Chromatograms of the trimethylsilyl ether derivatives of low-conversion $PO-SO_2$ copolymers made from the catalyst systems (A) Et_2Zn 10:1 and (B) Et_2Zn 20:1. The ratio following the catalyst is the $PO-SO_2$ charge ratio. The number (N) along the horizontal axis represents the number of PO units in the run. For N greater than 3, the relative molar run concentrations are given by the areas under the corresponding peaks. When N equals 1, 2, and 3, the areas must be multiplied by 2.0, 1.4, and 1.1, respectively. Tetraethylene glycol dimethyl ether is the internal standard (i). The remaining small peaks are impurities. The regular decrease in run concentrations beginning with N equal to 2 indicates the suitability of second-order Markoffian statistics to describe the monomer distribution.

monomer units. Sulfones, sulfonates, or sulfinites would not hydrolyze to form simple polypropylene glycol ethers and sodium sulfite.

A. The Et_2Zn-Catalyzed Copolymer. Figures 1 and 2 and Table I show the relative molar PO run concentrations obtained from glpc analysis of the polypropylene glycol ethers arising from hydrolysis of copolymers produced by three catalysts. The low-conversion monomer distribution generated by the Et_2Zn catalyst is the simplest of those shown (Figure 1). The relative concentrations of closed runs of PO, $[B(A)_NB]$, where A is PO and B is SO_2, decreases regularly beginning with N equal to 2. The conditional probabilities can be calculated from the run concentrations: $P(B/B)$, $P(BA/B)$, ... $P(BA_N/B)$ are the conditional probabilities that the next unit will be B given that the previous units are B, BA, ... BA_N, respectively. Since $P(B/B)$ is zero

TABLE II

CONDITIONAL PROBABILITIES FOR LOW-CONVERSION Et_2Zn-CATALYZED $PO-SO_2$ COPOLYMER,[a] $P(BA_N/B)$

N	Probability
0	0
1	0.071 ± 0.005
2	0.45 ± 0.02
3	0.51 ± 0.06
4	0.60 ± 0.11
5	0.58 ± 0.15
6	0.57 ± 0.20
7	0.7 ± 0.3
8	1 ± 1

[a] The increasing uncertainty in the conditional probabilities with increasing N is due to an accumulated error in the denominator of the expression for the probabilities in terms of the run concentrations.

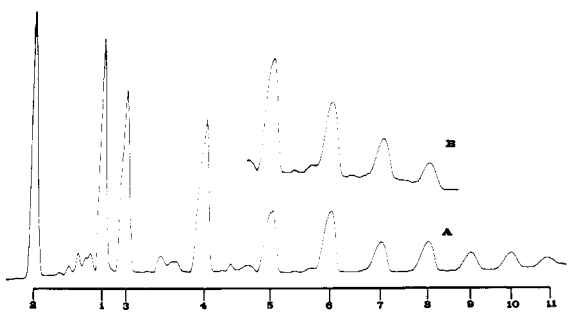

Figure 2. Chromatograms of the trimethylsilyl ether derivatives of the glycols obtained from hydrolysis of low-conversion $PO-SO_2$ copolymers made from the catalyst systems (A) $SnCl_4$ 7:1 and (B) $SnCl_4$ 1:1.

$$P(BA_N/B) = [B(A)_NB]/\left\{1 - \sum_{M=1}^{N-1}[B(A_M)B]\right\}$$

Conditional probabilities for the Et_2Zn 10:1 system are given in Table II. Since they are all constant when N is equal to or greater than 2, the suitability of second-order Markoffian statistics to describe the distribution (within experimental error) is indicated.[3b-5]

B. The $SnCl_4$-Catalyzed Copolymer. The monomer distribution generated by the $SnCl_4$ catalyst is more complicated. While the largest PO run concentration occurs when N equals 2, the decrease is by pairs of runs. Thus, the concentrations for N equal to 3 and 4 are equal, for N equal to 5 and 6 are equal, etc. (Figure 2A). This pair effect, which extends over runs of PO as long as twelve, gives a long-range order to the chain which is present in both low- and high-conversion copolymers made at higher charge ratios. The pair effect cannot be described in terms of PO units adding to the chain only in pairs since this would produce runs of only even length. At a $PO-SO_2$ charge ratio of 1:1, the pair effect has virtually disappeared (Figure 2B). Analysis[6] of the dependence of the pair

(4) B. D. Coleman, *J. Polym. Sci.*, **31**, 155 (1958); B. D. Coleman and T. G Fox, *ibid., Part A-1*, 3183 (1963).

(5) The same catalyst generates propylene oxide–maleic anhydride chains according to third-order Markoffian statistics: J. Schaefer, R. J. Katnik, and R. J. Kern, *Macromolecules*, **2**, 101 (1968).

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

effect on the comonomer charge ratio has shown that the chain can be described by non-Markoffian statistics.

In order to appreciate this conclusion, consider a growing copolymer chain which is associated with several different states or species. In the simplest case these states correspond to what the terminal unit in the chain happens to be. These states vary in their reactivity since, in general, a chain ending with A will react differently from a chain ending with B. As the chain propagates the terminal unit may change and this represents a transition between two states of the chain. This kind of a scheme produces a Markoffian chain since the propagation depends only on a finite number of previous events.

The $SnCl_4$-catalyzed PO–SO_2 chain may be considered non-Markoffian which means that chain growth depends on something other than the last few propagation steps. This other factor very probably is an equilibrium of the states of the chain. That is, a chain ending with A could undergo a transition to one ending with B without increasing the length of the chain if the two kinds of chain ends were in equilibrium. Such a transition would erase the memory of the last propagation step and complicate the propagation.

Obviously, the catalyst (which may be more elaborate than just the inorganic species) is somehow involved in facilitating the equilibrium. The run concentration pair effect requires that each species in equilibrium has at least a two-monomer unit long memory of the chain's history. Thus, more than just the terminal unit of the chain is involved. Furthermore, since the pair effect extends to very long runs of PO, it is unlikely that SO_2 units are directly involved. These questions are considered in more detail in the following paper in which a general mechanism is proposed which allows PO units, either singly or in pairs, to add to chain ends which are in equilibrium.[6]

C. The $SbCl_5$-Catalyzed Copolymer. The low-conversion monomer distribution generated by the $SbCl_5$ catalyst is more complicated than those generated by either the Et_2Zn or $SnCl_4$ catalyst systems. The dominant PO run concentration in the $SbCl_5$-catalyzed system changes from N equal to 3 to N equal to 2 as the PO–SO_2 comonomer charge ratio changes from 7:1 to 1:1. Furthermore, there is no regular decrease in run concentrations with increasing N, but what appears to be a decrease by trios. Thus, the concentrations of runs with N equal to 4, 5, and 6 are about equal and much larger than those with N equal to 7, 8, and 9 which, in turn, are about equal and larger than those with N equal to 10, 11, and 12. However, this trio effect is not as clearly defined as the pair effect, observed in the $SnCl_4$-catalyzed copolymers, and has a more complicated charge ratio dependence. The fact that there is no regular decrease in run concentrations means there is long-range order in these chains. That is, the distribution of run concentrations is *non*random. While this order has not been analyzed in detail, it seems reasonable to assume that, by analogy to the $SnCl_4$-catalyzed system, the monomer distribution is non-Markoffian and generated by a complicated mixture of catalyst species strongly interacting with one another.

2. Nmr Analysis of the Monomer Distribution. Figure 3 shows the 60-MHz nmr spectra of the methyl region of some PO–SO_2 copolymers. The spectra are very similar to the methyl region spectra of PO–MA copolymers[3] supporting the conclusion that the chain consists of sulfite linkages. In analogy with the PO–MA spectra, line assignments in terms of triads of monomers in the chain are given in Table III. PO methyl resonances in the central unit of the triads appear as doublets due to spin–spin coupling. The relative concentrations of these triads were estimated by simulating the methyl region spectra by seven channels of a Du Pont 310 curve resolver. An example of the simulation is given in Figure 3d. Since the head and tail structural isomerism within each triad (see Table III) is partially resolved at 60 MHz, the simulation of PO–SO_2 spectra is rather difficult. (The sulfur in the chain backbone apparently enhances chemical shift differences.) Triad concentrations in PO–SO_2 chains as a function of the comonomer charge ratio are given in Table IV. The triad charge ratio dependence is far more pronounced than for PO–MA chains.[3a]

Figure 3b (compared to 3a) shows a resonance in the methyl region at higher fields than observed for line 8 of the central methyl in (A)(*A*)(A) triads. Vacuum distillation of the low-conversion $SnCl_4$ 1:1 PO–SO_2 co-

TABLE III
LINE ASSIGNMENTS OF 60-MHz METHYL REGION SPECTRA OF PROPYLENE OXIDE–SULFUR DIOXIDE COPOLYMERS[a]

Line no.	Sequence[b]	Position (τ)
1	B(*A*)B	8.58
2	B*A*(A), (A)*A**B	8.63
3	B(*A*)B	8.68
4, 5	B*A*(A), (A)*A**B + B*A**(A), (A)*A*B	8.75
6	(A)(*A*)(A)	8.82
7	B*A**(A), (A)*A*B	8.87
8	(A)(*A*)(A)	8.91

[a] $CDCl_3$ as solvent at 35°. [b] A = $-CH(CH_3)CH_2O-$, A* = $-CH_2CH(CH_3)O-$, B = $-S(=O)O-$. Monomers in parentheses can have either sense of direction.

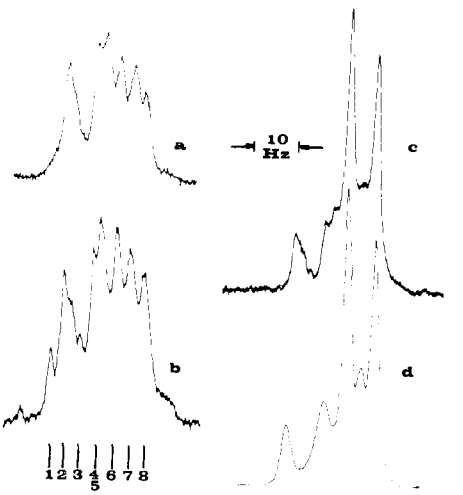

Figure 3. Methyl region spectra (60 MHz) of propylene oxide–sulfur dioxide copolymers made from the catalyst systems (a) Et_2Zn 10:1; (b) $SnCl_4$ 1:1; (c) $SnCl_4$ 10:1 (the $SnCl_4$ 10:1 is high-conversion material); (d) a Du Pont 310 curve resolver simulation of c.

TABLE IV
PROPYLENE OXIDE–SULFUR DIOXIDE MONOMER DISTRIBUTION FROM NMR ANALYSIS[a]

Catalyst	Initial $PO-SO_2$ charge ratio	Conversion	BAB	BAA, AAB[b]	AAA[b]
$SnCl_4$	10:1	0.86	0.00	0.51	0.49
	7:1	0.03	0.01	0.58	0.41
	3:1	0.03	0.02	0.64	0.34
	1:1	0.03	0.04	0.72	0.24
	1:3	0.03	0.05	0.80	0.15
Et_2Zn	10:1	0.02	0.01	0.75	0.24

[a] Relative triad concentrations obtained from computer simulation of methyl region. Estimated error for each triad is ±0.03. [b] A and A* are considered equivalent with respect to the monomer distribution.

polymer produced a small amount of a low-boiling liquid. After distillation the copolymer did not show these high field lines. The nmr spectrum of the distillable liquid had proton resonances in the typical regions of PO methine, methylene, and methyl groups in $PO-SO_2$ copolymers. The methyl region spectrum, however, was very complicated with tens of lines between τ 8.4 and 9.0. Hydrolysis of this liquid in the same manner as the copolymer produced 95% tripropylene glycol and 5% tetrapropylene glycol. At room temperature over a period of several weeks, the liquid formed a viscous resin whose nmr spectrum was now as simple as a typical $PO-SO_2$ copolymer spectrum.

These results are only consistent with the conclusion that the liquid is the cyclic copolymer of PO and SO_2 in almost exclusively a 3:1 ratio. The complicated methyl region nmr spectrum is due to the large number of possible geometrical isomers of the cyclic copolymer exactly analogous to the complicated spectrum and large number of geometrical isomers of the cyclic tetramer of PO produced by BF_3 during PO and MA copolymerization.[7] Of the three catalysts used in this study, Et_2Zn forms the cyclic copolymer the most readily and $SnCl_4$ the least readily. The cyclic copolymer always formed more readily at low charge ratio of PO to SO_2 (for example, 1:3) and during the later stages of a high-conversion copolymerization. Estimates of its concentration were made from the high field part of methyl region nmr spectra. The cyclic copolymer constituted no more than on the order of 5% of the total of the low charge ratio, low-conversion $PO-SO_2$ product, even for the Et_2Zn catalyst system. The data in Tables I, II, and IV have been corrected to remove estimated contributions from the cyclic copolymer.

The production of cyclic copolymer is the $PO-SO_2$ analog of the formation of cyclic ethers during the Friedel–Crafts catalyzed homopolymerization of ethylene oxide.[8] In the latter system, a molecular weight steady state supposedly results from a balance between a depolymerization reaction and the propagation processes. The depolymerization produces the cyclic ether.

The nmr observed triads of monomers in the chain can be independently predicted from the relative concentrations of closed runs of PO determined by glpc. These predictions are given in Table V and show reasonable agreement. The agreement is not as good as the corresponding internal check made in the PO–MA copolymer system.[3b] There are at least three reasons for the discrepancy in the $PO-SO_2$ system: (1) the computer simulation of the $PO-SO_2$ spectra is poorer than of the PO–MA spectra so that the experimental values for the triad concentrations are less accurate; (2) estimates of the contribution by cyclic copolymer to nmr and glpc analyses are not accurate; (3) the chain may contain some small percentage of nonsulfite links which could affect both nmr and glpc spectra.

TABLE V
PREDICTED NMR TRIADS FROM GLPC DETERMINED RUNS OF PROPYLENE OXIDE

Catalyst	$SnCl_4$	Et_2Zn
Initial $PO-SO_2$ charge ratio	7:1	10:1
Conversion, %	3	2
BAB (calcd)	0.006	0.026
(obsd)	0.01	0.01
BAA, AAB (calcd)	0.540	0.680
(obsd)	0.58	0.75
AAA (calcd)	0.453	0.294
(obsd)	0.41	0.24

3. The Structural Isomer Distribution in $PO-SO_2$ Copolymers. The head-to-head, head-to-tail, and tail-to-tail structural isomerism in $PO-SO_2$ copolymers, in closed runs of PO of length two and three, was determined by chromatographic analysis of the corresponding di- and tripropylene glycol ethers using a $HgCl_2$–Carbowax 20M column.[9] The relative concentrations of the diglycols of dimer isomers AA*, AA(A*A*), and A*A (from $SnCl_4$-catalyzed chains) were 0.24, 0.56, and 0.20, respectively, where A is $-CH(CH_3)CH_2O-$ and A* is $-CH_2CH(CH_3)O-$. The relative concentrations of the diglycols of trimer isomers AAA*-(AA*A*), A*AA*(AA*A) + A*AA(A*A*A), and AAA(A*A*A*) were 0.27, 0.48, and 0.25, respectively. Similar results were obtained from the other catalyst systems. For a structural isomer distribution that was totally random these six values would be 0.25, 0.50, and 0.25; 0.25, 0.50, and 0.25, respectively. Thus, the structural isomer distribution in closed runs of two and three PO units in low-conversion $PO-SO_2$ copolymers is random, within experimental error.[9] The same conclusion was reached for low-conversion PO–MA $SnCl_4$-catalyzed copolymers. The structural isomer distribution in the cyclic $PO-SO_2$ copolymer was also close to random.

The molecular weight of these copolymers is in the 1500–2000 range as determined by vapor phase osmometry, which is high enough so that severe end effects can be ignored.[3a] Of course, an end effect amounting to a few mole per cent of the total chain could conceivably be concentrated in any given run of PO. None of the conclusions reported are affected by this possibility. Once the cyclic copolymer had been removed, gel permeation chromatography showed a

(7) R. J. Katnik and J. Schaefer, *J. Org. Chem.*, **33**, 384 (1968).
(8) A. M. Eastham reviews these reactions in *Fortschr. Hochpolym.-Forsch.*, **2**, 18 (1960).
(9) Details of the separation and characterization of the di- and tripropylene glycol ethers are given in ref 5.

symmetrical molecular weight distribution with no major low molecular weight components.

Discussion

The PO–MA monomer distributions in copolymers made from $SnCl_4$ and $SbCl_5$ catalysts show no long-range order and have a weak, Markoffian dependence on charge ratio.[3] The PO–SO_2 monomer distributions in copolymers made from the same catalysts show a long-range order and have a strong, non-Markoffian dependence on charge ratio. These differences as well as all available distribution data can be understood by assuming that in both PO–MA and PO–SO_2 systems various numbers and combinations of monomers, coordinated in reaction spheres, are associated with the growing chain end by the catalyst. These coordinated species vary in their reactivity (that is, their ability to propagate the chain) depending on their composition. In the PO–MA case the species are not interacting, form the states of a third-order Markoffian chain (or chains), and can be connected only by propagation steps of the chain.[3] In the PO–SO_2 case the species are interacting, connected, for example, by equilibria, as well as propagation, and this strong interaction results in the more involved description as a non-Markoffian chain.[10]

(10) The Et_2Zn PO–SO_2 catalyst system is an exception. This may be related to the fact that cyclic copolymer is so readily produced rather than an interaction between catalytic species associated with long chains.

Equilibrium of Catalytic States in the Copolymerization of Propylene Oxide and Sulfur Dioxide[1]

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ABSTRACT: The monomer distribution in low-conversion propylene oxide–sulfur dioxide (PO–SO_2) copolymers catalyzed by $SnCl_4$ is characterized by a long-range order over runs of PO as long as twelve. This order is described in terms of the dynamic equilibrium of two catalytic states associated with the growing chain end. The resulting monomer distribution statistics are non-Markoffian. Values for the various rate constants involved in the propagation and equilibrium of the chain ends are obtained from the dependence of the long-range order on the comonomer charge ratio. Some other Markoffian and non-Markoffian schemes are shown to explain inadequately the available data.

Propylene oxide (PO) and sulfur dioxide (SO_2) can be copolymerized by the homogeneous catalyst $SnCl_4$ to form a poly(sulfite ether), $-S(=O)O(CH(CH_3)-CH_2O)_N-$. The monomer distributions in these copolymers have been determined by a combination of nmr analysis of the copolymer and gas–liquid partition chromatographic (glpc) analysis of the glycol ethers formed by hydrolysis of the copolymer.[2] The monomer distribution in copolymers made at high charge ratio (*i.e.*, ratio of concentrations of reactants) of PO to SO_2 shows an unusual long-range order over runs of PO as long as twelve. There are no consecutive SO_2 units in the chain. The distribution is characterized by equal or nearly equal concentrations of runs of PO of lengths $2N + 1$ and $2N + 2$ with these runs always less abundant than those of length $2N$ for all N. That is, instead of the concentrations of runs of PO decreasing in a regular fashion with increasing N (as predicted by Markoffian statistics and experimentally observed in some copolymer systems[2,3]) these concentrations decrease in pairs with increasing N (see Figure 1A). The monomer distributions in PO–SO_2 copolymers made at low charge ratio of PO to SO_2 fail to show this pair effect.

This paper presents a description of the monomer distribution in PO–SO_2 copolymers and its dependence on the comonomer charge ratio. The description involves the dynamic equilibrium of two of the catalytic states associated with the growing polymer chain. Each of these two states is capable of adding monomer to the chain in its own way and also has some knowledge of the chain's history. A chemical basis for such a model is suggested. The resulting distribution statistics are non-Markoffian. Descriptions which omit either the equilibrium or memory of these states will be shown to explain the available experimental data inadequately. The non-Markoffian description is an extention to copolymerizations of the multistate mechanism of homogeneous ionic homopolymerizations given by Coleman and Fox.[4]

Experimental Results

The details of the synthesis and characterization of low-conversion PO–SO_2 copolymers are given in the preceding paper.[2] Representative glpc spectra of the trimethylsilyl derivatives of hydrolyzed copolymers

(1) Parts of this paper were read at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) J. Schaefer, R. J. Kern, and R. J. Katnik, *Macromolecules*, 2, 107 (1968).

(3) J. Schaefer, R. J. Katnik, and R. J. Kern, *J. Amer. Chem. Soc.*, in press.

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