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]

Jacob Schaefer

Central Research Department, Monsanto Company, St. Louis, Missouri 63166.

Received December 28, 1967

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).

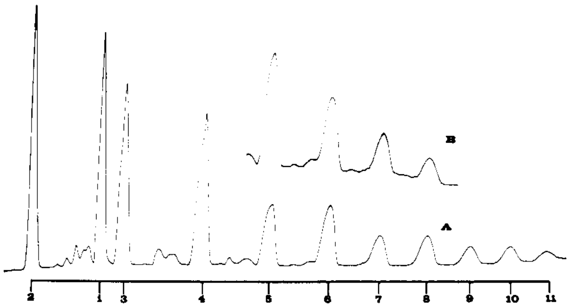

Figure 1. Chromatograms of the trimethylsilyl ether derivatives of the glycols obtained from hydrolysis of low-conversion PO–SO_2 copolymers made with the homogeneous catalyst $SnCl_4$ at a PO–SO_2 charge ratio of (A) 7 : 1 and (B) 1 : 1. The numbers (*N*) along the horizontal axis correspond to the numbers of PO units in the glycol. Numerical values for run concentrations are given in ref 2. Tetraethylene glycol dimethyl ether is the internal standard (i). Unusual line shapes are due to PO structural isomerism (head to head, head to tail, etc.) within the glycols. Remaining peaks are impurities.

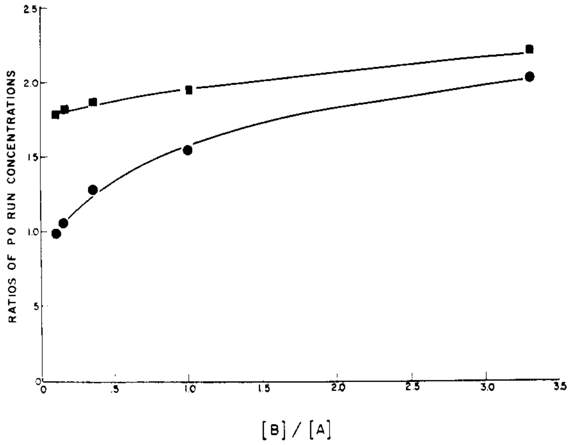

Figure 2. Experimental ratios of concentrations of runs of PO as a function of the reciprocal comonomer charge ratio: ■, $[B(A)_6B]/[B(A)_7B]$; ●, $[B(A)_5B]/[B(A)_6B]$. Within experimental error, $[B(A)_2B]/[B(A)_3B]$ = $[B(A)_6B]/[B(A)_7B]$ and $[B(A)_3B]/[B(A)_4B]$ = $[B(A)_5B]/[B(A)_6B]$.

made at different monomer charge ratios are given in Figure 1. (Reproducibility and accuracy of the glpc technique are also found in the preceding paper.) When *N*, the number of PO units in a run, is greater than 3, the relative molar response factors are all equal and so the relative concentrations of runs are equal to the relative areas of the corresponding peaks. When *N* equals 1, 2, and 3, the observed peak areas must be multiplied by 2.0, 1.4, and 1.1, respectively. Figure 1A shows the pair effect in which the concentrations of runs of length 5 and 6 are equal, 7 and 8 are equal, etc. Figure 1B and Figure 2 show the dependence of this pair effect on the charge ratio. At a charge ratio of 1 : 2, the pair effect has virtually disappeared and the decrease in run concentrations is almost regular for increasing *N*. In Figure 2, only the ratios of concentrations of runs of length 5, 6, and 7 have been plotted. Choosing any three consecutive run numbers (with the exceptions of runs of length one) will produce similar results. High- and low-conversion copolymers are alike in these respects.

Markoffian Description of the Monomer Distribution

A Markoffian description of two connected catalytic states *not* in dynamic equilibrium can involve the four states defined by

$$\begin{aligned} \{1\} &= AAM^1 \\ \{2\} &= AAM^2 \\ \{3\} &= ABM^1 \\ \{4\} &= BAM^1 \end{aligned} \qquad (1)$$

where A = PO, B = SO_2, and runs of B longer than one are not allowed. The experimentally observed extremely low concentration of BAB sequences can be described as a property of state $\{4\}$. The symbols M^1 and M^2 represent two different states of the reactive catalytic chain end. The catalyst system M remains with the chain end throughout the copolymerization and probably involves one or both monomers as well as the inorganic species.

The existence of a run concentration pair effect implies that the growing copolymer chain is somehow repetitively transmitting information over a length of two monomers in a way different from a chain end effect. The way in which M^1 and M^2 are connected gives rise to a pair effect as will be shown later. The pair effect cannot be explained by assuming that monomers add to the chain only by pairs since this would produce only runs of even lengths.

Propagation consists of the chain, growing from left to right, adding monomers and thereby undergoing transitions between the four states of eq 1. The addition probabilities *x*, *y*, and *z* are defined by

$$\begin{aligned} x &= P_{AAM^1/A} \\ y &= P_{AAM^2/A} \\ z &= P_{BAM^1/A} \end{aligned} \qquad (2)$$

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. The absence of consecutive B units requires that $P_{ABM^1/A} = 1$. These addition probabilities are related to the charge ratio by

$$\begin{aligned} x &= [A]k_{AAM^1/A}/([A]k_{AAM^1/A} + [B]k_{AAM^1/B}) \\ &= cr_1/(1 + cr_1),\ r_1 = k_{AAM^1/A}/k_{AAM^1/B} \end{aligned} \qquad (3)$$

where [A] and [B] are the concentrations of the unreacted monomers, the *k*'s are the rate constants for the processes indicated in the subscripts, and *c* = [A]/[B]. Similarly, we have

$$\begin{aligned} y &= cr_2/(1 + cr_2),\ r_2 = k_{AAM^2/A}/k_{AAM^2/B} \\ z &= cr_3/(1 + cr_3),\ r_3 = k_{BAM^1/A}/k_{BAM^1/B} \end{aligned} \qquad (4)$$

Since all the propagation probabilities depend only on a finite number of previous events, the description is Markoffian.

The transition probability matrix **P** connecting the four states is

$$\mathbf{P} = \begin{pmatrix} 0 & y & 0 & z \\ x & 0 & 0 & 0 \\ 1-x & 1-y & 0 & 1-z \\ 0 & 0 & 1 & 0 \end{pmatrix} \tag{5}$$

In this model the transitions $\{1\} \rightarrow \{1\}$ and $\{2\} \rightarrow \{2\}$ (with the addition of an A unit to the chain) are not allowed while the transitions $\{1\} \rightarrow \{2\}$ and $\{2\} \rightarrow \{1\}$ are allowed. Connecting the catalytic states M^1 and M^2 in this way provides the growing chain with a memory of a two monomer long repetition. This memory of the catalyst is distinct from the memory of the chain end.

P is a stochastic matrix allowing a simple solution of the eigenvalue equation

$$\mathbf{PV} = \lambda\mathbf{V} \tag{6}$$

where **V** is a four-element column vector whose components represent the relative concentrations of the steady-state (low conversion) distribution of the states $\{1\}$ to $\{4\}$ in the chain.[5] The eigenvalue λ is equal to unity.

Once a monomer is in the chain, whether it entered *via* M^1 or M^2 is not an experimental observable; M^1 and M^2 are not, of course, incorporated into the chain. In other words, M^1 and M^2 allow active chain end AA units to be distinguished as, say, AA^1 and AA^2 when in the catalytic state, although this distinguishing feature is not an experimental observable in the completed chain.

The solution of eq 6 is given by

$$\begin{aligned} \{1\}_s &= gz \\ \{2\}_s &= gxz \\ \{3\}_s &= g(1-xy) \\ \{4\}_s &= g(1-xy) \end{aligned} \tag{7}$$

where g is a constant.

Expressions for the relative concentrations of longer runs are immediately available from the shorter runs as shown by eq 8. The chain's two monomer long repetition is seen in equalities such as $[B(A)_6B]/[B(A)_4B] = [B(A)_8B]/[B(A)_6B] = xy$. This repetition gives rise to the run concentration pair effect (*e.g.*, $[B(A)_5B] = [B(A)_6B]$) when $y = 1/(2-x)$. For the $SnCl_4$-catalyzed PO–SO_2 low-conversion copolymer made at charge ratio $c = 7$, x and y are evaluated from the shorter runs as 0.65 and 0.75, respectively. With these parameters, the predicted values for the relative concentrations of runs of PO of length 5, 6, 7, and 8 are 1.00, 1.00, 0.54, and 0.54, respectively. The experimental values are 1.00, 0.96, 0.54, and 0.55, in good agreement.

$$\begin{aligned} [BAB] &= \{4\}_s(1-z) \\ [B(A)_2B] &= \{4\}_s z(1-x) \\ [B(A)_3B] &= \{4\}_s zx(1-y) \\ [B(A)_4B] &= \{4\}_s zxy(1-x) \end{aligned} \tag{8}$$

However, the Markoffian model completely fails to predict the observed dependence of the monomer distribution on charge ratio. The ratios plotted in Figure 2 are given by eq 9. Both ratios should give linear plots against $1/c$ with slopes and intercepts of the two plots related. The experimental plots are distinctly nonlinear and their slopes and intercepts are not related by eq 9.

$$\begin{aligned} [B(A)_5B]/[B(A)_6B] &= (1 + cr_1)/cr_2 \\ [B(A)_6B]/[B(A)_7B] &= (1 + cr_2)/cr_1 \end{aligned} \tag{9}$$

Any Markoffian model of a chain, growing one unit at a time, which attempts to describe the long-range order of PO–SO_2 copolymers by a shorter range memory will involve ratios of concentrations of long runs with a linear dependence on $1/c$ and so can be excluded.

Non-Markoffian Description of the Monomer Distribution

A plausible mechanism for generating a non-Markoffian monomer distribution in a copolymer made with a homogeneous catalyst is a copolymerization in which irreversible catalyst modifications occur with each new catalyst type adding monomers differently to the same growing chain.[6] For example, in the PO–SO_2 system at high charge ratio of PO to SO_2, the catalyst could be such that the Markoffian description of the previous section is applicable. At lower charge ratio, the catalyst system could be altered in such a way that some simpler Markoffian description is applicable. This irreversible change in the catalyst could be due either to a time and charge ratio dependent modification of the catalyst by a reaction with a rate constant comparable to the propagation rate, or to a charge ratio dependent modification which occurs in a short time compared to the propagation time. However, the fact that high- and low-conversion PO–SO_2 copolymers show identical pair effects makes the former catalytic modification unlikely for this system while the latter would not show the gradual disappearance of the pair effect as a functon of charge ratio shown in Figure 2. Thus, consecutive catalytic states connected by irreversible modifications are unlikely for the PO–SO_2 system.

It is also possible to show that the non-Markoffian monomer distribution produced by the sum of two different, independent Markoffian chains, one of which produces only runs of even length and the other only runs of odd length, fails to explain the charge ratio dependence. Sums of ordinary Markoffian chains fail to explain not only the charge ratio dependence but also the long-range run concentration pair effect.

However, other non-Markoffian models are possible. Coleman and Fox[4] have given a multistate description of homogeneous ionic homopolymerizations which leads to a non-Markoffian diastereosequence distribution. In their mechanism the growing polymer chain exists in either of two possible states which are in dynamic equilibrium, each capable of adding monomer with its own characteristic rate constant and stereoselectivity.

An analogous non-Markoffian multistate description of the monomer distribution in PO–SO_2 copolymers can be developed if, in the Markoffian description given in the previous section, the two connected catalytic states are allowed to be in dynamic equilibrium. The

---

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

(6) L. Peller, *ibid.*, **43**, 2355 (1965).

propagation scheme is given by reaction 10. The

$$\begin{aligned}
\mathrm{E}_1{}^{n}(\mathrm{AA}) + \mathrm{A} &\longrightarrow \mathrm{E}_2{}^{n+1}(\mathrm{AA}),\ k_{\mathrm{AA}^1/\mathrm{A}}\\
\mathrm{E}_1{}^{n}(\mathrm{AA}) + \mathrm{B} &\longrightarrow \mathrm{E}_1{}^{n+1}(\mathrm{AB}),\ k_{\mathrm{AA}^1/\mathrm{B}}\\
\mathrm{E}_1{}^{n}(\mathrm{AB}) + \mathrm{A} &\longrightarrow \mathrm{E}_1{}^{n+1}(\mathrm{BA}),\ k_{\mathrm{AB}^1/\mathrm{A}}\\
\mathrm{E}_1{}^{n}(\mathrm{BA}) + \mathrm{A} &\longrightarrow \mathrm{E}_1{}^{n+1}(\mathrm{AA}),\ k_{\mathrm{BA}^1/\mathrm{A}}\\
\mathrm{E}_1{}^{n}(\mathrm{BA}) + \mathrm{B} &\longrightarrow \mathrm{E}_1{}^{n+1}(\mathrm{AB}),\ k_{\mathrm{BA}^1/\mathrm{B}} \qquad (10)\\
\mathrm{E}_2{}^{n}(\mathrm{AA}) + \mathrm{A} &\longrightarrow \mathrm{E}_1{}^{n+1}(\mathrm{AA}),\ k_{\mathrm{AA}^2/\mathrm{A}}\\
\mathrm{E}_2{}^{n}(\mathrm{AA}) + \mathrm{B} &\longrightarrow \mathrm{E}_1{}^{n+1}(\mathrm{AB}),\ k_{\mathrm{AA}^2/\mathrm{B}}\\
\mathrm{E}_1{}^{n}(\mathrm{AA}) &\longrightarrow \mathrm{E}_2{}^{n}(\mathrm{AA}),\ \lambda_{12}\\
\mathrm{E}_2{}^{n}(\mathrm{AA}) &\longrightarrow \mathrm{E}_1{}^{n}(\mathrm{AA}),\ \lambda_{21}
\end{aligned}$$

condition of a polymer molecule is given by $\mathrm{E}_i{}^n\ (\alpha)$. The degree of polymerization n is assumed to be large so that end effects are neglected; α defines the growing chain end, and i denotes the state of the catalyst. The rate constants for the only allowed transitions of the chain, growing from left to right, are indicated in eq 10 and depend on the chain end and the catalytic state. Rate constants λ_{12} and λ_{21} connect the two catalytic states in a way which does not propagate the chain. All rate constants are assumed independent of n and charge ratio. The concentrations of the monomers are given by [A] and [B] and are constant throughout a given polymerization (low conversion). Concentrations are used even though solutions are nonideal.

The copolymerization scheme of eq 10 differs from the Coleman–Fox mechanism in three ways: (1) two different monomers are added to the chain instead of one; (2) the last two monomers in the chain affect propagation instead of just the last one; (3) the two catalytic states are connected by propagation as well as equilibrium transitions.

The motivation for feeling that this sort of a mechanism might be applicable can be gained by considering the transitions available to states $\{1\}$ and $\{2\}$: $\{1\} \rightarrow \{2\}$, $\{1\} \rightleftarrows \{2\}$, and $\{2\} \rightarrow \{1\}$. The notation of eq 1 is used, but now states $\{1\}$ and $\{2\}$ are in equilibrium as well as connected by propagation of the chain. These transitions occur with different rate constants. If the rate constants are such that at high charge ratio of PO to SO_2 virtually every polymer chain in state $\{1\}$ goes to state $\{2\}$ by a propagation step and returns to state $\{1\}$ from state $\{2\}$ by another propagation step, then the mechanism of eq 10 approaches the Markoffian mechanism of eq 5. This produces the run concentration pair effect as noted in the text following eq 8. When the charge ratio is lower, the concentration of PO is lower, and the probability of a polymer chain in state $\{1\}$ going to state $\{2\}$ by a propagation step is correspondingly reduced. That is, some of the chains in state $\{1\}$ will go to state $\{2\}$ by a nonpropagating step. However, if λ_{21} (of eq 10) is very small, all the chains in state $\{2\}$ will still go to state $\{1\}$ by a propagation step. When the charge ratio is very low, virtually every polymer chain in state $\{1\}$ goes to state $\{2\}$ by a nonpropagating step with a rate constant λ_{12}. State $\{1\}$ has become a dummy variable. The scheme is now equivalent to a normal Markoffian mechanism which produces run concentrations which decrease uniformly with increasing length. Thus, the mechanism of eq 10 seems capable of explaining the appearance of the pair effect at high charge ratio and its gradual disappearance with lower charge ratios by a model which is really no more complicated than the Markoffian description of eq 5.

Physically, the scheme may be considered the description of a process in which monomers can be added to the *completed* chain either singly or by pairs. If $\{1\}$ = AAM and now $\{2\}$ is written as AM:A (where the colon represents a monomer bound to the catalyst in some sort of a coordination sphere but not yet part of the completed chain), then the propagation step $\{2\} \rightarrow \{1\}$ is given by AM:A + A → [AM:A_2] → AAAM. Here, A_2 represents an intermediate, coordinated PO–dimer (probably a six-membered ring attached to the tin by one of the two oxygens in the ring). The propagation step $\{1\} \rightarrow \{2\}$ represents the coordination of a new PO unit and the equilibrium steps connecting the two states represent a single PO unit entering (or leaving) the completed chain from (or to) the coordination sphere of the catalyst. States $\{3\}$ and $\{4\}$ and monomer B can be introduced analogously. The reasonable idea of monomers such as PO coordinated by catalyst systems such as $SnCl_4$–PO–SO_2 before entering the completed chain has been discussed and documented in detail before.[3,7,8] Note that even though dimers are formed before entering the completed chain, propagation is by single units. An unreasonable, concerted, trimolecular (chain end and two monomers) propagation step need not be assumed.

The rate constant, $k_{\mathrm{BA}^1/\mathrm{B}}$ will be set identically to zero, reflecting the experimentally observed fact that BAB sequences are almost never observed. The function $R(\mathrm{AAA},t,1\,|\,j)$ is the probability that a polymer molecule is in the state $\mathrm{E}_j{}^n(\mathrm{AA})$ at time $t + \tau_n$, given that at time τ_n $\mathrm{E}_1{}^{n-1}(\mathrm{AA}) \rightarrow \mathrm{E}_2{}^n(\mathrm{AA})$. Probabilities $R(\mathrm{AAA},t,2\,j)$ (j = 1, 2) are defined similarly except at time τ_n $\mathrm{E}_2{}^{n-1}(\mathrm{AA}) \rightarrow \mathrm{E}_1{}^n(\mathrm{AA})$. These functions[9] of t are independent of n and τ_n and obey the differential equations

$$\begin{aligned}
\mathrm{d}R(\mathrm{AAA},t,i\,|\,1)/\mathrm{d}t = -\ \{k_{\mathrm{AA}^1/\mathrm{A}}[\mathrm{A}] + k_{\mathrm{AA}^1/\mathrm{B}}[\mathrm{B}] +{}&\\
\lambda_{12}\}R(\mathrm{AAA},t,i\,|\,1) + \lambda_{21}R(\mathrm{AAA},t,i\,|\,2)&\\
\mathrm{d}R(\mathrm{AAA},t,i\,|\,2)/\mathrm{d}t = -\ \{k_{\mathrm{AA}^2/\mathrm{A}}[\mathrm{A}] + k_{\mathrm{AA}^2/\mathrm{B}}[\mathrm{B}] +{}&\\
\lambda_{21}\}R(\mathrm{AAA},t,i\,|\,2) + \lambda_{12}R(\mathrm{AAA},\ t,i\,|\,1)&
\end{aligned} \qquad (11)$$

where i is 1 and 2. The initial conditions are

$$\begin{aligned}
R(\mathrm{AAA},0,1\,|\,1) &= 0\\
R(\mathrm{AAA},0,1\,|\,2) &= 1\\
R(\mathrm{AAA},0,2\,|\,1) &= 1\\
R(\mathrm{AAA},0,2\,|\,2) &= 0
\end{aligned} \qquad (12)$$

Even though the rate constants depend only on the last two units in the chain, specifying the last three units in defining the R functions permits a specification of the initial conditions. A similar simultaneous differential equation is obtained when the AAA index of the R functions is replaced by the BAA index, but now with the initial conditions

$$\begin{aligned}
R(\mathrm{BAA},0,1\,|\,1) &= 1\\
R(\mathrm{BAA},0,1\,|\,2) &= 0
\end{aligned} \qquad (13)$$

The functions $R(\mathrm{BAA},t,2\,|\,j)$ (j = 1, 2) are zero since A adding to a chain with i = 2 and ending with BA is not

---

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

(8) J. Schaefer, R. J. Kern, and R. J. Katnik, *Macromolecules*, **2**, 101 (1968).

(9) Coleman and Fox discuss the properties of these functions in somewhat more detail in ref 4.

allowed by eq 10. The matrices **BAA** and **AAA** have the elements

$$\begin{aligned}(\mathbf{BAA})_{ij} &= b_{ij}\\ (\mathbf{AAA})_{ij} &= a_{ij}\end{aligned} \tag{14}$$

where

$$\begin{aligned}b_{ij} &= \int_0^\infty R(\mathrm{BAA},t,i\,|\,j)\mathrm{d}t\\ a_{ij} &= \int_0^\infty R(\mathrm{AAA},t,i\,|\,j)\mathrm{d}t\end{aligned} \tag{15}$$

The matrices **BAA/A**, **BAA/B**, **AAA/A**, and **AAA/B** have elements which give the probability that the $(n + 1)$th unit was added when the chain was in catalytic state j, given that the nth unit was added when the chain was in state i; for example

$$\begin{aligned}(\mathbf{BAA/A})_{12} &= [\mathrm{A}]k_{\mathrm{AA^2/A}}b_{12}\\ &= b_{12}(\mathrm{A})\end{aligned} \tag{16}$$

is the probability that the $(n + 1)$th unit is an A unit added when the chain ending with BAA was in catalytic state 2, given that the nth unit was added when the chain was in catalytic state 1. The other matrix elements are defined in an analogous manner. With the fact that

$$\lim_{t\to\infty} R(\alpha,t,i\,|\,j) = 0 \tag{17}$$

for all α, i, and j, the a_{ij} and b_{ij} terms can be obtained from eq 11–15 and are given by

$$\begin{aligned}b_{11} &= (k_{\mathrm{AA^2/A}}[\mathrm{A}] + k_{\mathrm{AA^2/B}}[\mathrm{B}] + \lambda_{21})/D\\ b_{12} &= \lambda_{12}/D\\ b_{21} &= 0\\ b_{22} &= 0\\ a_{11} &= \lambda_{21}/D\\ a_{12} &= (k_{\mathrm{AA^1/A}}[\mathrm{A}] + k_{\mathrm{AA^1/B}}[\mathrm{B}] + \lambda_{12})/D\\ a_{21} &= (k_{\mathrm{AA^2/A}}[\mathrm{A}] + k_{\mathrm{AA^2/B}}[\mathrm{B}] + \lambda_{21})/D\\ a_{22} &= \lambda_{12}/D\end{aligned} \tag{18}$$

where $D = (k_{\mathrm{AA^1/A}}[\mathrm{A}] + k_{\mathrm{AA^1/B}}[\mathrm{B}] + \lambda_{12})(k_{\mathrm{AA^2/A}}[\mathrm{A}] + k_{\mathrm{AA^2/B}}[\mathrm{B}] + \lambda_{21}) - \lambda_{12}\lambda_{21}$. The experimentally observed ratios of concentrations of runs of PO can now be obtained from eq 15, 16, and 18 and are given by

$$\begin{aligned}[\mathrm{BAAB}]/[\mathrm{BAAAB}] &= \{b_{11}(\mathrm{B}) + b_{12}(\mathrm{B})\}/\\ &\quad \{b_{11}(\mathrm{A})a_{11}(\mathrm{B}) + b_{12}(\mathrm{A})a_{21}(\mathrm{B}) +\\ &\quad b_{11}(\mathrm{A})a_{12}(\mathrm{B}) + b_{12}(\mathrm{A})a_{22}(\mathrm{B})\}\\ [\mathrm{BAAAB}]/[\mathrm{BAAAAB}] &= \Big\{\sum_{i,j=1,2} b_{1i}(\mathrm{A})a_{ij}(\mathrm{B})\Big\}/\\ &\quad \Big\{\sum_{i,j,k=1,2} b_{1i}(\mathrm{A})a_{ij}(\mathrm{A})a_{jk}(\mathrm{B})\Big\}\end{aligned} \tag{19}$$

Since the propagation probabilities depend on equilibrium transitions of the chain in addition to a finite number of previous events, the description is non-Markoffian.[4] That is, the conditional probability for B to add to a chain ending with BA_N does not become a constant with increasing N. In the limit of $\lambda_{12} = \lambda_{21} = 0$, the ratios in eq 19 go to

$$\begin{aligned}[\mathrm{BAAB}]/[\mathrm{BAAAB}] &= (1 + cr_2)/cr_1\\ [\mathrm{BAAAB}]/[\mathrm{BAAAAB}] &= (1 + cr_1)/cr_2\end{aligned} \tag{20}$$

where c_1, r_1, and r_2 have been defined earlier. That is, as the probability for the chain to make a transition without adding a monomer unit goes to zero, the non-Markoffian description goes to the Markoffian description of the previous section. (Note that $k_{\mathrm{AAM^i/A}}$ equals $k_{\mathrm{AA^i/A}}$, etc.)

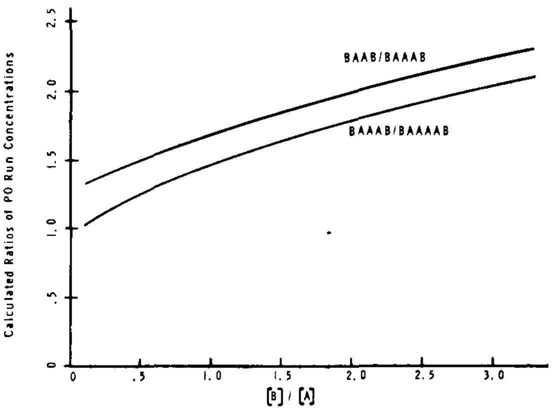

Figure 3. Calculated ratios of concentrations of runs of PO as a function of the reciprocal comonomer charge ratio using the non-Markoffian model of eq 10 with $k_{\mathrm{AA^1/A}} = k_{\mathrm{AA^2/A}}$, $\lambda_{21} = 0$, $r_1 = 0.253$, $r_2 = 9.286$, $k_1 = 2.646$, and $[\mathrm{A}] + [\mathrm{B}] = 0.612$. See text for definitions. Only ratios of parameters are significant.

Discussion

All of the large number of parameters involved in eq 10 cannot be reliably evaluated from the available experimental data. However, some of the properties of the non-Markoffian model in predicting the results of Figure 2 can be seen if we assume $[\mathrm{A}] + [\mathrm{B}] \sim 10$, $r_1/r_2 \sim 1$, $k_{\mathrm{AA^1/A}} = k_{\mathrm{AA^2/A}} \sim 10$, and λ_{12} and $\lambda_{21} \sim 10$. Then the most important terms in the ratios of eq 19 will be those which contain the highest power of $[\mathrm{A}] + [\mathrm{B}]$ for large $[\mathrm{A}]/[\mathrm{B}]$ and are given by

$$\begin{aligned}[\mathrm{BAAB}]/[\mathrm{BAAAB}] &= (k_2 + [\mathrm{A}] + [\mathrm{B}]/r_2)r_2/[\mathrm{A}]r_1\\ [\mathrm{BAAAB}]/[\mathrm{BAAAAB}] &= (k_1 + [\mathrm{A}] + [\mathrm{B}]/r_1)r_1/[\mathrm{A}]r_2\end{aligned} \tag{21}$$

where $k_1 = \lambda_{12}/k_{\mathrm{AA^1/A}}$ and $k_2 = \lambda_{21}/k_{\mathrm{AA^1/A}}$.

Equation 21 shows that the non-Markoffian model predicts that the run-concentration ratios depend nonlinearly on the charge ratio, that $[\mathrm{B(A)_3B}]/[\mathrm{B(A)_4B}]$ can depend more strongly on the charge ratio than $[\mathrm{B(A)_2B}]/[\mathrm{B(A)_3B}]$, and that as the charge ratio becomes very large these two ratios are not reciprocals of one another. All of these results are observed experimentally.[10] The long-range order that PO–$\mathrm{SO_2}$ copolymers exhibit in this charge ratio region, through the repetition of the run-concentration pair effect with increasing length of runs of PO, is also predicted by the non-Markoffian model. For increasing N, run-concentration ratios will, in turn, first involve terms containing k_2 and then terms containing k_1. That is, eq 21 is repeated for increasing N. This result depends directly on the boundary conditions of eq 12 and 13 and hence on the memory of the catalytic states. Thus, if $[\mathrm{B(A)_3B}]/[\mathrm{B(A)_4B}]$ and $[\mathrm{B(A)_2B}]/[\mathrm{B(A)_3B}]$ are about 1 and 2, respectively, for a

---

(10) Recall that experimentally, $[\mathrm{B(A)_2B}]/[\mathrm{B(A)_3B}] = [\mathrm{B(A)_6B}]/[\mathrm{B(A)_7B}]$ and $[\mathrm{B(A)_3B}]/[\mathrm{B(A)_4B}] = [\mathrm{B(A)_5B}]/[\mathrm{B(A)_6B}]$.

high charge ratio of PO to SO_2, then $[B(A)_5B]/[B(A)_6B]$ and $[B(A)_4B]/[B(A)_5B]$ will also be about 1 and 2, respectively.[10]

In general, the expressions for the run-concentration ratios are more involved than eq 21. Figure 3 shows the calculated $[B(A)_2B]/[B(A)_3B]$ and $[B(A)_3B]/[B(A)_4B]$ ratios obtained for $k_{AA^1A} = k_{AA^2A}$ and $\lambda_{21} = 0$ with the other parameters varied to give a reasonable fit to the experimental data ($r_1 = 0.253$, $r_2 = 0.286$, $k_1 = 2.646$, and $[A] + [B] = 0.612$; the sum of [A] and [B] is assumed a constant since no solvent is used in the copolymerization.) Although this simplified model does not give a perfect fit between calculated and observed values of the run-concentration ratios, the essential features are predicted: a nonlinear dependence on the charge ratio with the curvature in the right direction, a slightly stronger charge ratio dependence for $[B(A)_2B]/[B(A)_3B]$, and intercepts for the two ratios which are not reciprocals. The boundary conditions of eq 12 and 13 ensure a tendency for the model to repeat the pair effect with increasing run length, but with a somewhat different charge ratio dependence. The differences are not outside experimental error limits.

The non-Markoffian model presented can account for all of the available $SnCl_4$-catalyzed PO–SO_2 monomer distribution data. Such an agreement does not, of course, constitute a *proof* of the applicability of the model to the real system. Further checks and tests are desirable. Since an equilibrium of catalytic species is an hypothesis of the model, changing the reaction conditions to affect the equilibrium (and so the monomer distribution) in a predictable way would be appropriate. This might be achieved by variation of the polymerization temperature, or perhaps the introduction of an inert solvent. Unfortunately, the danger in this sort of an approach is that any change in conditions which might affect the equilibrium might also change other aspects of the rather involved reaction system[2] so that the same *kind* of polymerization may no longer result.

Polarized Infrared Studies of Amorphous Orientation in Polyethylene and Some Ethylene Copolymers[1a]

B. E. Read[1b] and R. S. Stein

Polymer Research Institute, University of Massachusetts,
Amherst, Massachusetts.
Received November 6, 1967

ABSTRACT: Measurements have been made of the dichroic ratios of a number of infrared bands for uniaxially deformed low-density polyethylene. In order to characterize the amorphous orientation in the polymer, orientation functions have been derived from the results on the conformationally sensitive amorphous bands at 1368, 1352, 1303, and 1078 cm^{-1}. In conjunction with X-ray data and infrared dichroism data on the crystalline 1894-cm^{-1} band, amorphous orientation functions have also been derived from the 2016-cm^{-1} band which appears to contain a normal amorphous component. The results indicate that extended *trans* sequences in the amorphous phase orient to a larger extent than isolated *trans* bonds flanked by *gauche* bonds. Results on the bands at 720 and 730 cm^{-1} appear to show discrepancies when compared with the data from the other bands, and possible reasons for this apparent inconsistency are suggested. Amorphous orientation functions have also been derived from the $C{\equiv}N$ stretching band at 2250 cm^{-1} in a copolymer of ethylene and (2 wt %) acrylonitrile. The bands at 2016 and 1894 cm^{-1} have also been analyzed for this copolymer, in addition to a $C{=}O$ stretching band at 1740 cm^{-1} due apparently to thermal oxidation. Infrared dichroism results are also discussed for a copolymer of ethylene and (4.1 mol %) methacrylic acid in which 70% of the -COOH groups are neutralized with sodium hydroxide.

A considerable amount of work has been reported on the orientation of the crystalline phase of deformed partially crystalline polymers, and the X-ray technique has figured prominently in these investigations.[2–6] Several studies have also been made of the effect of a deformation on the orientation of the amorphous regions. These include studies involving a combination of birefringence and X-ray methods.[2a,4,6] Amorphous orientation has also been investigated by incorporating dye molecules into the amorphous phase and making measurements of visible dichroism.[7–9] In addition, studies of the polarization of fluorescence have been made using samples containing fluorescent molecules in the amorphous regions.[10] The two latter investigations suffer from the disadvantage that the

---

(1) (a) Supported in part by grants from the National Science Foundation and the Petroleum Research Fund and in part by a contract with the Office of Naval Research. (b) Work carried out while on leave of absence from the Division of Molecular Science, National Physical Laboratory, Middlesex, England, which is the present address.

(2) (a) R. S. Stein, "Newer Methods of Polymer Characterization," B. Ke, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter IV, p 155; (b) S. Hoshino, J. Powers, D. G. LeGrand, H. Kawai, and R. S. Stein, *J. Polym. Sci.*, **58**, 185 (1962).

(3) I. L. Hay and A. Keller, *Kolloid Z.*, **204**, 43 (1965).

(4) R. J. Samuels, *J. Polym. Sci., Part A*, **3**, 1741 (1965).

(5) C. R. Desper and R. S. Stein, *J. Appl. Phys.*, **37**, 3990 (1966).

(6) K. Fujino, H. Kawai, T. Oda, and H. Maeda, *Proc. Intern. Congr. Rheol., 4th*, Providence, 1963, Part 3, 501 (1965).

(7) D. Patterson and I. M. Ward, *Trans. Faraday Soc.*, **53**, 1516 (1957).

(8) R. Yamada and R. S. Stein, *J. Polym. Sci., Part B*, **2**, 1131 (1964).

(9) R. Yamada, C. Hayashi, and S. Onogi, *Intern. Symp. Macromol. Chem., Tokyo*, **8**, 160 (1966).