Oxidation products from the xylenol analogs in Table IX were isolated after treatment of the phenols with oxygen in 15 ml of pyridine containing 20 mg of peroxidized Cu_2Cl_2. Crude product was isolated by pouring into 100 ml of dilute (5:1) hydrochloric acid.

Mesitol (IA, 816 mg, 6 mmol) consumed 3.6 mmol of O_2 in 20 hr. The crude product (617 mg, mp 108–185°) left 109 mg, mp 190–220° on benzene extraction, 0.76 mequiv of peroxide/g. *Anal.* Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 76.76; H, 7.60. Evaporation of the benzene and methanol extraction left 172 mg: mp 163–177°; $[\eta]$ 0.05 (benzene); 0.46 mequiv of peroxide/g, nmr ($CDCl_3$) δ 2.29 (3 H), 2.35 (4 H), 4.68 (1.3 H), 6.85 (0.4 H), and 7.18 (1.6 H). From the initial acid mother liquor, ether extraction yielded 167 mg, recrystallized from water as white needles (63 mg, 7%), of **4-formyl-2,6-xylenol,** mp 112–114° (lit.[21] mp 113.5–114°), identified further by comparison of the ir spectrum with that of authentic material.[21]

4-Hydroxymethyl-2,6-xylenol (IE, 608 mg, 4 mmol) consumed 2.45 mmol of O_2 in 4 hr. The crude initial precipitate, 293 mg, mp 108–145°, left 80 mg of methanol-insoluble white powder, identified as **polyxylenol:** mp 185–205°, nmr ($CDCl_3$) δ 2.09 (6 H), and 6.49 (2 H). From ether extraction of the original acid mother liquor, 185 mg (31%) of **4-formyl-2,6-xylenol,** mp 107–113°, was recovered.

4-Ethoxymethyl-2,6-xylenol (IG, 720 mg, 4 mmol) consumed 2.04 mmol of O_2 in 20 hr. There was no dilute hydrochloric acid insoluble product. Ether extraction gave 558 mg, mp 102–107°, which was recrystallized to give 438 mg (73%) of **4-formal-2,6-xylenol,** mp 110–113°, identical with authentic material[21] by ir spectra.

4-*tert*-Butyl-2,6-xylenol (ID, 534 mg, 3 mmol) consumed 2.07 mmol of O_2 in 20 hr. The crude precipitate, 496 mg, mp 110–130°, left 239 mg of methanol-insoluble amber powder, mp 168–180°, identified as an oligomer of polyxylenol by nmr ($CDCl_3$) [δ 1.33 (2.5 H), 2.09 (4 H), 2.14 (2 H), 6.47 (1.3 H), 6.98 (0.2 H), and 7.09 (0.4 H)]. Its ir spectrum ($CHCl_3$) showed no OH and only very weak $C{=}O$ absorbance.

4-Methoxy-2,6-xylenol (IF, 608 mg, 4 mmol) consumed 2.9 mmol of O_2 in 20 hr. The crude amber precipitate weighed 517 mg: mp 65–90°; 1.58 mequiv of peroxide/g; nmr ($CDCl_3$) δ 1.50 (0.2 H), 1.90 (0.4 H), 2.17–2.25 (3.4 H), 3.48–3.71 (4.25 H), 4.71 (9.3 H), and 6.61–7.0 (2 H). These data are in reasonable accord with a product containing 0.25 mol of dimer peroxide per mole of *o*-quinomethane oligomer, contaminated with 1 mol of water.

Durenol (592 mg, 4 mmol) was oxidized as above but with 15 ml of benzene added. In 1 hr, 2.28 mmol of O_2 was consumed. After adding another 20 ml of benzene and extracting with hydrochloric acid, 160 mg of almost colorless white solid was filtered from the benzene layer: mp 310–345°; ir (KBr), cm^{-1} (% absorbance) 1090 (93), 1230 (96), 1360 (78), 1390 (82), 1455 (85), and 2910 (45). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 79.47; H, 8.21. Further washing of the benzene fitrate, evaporation, and extraction with petroleum ether (30–60°) left 106 mg: mp 250–330°, $[\eta]$ 0.06 (benzene), nmr ($CDCl_3$) δ 1.99, ir identical with that of the insoluble polymer. Evaporation of the petroleum ether and methanol extraction gave 46 mg of duroquinone, mp 109–110° (lit.[22] 110–111°).

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(21) J. Thiele and H. Eichwede, *Justus Liebigs Ann. Chem.*, **311**, 363 (1900).

(22) L. I. Smith and F. J. Dobrovolny, *J. Amer. Chem. Soc.*, **48**, 1420 (1926).

Block-Frequency Distribution of Copolymers

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ABSTRACT: The fraction of molecules of a statistical copolymer which has a given number of blocks of specified length of one comonomer has been derived by a Markov-chain approach, while the corresponding weight fraction has been calculated by a Monte Carlo method. Attention is directed both at blocks of a given length and at blocks above a given minimum length. These quantities are of interest because the distribution of blocks which are long enough to segregate into crystalline or glassy domains governs the physical properties of block copolymers.

Copolymer properties can be profoundly influenced by the presence of blocks, *i.e.*, long sequences, of one of the constituent monomers, especially if these are long and numerous enough to segregate into separate phases of glassy or crystalline domains. Among copolymers with such long blocks, one can distinguish several types, notably block copolymers made by sequential homopolymerization (*e.g.*, ABA triblock polymers) and statistical copolymers made by conventional copolymerization with monomer concentrations and reactivity ratios which lead to block structures. This paper concerns itself only with statistical copolymers.

Many copolymers are of interest in which the molecules consist of long blocks capable of participating in glassy or crystalline domains separated by amorphous chains. The glassy or crystalline domains form tie points, *i.e.*, quasi-cross-links, which bind the amorphous chains into a network resembling that of conventionally cross-linked elastomers, and the reversible nature of such tie points confers upon some of these materials the special properties which permit their use as thermoplastic elastomers.

In statistical copolymers of this type there are some molecules which have no block long enough to participate in a glassy or crystalline domain and which are thus not tied into the network at all, while others have only one such block which does not provide any elastically effective chain, except possibly by means of chain entanglements. In order to predict the quantity of such elastically inferior molecules in the copolymer, one needs to know the block-frequency distribution, defined here as the fraction of copolymer molecules with a given number of blocks of specified length.

In a copolymer of any number of different comonomers, let us designate the monomer of interest, *i.e.*, the one capable of participating in glassy or crystalline domains, as monomer A and its sequences as A blocks. The block-length distribu-

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[1] Contribution No. 258.

tion, *i.e.*, the probability of finding A blocks of specified length in the whole copolymer and the *mean* number of such A blocks per n-mer, can be derived by standard combinatorial methods.[2] The block-frequency distribution represents a more complex problem.

The work in this paper addresses itself to two block-frequency distributions: (1) the mole fraction, *i.e.*, the fraction of the total number of *molecules* in the whole copolymer with i A blocks of length k or longer, or of exactly length k, and (2) the weight fraction, *i.e.*, the fraction of the total number of *monomer units* in such molecules. An exact, general, closed-form solution of (1) will be derived by a Markov-chain formalism.[3] Distribution 2 is of greater relevance to the elastic properties of copolymers, since it reflects the total quantity of material which does not contribute to the elastic network. However, a closed-form solution of (2) has so far eluded us, and this problem has been treated numerically by a Monte Carlo method, a treatment more widely used for polymer conformation[4] than for copolymerization statistics. The approach to both problems has been kept general enough to be applicable to condensation as well as to addition copolymerization with any number of different comonomers, to any type of initiation mechanism, and to any type of single-chain termination. The treatment applies to any system with constant transition probabilities, *e.g.*, continuous copolymerization in a well-stirred reactor, the prevailing industrial practice of copolymer synthesis; batch copolymerization to low conversion; and equilibrium copolymerization. It is not directly applicable to systems with varying transition probabilities, such as are caused by the compositional drift during batch copolymerization to high conversion.

Definitions

For the present purpose, attention is directed to only one of the different comonomers, labeled A, while all the other comonomers are collectively labeled O. An A block of length k is defined as a sequence of exactly k A units bordered at beginning and end by O units (*i.e.*, units other than A). The basic parameters of the treatment are the transition probabilities P_{aa}, P_{ao}, P_{oa}, P_{oo}, defined in the customary way: P_{ij} is the conditional probability of the occurrence of monomer J, given that the preceding monomer unit is an I. They can, of course, also be defined in the corresponding kinetic terms.[3] The termination probabilities are defined as follows: T_a is the probability of chain termination after an A unit, T_o after a non-A. Accordingly, the normalization conditions are

$$\begin{aligned} P_{aa} + P_{ao} + T_a &= 1 \\ P_{oa} + P_{oo} + T_o &= 1 \end{aligned} \qquad (1)$$

Other basic relations follow directly from these definitions: $P(k)$, the probability that a given A block has length k, is given by

$$P(k) = (1 - P_{aa})P_{aa}^{k-1} \qquad (2)$$

the mean length of A blocks, $\bar{k}$, by

$$\bar{k} = 1/(1 - P_{aa}) \qquad (3)$$

the mean number of A blocks of any length in an n-mer, $B(n)$, by

$$B(n) = nX_a(1 - P_{aa}) \qquad (4)$$

where X_a is the mole fraction of A units in the copolymer; and the mean number of A blocks of length k in an n-mer, $C(n, k)$, by

$$C(n, k) = B(n)P(k) = nX_a(1 - P_{aa})^2 P_{aa}^{k-1} \qquad (5)$$

Mole Fraction with *i* A Blocks of Length *k* or Above

This problem is approached by the Markov-chain formulation for success runs[5a] combined with distribution-generating functions.[5b] The generating function $F(s)$ of a series of real numbers, $C_0, C_1, C_2, \ldots$, is defined as

$$F(s) \equiv C_0 + C_1 s + C_2 s^2 + \ldots C_n s^n + \ldots \qquad (6)$$

where s is a dummy variable which can take on values between 0 and 1. Generating functions are particularly useful if they are expressible in closed form, rather than as infinite series. In such cases, the moments of the distribution can be generated directly,[5a] and the distribution itself can be recovered by expanding the generating function in a McLaurin series, so that

$$C_i = F^{(i)}(0)/i! \qquad (7)$$

where the superscript (i) refers to the ith derivative with respect to s.

To adapt the Markov-chain formalism to A blocks of length k or above, we proceed along the monomer units of the copolymer chain from one end to the other, defining the *states* of the system as follows: (1) whenever a unit other than an A occurs, it is in state O; (2) when the first A unit occurs, either at the beginning or after a non-A, it is in state A_1; (3) with further A units, it goes successively to states A_2, A_3, A_4, . . . , A_k, remaining in state A_k after this; (4) on termination, the chain goes to state T and remains there. For example, the molecule

AOAOOAAAOOOAAAAAOAAAAOO

corresponds to the following series of states for $k = 3$

$$A_1OA_1OOA_1A_2A_3OOOA_1A_2A_3A_3A_3OA_1A_2A_3A_3OOTTT\ldots T\ldots$$

The transition table for this model, which defines the matrix **Q**, is shown in eq 8, in which we ignore the dummy variable s for the moment. The matrix elements Q_{gh} (where g and h refer to row and column, respectively, and can take on values 0, A_1, A_1, . . . , A_k, and T) represent the probabilities of going from state g to state h in one step. Similarly, the elements $Q_{gh}^{(n)}$ of its nth power, $\mathbf{Q}^n$, represent the probability of going from state g to state h in n steps.

It is evident that the number of A blocks of length k or above is equal to the number of transitions from state A_{k-1} to state A_k, which is where s appears in **Q**. Thus $Q_{gh}^{(n)}$ is a polynomial in s, with the coefficient of s^i representing the probability of passing from state A_{k-1} to state A_k exactly i times in going from state g to state h in n steps, *i.e.*, it is the corresponding generating function (*cf.* eq 6).

Since chains can start with A units or non-A units, the respective initiation probabilities I_a and I_o must be taken into

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(2) See, *e.g.*, G. E. Ham, Ed., "Copolymerization," Interscience, New York, N. Y., 1964, pp 5–8.

(3) H. K. Frensdorff and R. Pariser, *J. Chem. Phys.*, 39, 2303 (1963).

(4) G. G. Lowry, Ed., "Markov Chains and Monte Carlo Calculations in Polymer Science," Marcel Dekker, New York, N. Y., 1970.

(5) W. Feller, "Introduction to Probability Theory and Its Applications," 3rd ed, Wiley, New York, N. Y., 1968, (a) Chapter XV; (b) Chapter XI.

$$\mathbf{Q} \equiv \begin{array}{c|cccccccc}
 & \mathrm{O} & \mathrm{A}_1 & \mathrm{A}_2 & \mathrm{A}_3 & \cdots & \mathrm{A}_{k-2} & \mathrm{A}_{k-1} & \mathrm{A}_k & \mathrm{T} \\
\hline
\mathrm{O} & P_{oo} & P_{oa} & 0 & 0 & \cdots & 0 & 0 & 0 & T_o \\
\mathrm{A}_1 & P_{ao} & 0 & P_{aa} & 0 & \cdots & 0 & 0 & 0 & T_a \\
\mathrm{A}_2 & P_{ao} & 0 & 0 & P_{aa} & \cdots & 0 & 0 & 0 & T_a \\
\mathrm{A}_3 & P_{ao} & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & T_a \\
\cdot & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & & \cdot & \cdot & \cdot & \cdot \\
\mathrm{A}_{k-2} & P_{ao} & 0 & 0 & 0 & \cdots & 0 & P_{aa} & 0 & T_a \\
\mathrm{A}_{k-1} & P_{ao} & 0 & 0 & 0 & \cdots & 0 & 0 & sP_{aa} & T_a \\
\mathrm{A}_k & P_{ao} & 0 & 0 & 0 & \cdots & 0 & 0 & P_{aa} & T_a \\
\mathrm{T} & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 1
\end{array} \qquad (8)$$

account. Then $F(s)$, defined by

$$F(s) = \lim_{n\to\infty} (I_o Q_{\mathrm{OT}}^{(n)} + I_a Q_{\mathrm{A_1T}}^{(n)}) \qquad (9)$$

is the generating function for the desired distribution, the fraction of molecules of the whole copolymer having i A blocks of length k or longer. By taking the limit as n goes to infinity, all chain lengths are included in the proper proportion according to the termination probabilities T_a and T_o, which thus produce the appropriate DP distribution.

Evaluation of eq 9 requires a tractable expression for $\mathbf{Q}^n$. The nth power of any square matrix $\mathbf{Q}$ of order m with real, distinct roots λ_i can be expressed in terms of these roots[6]

$$\mathbf{Q}^n = \sum_{i=1}^{m} \lambda_i^n \mathbf{B}_i \qquad (10)$$

where the "spectral matrix" $\mathbf{B}_i$ is the matrix product of the column and row eigenvectors corresponding to the ith root λ_i. It can be shown that the matrix $\mathbf{Q}$ of eq 8 has one root of unity and that all other roots have absolute values of less than unity.[6] Thus as n grows without limit, all the terms in eq 10 vanish except the one corresponding to the root of unity, and it becomes simply

$$\lim_{n\to\infty} \mathbf{Q}^n = \mathbf{B}_1 \qquad (11)$$

where $\mathbf{B}_1$ is the matrix product of the eigenvectors of $\mathbf{Q}$ for the root of unity. This can be derived in closed form by solving the matrix equation $\mathbf{B}_1\mathbf{Q} = \mathbf{Q}\mathbf{B}_1 = \mathbf{B}_1$ to give (12). The terms D and C of eq 12 are defined by eq 13 and 14.

$$B_1 = \begin{array}{c|cccccc}
 & \mathrm{A} & \mathrm{A}_1 & \mathrm{A}_2 \ldots \mathrm{A}_{k-1} & \mathrm{A}_k & \mathrm{T} \\
\hline
\mathrm{O} & 0 & 0 & 0 \ldots 0 & 0 & C[1 - T_a P_{oa} P_{aa}^{k-1}(1 - s)/D] \\
\mathrm{A}_1 & 0 & 0 & 0 \ldots 0 & 0 & C[1 - P_{aa}^{k-1}(1 - s)] \\
\mathrm{A}_2 & 0 & 0 & 0 \ldots 0 & 0 & C[1 - P_{aa}^{k-2}(1 - s)] \\
\cdot & \cdot & \cdot & \cdot \quad \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot \quad \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot \quad \cdot & \cdot & \cdot \\
\mathrm{A}_{k-1} & 0 & 0 & 0 \ldots 0 & 0 & C[1 - P_{aa}(1 - s)] \\
\mathrm{A}_k & 0 & 0 & 0 \ldots 0 & 0 & C \\
\mathrm{T} & 0 & 0 & 0 \ldots 0 & 0 & 1
\end{array} \qquad (12)$$

$$D \equiv (1 - P_{oo})T_a + P_{ao}T_o \qquad (13)$$

$$C \equiv [1 + P_{ao}P_{oa}P_{aa}^{k-1}(1 - s)/D]^{-1} \qquad (14)$$

Equations 11 and 12 show that in the limit $\mathbf{Q}^n$ is a matrix with nonzero elements only in the T column, *i.e.*, all chains eventually end up in state T, in accordance with our model which requires that all molecules are eventually terminated. The first two elements are the quantities required in eq 9

$$\lim_{n\to\infty} Q_{\mathrm{OT}}^{(n)} = C[1 - T_a P_{oa} P_{aa}^{k-1}(1 - s)/D] \qquad (15)$$

and

$$\lim_{n\to\infty} Q_{A_1\mathrm{T}}^{(n)} = C[1 - P_{aa}^{k-1}(1 - s)] \qquad (16)$$

For simplicity's sake, we assume that termination is equally likely for all comonomers

$$T \equiv T_a = T_o \qquad (17)$$

and that initiation is proportional to the mole fractions of the comonomers, X_a and X_o, which are readily expressed in terms of the transition probabilities[3]

$$\begin{aligned} I_a &= X_a = P_{oa}/(P_{ao} + P_{oa}) = P_{oa}/\rho \\ I_o &= X_o = P_{ao}/(P_{ao} + P_{oa}) = P_{ao}/\rho \end{aligned} \qquad (18)$$

The frequently recurring factor ρ, which is defined by

$$\rho \equiv P_{ao} + P_{oa} \qquad (19)$$

is a measure of the randomness of the copolymer.[3] While these two assumptions are not necessary for the subsequent treatment, they simplify the resulting expressions considerably. Substitution of eq 15–18 into eq 9 and collection of

(6) M. S. Bartlett, "Introduction to Stochastic Processes," The University Press, Cambridge, England, 1962, Chapter 2.

TABLE I
FREQUENCY DISTRIBUTION WITH ZERO AND ONE A BLOCK OF LENGTH k OR ABOVE[a]

$\bar{N}$	k	X_a	$100X(0, k)$ Eq 24	$100X(0, k)$ M.C.	$100W(0, k)$ M.C.	$100X(1, k)$ Eq 24	$100X(1, k)$ M.C.	$100W(1, k)$ M.C.
100	1	0.80	0.249	0.255	0.0032	5.98	6.08	0.327
100	1	0.80	0.249	0.258	0.0032	5.98	5.89	0.302
100	2	0.80	1.80	1.72	0.0323	7.32	7.47	0.554
100	3	0.80	3.68	3.75	0.123	8.89	8.96	0.923
100	3	0.80	3.68	3.77	0.124	8.89	8.88	0.920
100	3	0.80	3.68	3.69	0.119	8.89	8.87	0.902
100	4	0.80	5.96	5.77	0.273	10.7	10.5	1.42
100	5	0.80	8.69	8.62	0.583	12.7	12.8	2.37
100	5	0.80	8.69	8.63	0.624	12.7	12.7	2.30
100	10	0.80	30.2	29.9	7.83	23.9	23.7	14.0
100	3	0.35	25.3	25.5	6.34	20.3	20.1	10.2
100	3	0.50	11.7	11.8	1.34	12.6	12.6	2.95
100	3	0.65	6.23	6.37	0.377	9.16	9.05	1.21
100	3	0.70	5.18	5.23	0.250	8.71	8.83	1.05
100	3	0.75	4.35	4.38	0.174	8.59	8.66	0.940
100	3	0.80	3.68	3.69	0.119	8.89	8.87	0.902
100	3	0.88	2.85	2.88	0.0702	11.0	11.0	1.28
100	3	0.95	2.31	2.29	0.0414	19.1	19.1	3.69
10	3	0.80	30.5	30.6	8.29	41.5	41.5	33.1
30	3	0.80	11.7	11.7	1.20	24.0	23.9	7.58
100	3	0.80	3.68	3.69	0.119	8.89	8.87	0.902
300	3	0.80	1.25	1.25	0.0136	3.15	3.15	0.109
1000	3	0.80	0.376	0.376	0.0012	0.967	0.965	0.0101
3000	3	0.80	0.125	0.126	0.0001	0.325	0.324	0.0011
10000	3	0.80	0.0376	0.0377	<0.0001	0.0976	0.0973	0.0001

[a] Equation 24, closed-form solution; M.C., Monte Carlo method, 2000 trials per run.

terms gives the generating function explicitly

$$F(s) = (C/\rho)\{P_{oa}[1 - P_{ao}P_{aa}^{k-1}(1 - s)/(\rho + T)] + P_{oa}[1 - P_{aa}^{k-1}(1 - s)]\} \quad (20)$$

$$= G\{[T + E(1 - s)]^{-1} - (1 - P_{aa})^{-1}\} - T/\rho \quad (21)$$

where

$$E \equiv P_{ao}P_{oa}P_{aa}^{k-1}/(\rho + T) \quad (22)$$

and

$$G \equiv T(1 - P_{aa})(\rho + T)/(P_{ao}\rho) \quad (23)$$

The distribution corresponding to this generating function can now be derived by successive differentiations of eq 21 (*cf.* eq 7). The fraction of molecules with i A blocks of k or more units, $X(i, k)$, is then given by

$$X(i, k) = F^{(i)}(0)/i! = G(1 + T/E)^{-i-1}/E \quad \text{for } i \geq 1$$

and

$$X(0, k) = F(0) = G(1 + T/E)^{-1}/E - G/(1 - P_{aa}) - T/\rho \quad (24)$$

where the groups of transition probabilities, E, G, and ρ are as given in eq 22, 23, and 19.

It can be seen that this block-frequency distribution is geometric for $i \geq 1$. Its mean, $\bar{i}$, can be directly derived from the generating function

$$\bar{i} = F^{(1)}(1) = GE/T^2 = (1 - P_{aa})P_{oa}P_{aa}^{k-1}/(\rho T) \quad (25)$$

The number-average degree of polymerization $\bar{N}$ is the reciprocal of the termination probability T. With this substitution and eq 18, the mean number of A blocks of length k or above per molecule is

$$\bar{i} = \bar{N}X_a(1 - P_{aa})P_{aa}^{k-1} \quad (26)$$

which corresponds, as it must, to the summation of eq 5 from k to infinity, except for the substitution of the number average for the monodisperse degree of polymerization. Table I shows $X(0, k)$ and $X(1, k)$ for selected values of the parameters, but discussion of the results will be deferred to the end of this paper.

Mole Fraction with *i* A Blocks of Length *k*

As discussed above, some copolymer properties depend on the presence of long blocks which can participate in crystalline or glassy domains, but such participation would not be confined to a particular block length but rather to all blocks above a certain minimum size. Hence, the present problem is of less inherent interest than that treated in the previous section; but since it yields to the same approach, it is included here.

The Markov-chain model for this case is equivalent to the one used above, except that the states are numbered up to A_{k+1}, so that our sample molecule of the previous section gives rise to the following series of states for $k = 3$

$$A_1OA_1OOA_1A_2A_3OOOA_1A_2A_3A_4A_4OA_1A_2A_3A_4OOTTT\ldots T\ldots$$

The transition table for this model, the matrix **R**, differs slightly from that of eq 8. **R** is given by eq 27. This time the dummy variable is placed to reflect the transition from state A_k to state O, which occurs when, and only when, an A block of length k is completed. The matrix **R**, like **Q**, has only one root of unity and none above, so the equivalent of eq 11 holds. Solution for the eigenvectors is again possible in closed form, and leads to eq 28; H is given by (29)

$$\mathbf{R} \equiv \begin{array}{c|ccccccccc} & \mathrm{O} & \mathrm{A}_1 & \mathrm{A}_2 & \mathrm{A}_3 & \cdots & \mathrm{A}_{k-1} & \mathrm{A}_k & \mathrm{A}_{k+1} & \mathrm{T} \\ \hline \mathrm{O} & P_{oo} & P_{oa} & 0 & 0 & \cdots & 0 & 0 & 0 & T_o \\ \mathrm{A}_1 & P_{ao} & 0 & P_{aa} & 0 & \cdots & 0 & 0 & 0 & T_a \\ \mathrm{A}_2 & P_{ao} & 0 & 0 & P_{aa} & \cdots & 0 & 0 & 0 & T_a \\ \mathrm{A}_3 & P_{ao} & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & T_a \\ \vdots & \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots \\ \mathrm{A}_{k-1} & P_{ao} & 0 & 0 & 0 & \cdots & 0 & P_{aa} & 0 & T_a \\ \mathrm{A}_k & sP_{ao} & 0 & 0 & 0 & \cdots & 0 & 0 & P_{aa} & T_a \\ \mathrm{A}_{k+1} & \mathrm{P}_{ao} & 0 & 0 & 0 & \cdots & 0 & 0 & P_{aa} & T_a \\ \mathrm{T} & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 1 \end{array} \tag{27}$$

$$\lim_{n \to \infty} \mathbf{R}^n = \begin{array}{c|ccccccl} & \mathrm{O} & \mathrm{A}_1 & \mathrm{A}_2 & \cdots & \mathrm{A}_k & \mathrm{A}_{k+1} & \mathrm{T} \\ \hline \mathrm{O} & 0 & 0 & 0 & \cdots & 0 & 0 & H(1 - P_{aa})/P_{ao} \\ \mathrm{A}_1 & 0 & 0 & 0 & \cdots & 0 & 0 & T_a/(1 - P_{aa}) + H[1 - (1 - P_{aa})P_{aa}{}^{k-1}(1 - s)] \\ \mathrm{A}_2 & 0 & 0 & 0 & \cdots & 0 & 0 & T_a/(1 - P_{aa}) + H[1 - (1 - P_{aa})P_{aa}{}^{k-2}(1 - s)] \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots \\ \mathrm{A}_{k-1} & 0 & 0 & 0 & \cdots & 0 & 0 & T_a/(1 - P_{aa}) + H[1 - (1 - P_{aa})P_{aa}(1 - s)] \\ \mathrm{A}_k & 0 & 0 & 0 & \cdots & 0 & 0 & T_a/(1 - P_{aa}) + H[1 - (1 - P_{aa})(1 - s)] \\ \mathrm{A}_{k+1} & 0 & 0 & 0 & \cdots & 0 & 0 & T_a/(1 - P_{aa}) + H \\ \mathrm{T} & 0 & 0 & 0 & \cdots & 0 & 0 & 1 \end{array} \tag{28}$$

and D is as defined by eq 13.

$$H \equiv DP_{ao}/\{(1 - P_{aa})[P_{ao}P_{oa}P_{aa}{}^{k-1}(1 - P_{aa})(1 - s) + D]\} \tag{29}$$

With the assumptions of eq 17 and 18 and the introduction of the first two elements of the T column of eq 28 into eq 9, the generating function becomes

$$F'(s) = H(1 - P_{aa})/\rho + (P_{oa}/\rho)\{T(1 - P_{aa}) + H[1 - (1 - P_{aa})P_{aa}{}^{k-1}(1 - s)]\} \tag{30}$$

$$= (T/\rho)\{(\rho + T)/[(1 - P_{aa})E(1 - s) + T] - 1\} \tag{31}$$

where E is as defined by eq 22. The block-frequency distribution itself, $Y(i, k)$, *i.e.*, the fraction of molecules with i A blocks of exactly k units, is then given by

$$Y(i, k) = F'^{(i)}(0)/i! = (\rho + T)(1 + 1/I)^{-n}/[\rho(1 + I)] \quad \text{for } i \geq 1 \tag{32}$$

and

$$Y(0, k) = F'(0) = (\rho + T)/[\rho(1 + I)] - 1 \tag{33}$$

where

$$I \equiv P_{ao}P_{oa}P_{aa}{}^{k-1}(1 - P_{aa})/[T(\rho + T)] \tag{34}$$

which is again a geometric distribution.

The mean number of A blocks of length k per molecule, $\bar{\jmath}$, is given by

$$\begin{aligned} \bar{\jmath} &= F'^{(1)}(1) = P_{ao}P_{oa}P_{aa}{}^{k-1}(1 - P_{aa})/(\mathrm{T}\rho) \\ &= \bar{N}X_aP_{ac}P_{aa}{}^{k-1}(1 - P_{aa}) \end{aligned} \tag{35}$$

which is seen to agree with eq 5, when $1 - P_{aa}$ is substituted for P_{ao}, which is valid for a high polymer, *i.e.*, one for which T is much smaller than P_{ao} (*cf.* eq 1).

Weight Fraction with *i* A Blocks of Length *k* or Above

In principle, it should be possible to derive this weight-fraction block-frequency distribution in a straightfoward way: the fraction of molecules of an n-mer, as opposed to a whole copolymer as treated above, with i A blocks of length k or above, is established, and this is then summed over all n with the geometric DP distribution as weighting factor. The generating function for the n-mer can be formulated in terms of a transition matrix just like that of eq 8 but with the T row and column omitted. What is required is the nth power of this matrix, rather than the limit as n approaches infinity, and thus all the roots and eigenvectors, rather than only those of the unit root, have to be used in the spectral expansion (eq 10). However, the roots are irrational numbers and, therefore, the generating function cannot be obtained in closed form. Nor have we been able to devise any other approach which gives a closed-form solution to this problem.

The most appropriate numerical approach is the Monte Carlo method which is, in fact, computer experimentation. To apply it to the present system, one uses the computer to construct a large number of copolymer molecules of n monomer units in accordance with an appropriate set of P_{ij}. These molecules are then examined to see how many have zero, one, two, etc., A blocks of length k or above. Finally summation over n with weight factors furnished by the geometric DP distribution results in the desired block-frequency distribution.

The detailed computing procedure is as follows. Each *run* pertains to a specific set of X_a, P_{aa}, P_{ao}, P_{oa}, P_{oo}, and k. Initiation is assumed to be proportional to X_a and X_o. A *trial* is started by generating a random number N_1 between zero and unity; if N_1 is less than X_a, the first unit is an A; if N_1 is more than X_a, the first unit is an O. Then a second

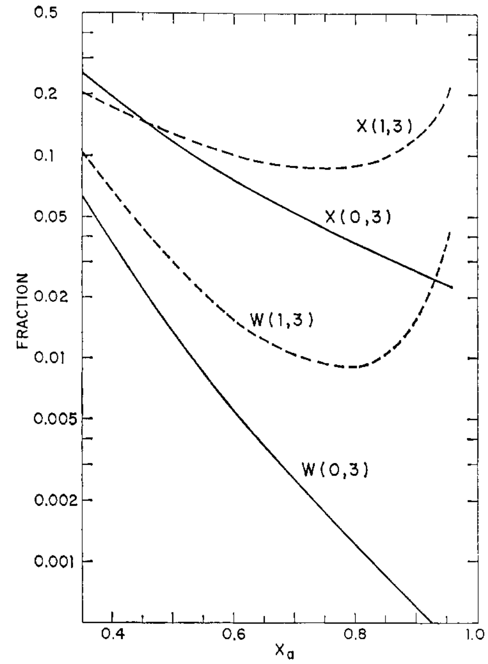

Figure 1. Effect of overall mole fraction of monomer A (X_a) on fraction of molecules with zero or with one A block of length three or more. $\bar{N} = 100$.

random number N_2 is generated. The second unit is an A if the first unit is an A and $N_2 < P_{aa}$ or if the first unit is an O and $N_2 < P_{oa}$; otherwise, the second unit is an O. Successive units are added in the same way until the first uninterrupted sequence of k A units occurs. At this point, the total number of monomer units h_1 is noted, and the trial is continued, the total number of monomer units, h_2, h_3, . . . , being noted when the second, third, etc., A block of length k or above occurs. When a suitable number of monomer units has been added, *i.e.*, the DP is high enough, the trial is terminated and a new trial is initiated. Each run consists of an appropriately large number of trials, N_t.

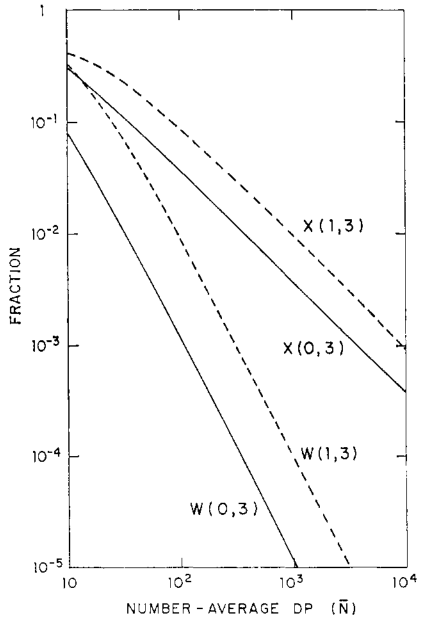

Figure 2. Effect of number-average DP ($\bar{N}$) on fraction of molecules with zero or with one A block of length three or more. $X_a = 0.8$.

The fraction of molecules of given n which have i A blocks of length k or longer, $\phi(i, k, n)$, is established as follows. N_t molecules of each n are considered: those with $h_1 > n$ are taken to have no A block of length k or above, those with $h_2 > n > h_1$ to have one such block, etc. Division of these numbers by N_t gives $\phi(i, k, n)$. Summation over all n then gives the required weight fraction, $W(i, k)$, of the title of this section, the weighting factors coming from the geometric distribution which copolymers generally obey,[3] though the more complete double geometric distribution[3] could also be used, if necessary.

$$W(i, k) = \bar{N}^{-2}\sum_{n=1}^{h_i^*} n(1 - 1/\bar{N})^{n-1}\phi(i, k, n) \qquad (36)$$

where h_i^* designates the highest h_i encountered during the particular run and $\bar{N}$ the number-average DP. Of course, the corresponding mole fraction, which was derived in closed form above (eq 24), is also obtainable from the Monte Carlo runs.

$$X(i, k) = \bar{N}^{-1}\sum_{n=1}^{h_j^*}(1 - 1/\bar{N})^{n-1}\phi(i, k, n) \qquad (37)$$

While this procedure uses the same set of Monte Carlo trials over and over again for all different n-mers, an independent set of trials for each n-mer would represent sounder statistics. However, such a procedure would increase the volume of computation by several orders of magnitude and make extensive calculations impractical. This lack of complete independence of trials should matter less and less as the number of trials per run increases, and it is possible to test whether the number of trials is adequate by comparing $X(i, k)$ calculated by means of eq 24 with the corresponding value obtained by the Monte Carlo Method.

Numerical calculations[7] were carried out for a range of values of the parameters (Table I) subject to the following assumptions: random copolymerization and initiation proportional to mole fraction which corresponds to

$$P_{aa} = P_{oa} = X_a = 1 - X_o = 1 - P_{ao} = 1 - P_{oo} \qquad (38)$$

Two thousand trials per run turned out to be an adequate number, as shown by the consistency of repeat runs in Table I. Above all, the good agreement between the Monte Carlo and the closed-form mole fractions in Table I demonstrates not only the adequacy of the Monte Carlo calculation, but also the correctness of the Markov-chain derivation.

Results of the calculations (Table I, Figures 1 and 2) illustrate the effects of varying k, the minimum A-block length; X_a, the mole fraction of A-units; and $\bar{N}$, the number-average DP.

As expected, the fraction of molecules with zero or one A block of length k or above, *i.e.*, the "elastically inferior" molecules discussed in the introduction, increases with k. In all cases, the weight fraction is much lower than the mole fraction, since the shortest molecules of the geometric distribution are most likely to have few long blocks.

As the mole fraction X_a increases, the fraction of polymer without long A blocks decreases, but the fraction with exactly one block goes through a minimum (Figure 1). This is a

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(7) Computations were done on an IBM 360 with DURAX remote terminal. The simple program (less than 100 Fortran IV statements including the random-number subroutine) is available from the author on request.

reasonable effect: If X_a is near unity, many molecules will have just one very long A block. In contrast, when X_a is small, occurrence of more than one long A block is very unlikely, so that the probability of just one such block per molecule is relatively large. Between these two maxima, then, there is a minimum. The existence of this minimum is implicit in eq 24 which, on differentiation subject to the assumptions of eq 38, predicts a minimum in $X(i, k)$ at $X_a = k/(k + 1)$, *i.e.*, at $X_a = 0.75$ for $k = 3$, where it is indeed observed (Figure 1).

Figure 2 shows that the mole fraction with zero or one long A block varies approximately as the reciprocal of the DP, $\bar{N}$, as predicted by eq 24 (G is roughly proportional to T, the reciprocal of $\bar{N}$, while E is nearly independent of T). The weight fractions, on the other hand, can be seen to vary inversely as the square of $\bar{N}$, except at the lowest $\bar{N}$.

The Photochemistry of Ketone Polymers. IV. Photolysis of Methyl Vinyl Ketone Copolymers

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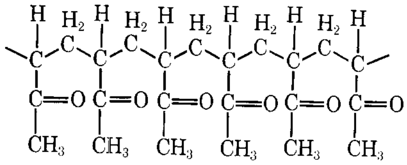
Received October 13, 1970

ABSTRACT: Studies have been made of the photolysis of copolymers of methyl methacrylate (MMA) and methyl vinyl ketone (MVK) containing minor amounts of MVK. It is shown that under conditions where there is sufficient molecular mobility (in solution or in the solid phase above T_g), the quantum yield for the process which leads to main-chain scission is 0.20 ± 0.02, nearly an order of magnitude higher than for poly-MVK itself. This is unexpected, because most of the ketone groups are surrounded by MMA units and consequently no γ hydrogens are available to form the cyclic six-membered ring postulated as the transition state for the Norrish type II process. It is suggested that in this case the scission might occur through a seven-membered intermediate, and the δ hydrogen is abstracted. The higher quantum yield for scission of the copolymer indicates that the isolated carbonyl group may be precluded from energy exchange along the polymer chain.

Early studies by Guillet and Norrish[1] and Wissbrun[2] on the photolysis of poly(methyl vinyl ketone) (poly-MVK) demonstrated that the primary photolytic steps involved the Norrish type I and type II reactions typical of low molecular weight aliphatic ketones. At ordinary temperatures the quantum yield for the type II reaction in polymer systems is considerably greater than that for the type I, and the type II reaction represents the major degradation mechanism for polymers containing ketone groups in the backbone or in side chains adjacent to the main chain of the polymer. Recent studies by Guillet and Hartley[3] on the photolysis of ethylene–carbon monoxide copolymers confirm that the type II reaction, which involves a split in the backbone of the chain at the carbon bond α–β to the absorbing carbonyl appears to involve the transient formation of a cyclic six-membered ring involving the hydrogen on the γ-carbon atom. If this is the case, one might expect that the photochemistry of a copolymer system involving methyl vinyl ketone would be affected by the groups adjacent to the ketone monomer in the polymer chain. For example, in poly(methyl vinyl ketone) the general structure is as shown in I. If a central ketone group absorbs a quantum of light, hydrogen is available on the γ-carbon atoms in the chain provided from the adjacent MVK monomer units. However, if one prepares, for example, a copolymer of methyl vinyl ketone and methyl methacrylate containing only a minor amount of MVK, the polymer structure will consist predominantly of units such as shown in II. In this case, as pointed out by Golemba,[4] there are no protons on the γ-carbon atoms which are instead substituted by methyl groups from the MMA units adjacent to the absorbing ketone groups. In this instance, since the six-membered ring transition state can no longer form, one might expect that the quantum yield for the type II photochemical process would be reduced. In the present work, studies were made of the photolytic behavior of copolymers of methyl vinyl ketone with both methyl methacrylate and methyl acrylate, to determine the effect of adjacent monomer units on the photochemistry of the system.



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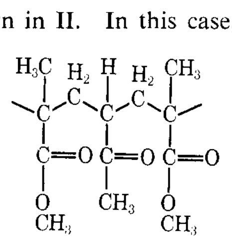

II

Experimental Section

The copolymers were prepared by free-radical polymerization in sealed tubes under vacuum using lauroyl or benzoyl peroxide as initiator. The polymers were dissolved in benzene and reprecipitated several times with methanol to remove catalyst residues and unreacted monomer, then dried to constant weight under vacuum. A summary of the polymers used and their properties is given in Table I.

The irradiation was carried out in benzene solution using the

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(1) J. E. Guillet and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **233**, 153 (1955).

(2) K. F. Wissbrun, *J. Amer. Chem. Soc.*, **81**, 58 (1959).

(3) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165 (1968).

(4) F. J. Golemba, Ph.D. Thesis, University of Toronto, 1970.