[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH AT THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Intramolecular Condensations in Vinyl Copolymers[1]

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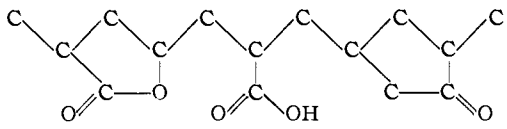
Intramolecular condensation reactions have been successfully employed to elucidate the structure of polymers such as polyvinyl chloride[2] polyvinyl methyl ketone[3,4,5] and polyisopropenyl methyl ketone.[6] These reactions have been subjected to statistical treatment, and the agreement between experimental results and theoretical calculations based on a 1,3-structure has established a head-to-tail addition mechanism for vinyl polymerization.

It has been suggested[7] that the copolymer of vinyl acetate and acrylic acid could be studied by hydrolyzing the acetate group and allowing the resulting hydroxyl to lactonize with the carboxyl groups present. The Flory statistical treatment[2a] is not directly applicable to such a system. It is the purpose of this paper to extend these statistics to cover the case of intramolecular condensations between unlike substituents. The example given above will be used as a model in the subsequent derivation.

We will assume a head-to-tail configuration for the copolymer, giving rise to a γ-hydroxy acid structure along the chain. We will further assume that γ-lactonization takes place to the complete exclusion of cross-linking by esterification. This is in accord with the known behavior of γ-hydroxy acids.

It is clear that lactonization cannot be quantitative since an acrylic acid segment flanked by two other acid segments is incapable of reaction. A similar situation exists for the vinyl alcohol segments. Furthermore, there exists the possibility of isolation of functions in alternating sequences. Thus we may find a carboxyl group whose neighbors are lactonized hydroxyl groups and which consequently cannot react.



In the discussion which follows we will focus our attention on the carboxyl groups, as these are the more readily determinable. We will use M_1 and M_2 to designate vinyl alcohol and acrylic acid segments, respectively. Thus an alternating sequence is of the form $M_1M_2M_1M_2M_1M_2$. Starting from a point in the chain where we find an M_1–M_2 (or an M_2–M_1) pair we advance along the chain in both directions until we reach breaks in the alternation pattern (*i. e.*, an M_1–M_1 or an M_2–M_2 pair). We next draw lines which separate the members of the like pairs thus found. By continuing this operation throughout the system, we will divide it into sequences which are either pure alternating or "straight" (*i. e.*, all M_1 or all M_2). The length of an alternating sequence is defined as the number of M_1 or M_2 groups (whichever is the smaller) that it contains.

We see that there are four possible types of alternating sequence.

I $M_1 \mid (M_1M_2)_nM_1 \mid M_1$
II $M_1 \mid (M_1M_2)_n \mid M_2$
III $M_2 \mid (M_2M_1)_nM_2 \mid M_2$
IV $M_2 \mid (M_2M_1)_n \mid M_1$

Let

N = total number of monomer molecules that have polymerized
m_1 = mole fraction of M_1 in copolymer
m_2 = mole fraction of M_2 in copolymer

Therefore

Nm_1 = total M_1 in copolymer
Nm_2 = total M_2 in copolymer

The total number of sequences of type I and length n is given by the product of the number of M_1 segments and the probability that an M_1 segment is followed by an alternating sequence of the desired type. Representing this quantity by A_n^I we have[8]

$$(1)\quad A_n^{\mathrm{I}} = Nm_1P_{11}^2P_{12}^nP_{21}^n$$

Similarly

$$(2)\quad A_n^{\mathrm{II}} = Nm_1P_{11}P_{22}P_{12}^nP_{21}^{n-1}$$
$$(3)\quad A_n^{\mathrm{III}} = Nm_2P_{22}^2P_{12}^nP_{21}^n$$
$$(4)\quad A_n^{\mathrm{IV}} = Nm_2P_{22}P_{11}P_{12}^{n-1}P_{21}^n$$

The constants P_{11}, P_{12}, etc., in the above equations are the propagation probabilities of the copolymer system. Thus P_{12} is the probability that, during the copolymerization process, a growing free radical chain of the type M^{1*} will react with a monomer molecule of type M_2.[8]

The number of alternations of type M_1M_2 must obviously be equal to the number of type M_2M_1.

(1) Presented before the High Polymer Forum at the 115th Meeting of the American Chemical Society, San Francisco, California, March–April, 1949.

(2) (a) P. Flory, THIS JOURNAL, **61**, 1518 (1939); (b) C. S. Marvel, Sample and Roy, *ibid.*, **61**, 3241 (1939).

(3) P. Flory, *ibid.*, **64**, 177 (1942).

(4) F. T. Wall, *ibid.*, **64**, 269 (1942).

(5) C. S. Marvel and C. L. Levesque, *ibid.*, **60**, 280 (1938).

(6) C. S. Marvel, Riddle and Corner, *ibid.*, **64**, 92 (1942).

(7) E. Merz, T. Alfrey and G. Goldfinger, *J. Polymer Sci.*, **1**, 75 (1946).

(8) The propagation probabilities used here refer to the system vinyl acetate–acrylic acid. P_{12} is the probability that, during the copolymerization process, a growing free radical chain of the type M_1 will react with a monomer molecule of type M_2, and similarly for the other P terms. A complete discussion of these propagation probabilities may be found in T. Alfrey, *Trans. N. Y. Acad. Sci.*, **10**, 298 (1948). An earlier paper discusses the same subject but employs a different type of symbolism, T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

This is expressed mathematically by the equation

$$(5) \quad m_2P_{21} = m_1P_{12}$$

We may consequently rewrite equations (1) and (2) in the form

$$(6) \quad A_n^{\mathrm{I}} = Nm_2P_{11}^2P_{12}^{n-1}P_{21}^{n+1}$$
$$(7) \quad A_n^{\mathrm{II}} = Nm_2P_{11}P_{22}P_{12}^{n-1}P_{21}^{n}$$

It is now necessary to calculate on a statistical basis the number of carboxyl groups that will be isolated in the various alternating sequences. Flory[2a] has derived an expression for the average number of chlorine atoms remaining in a sequence of v nyl chloride segments after the random removal of chlorine from 1,3-positions (*e. g.*, by the action of metallic zinc). According to this treatment, S_n chlorine atoms will remain after exhaustive dechlorination of a sequence of n vinyl chloride groups, where

$$S_n = \sum_{i=0}^{n-1} (n - i)\frac{(-2)^i}{i!}$$

Let us consider an alternating sequence of type I and length n. The lactonization of such a sequence is statistically identical with the removal of chlorine from a sequence of $2n + 1$ vinyl chloride groups. Thus S_{2n+1} gives the total number of uncombined alcohol and acid groups. Since the number of alcohol groups is greater by one than the number of acid groups both before and after lactonization, we may write for the number of remaining acid groups

$$(9) \quad S_n^{\mathrm{I}} = (S_{2n+1} - 1)/2$$

A similar treatment for the other types of alternating sequences gives

$$(10) \quad S_n^{\mathrm{II}} = S_{2n}/2$$
$$(11) \quad S_n^{\mathrm{III}} = (S_{2n+1} + 1)/2$$
$$(12) \quad S_n^{\mathrm{IV}} = S_{2n}/2$$

We may now write an expression for the total number of carboxyl groups that may be expected to be isolated in alternating sequences of all types, *viz.*

$$(13) \quad \sum_{n=1}^{\infty} (S_n^{\mathrm{I}}A_n^{\mathrm{I}} + S_n^{\mathrm{II}}A_n^{\mathrm{II}} + S_n^{\mathrm{III}}A_n^{\mathrm{III}} + S_n^{\mathrm{IV}}A_n^{\mathrm{IV}})$$

It remains to find the number of carboxyl groups that remain unlactonized because they are adjacent to other carboxyl groups. Consider such a sequence $M_1M_2M_2M_2\cdots M_2M_2M_1$. The first and last M_2 groups have already been counted in the alternating sequences flanking the sequence of M_2 groups. The remainder constitute the unlactonizable acid groups and the amount of such material is given by

$$\sum_{n=3}^{\infty} (n - 2) \times [\text{total number of } M_2 \text{ sequences of length } n]$$

In view of what has been said above, the bracketed quantity may be shown to be equal to

$$Nm_1P_{12}P_{21}P_{22}^{n-1} = Nm_2P_{21}^2P_{22}^{n-1}$$

so that the total number of unlactonizable acid groups of this type is given by

$$\sum_{n=3}^{\infty} (n - 2) \times Nm_2P_2^2P_{22}^{n-1}$$

Making use of the relationship $1 - P_{22} = P_{21}$, this reduces to

$$(14) \quad Nm_2P_{22}^2$$

Combining (13) and (14) we have the total number of unlactonized acid groups. Dividing by Nm_2, the total acid present initially, we have the desired quantity f, the *fraction* of the total acid that remains unlactonized.

$$(15) \quad f = \frac{1}{Nm_2}\sum_{n=1}^{\infty} (S_n^{\mathrm{I}}A_n^{\mathrm{I}} + S_n^{\mathrm{II}}A_n^{\mathrm{II}} + S_n^{\mathrm{IV}}A_n^{\mathrm{III}} + S_n^{\mathrm{IV}}A_n^{\mathrm{IV}}) + P_{22}^2$$

Substituting from equations (3), (4), (6), (7), (9), (10), (11) and (12)

$$f = \frac{1}{2}(P_{11}^2P_{21}^2 + P_{22}^2P_{12}P_{21})\sum_{n=1}^{\infty}(P_{12}P_{21})^{n-1}S_{2n+1} - \frac{1}{2}(P_{11}^2P_{21}^2 - P_{22}^2P_{12}P_{21})\sum_{n=1}^{\infty}(P_{12}P_{21})^{n-1} + (P_{11}P_{22}P_{21})\sum_{n=1}^{\infty}(P_{12}P_{21})^{n-1}S_{2n} + P_{22}^2$$

$$(16) \quad f = P_{22}^2 - \frac{P_{11}^2P_{21}^2}{2(1 - P_{12}P_{21})} + \frac{P_{22}^2P_{12}P_{21}}{2(1 - P_{12}P_{21})} + \frac{1}{2}(P_{11}^2P_{21}^2 + P_{22}^2P_{12}P_{21})\sum_{n=1}^{\infty}P^{n-1}S_{2n+1} + P_{11}P_{22}P_{21}\sum_{n=1}^{\infty}P^{n-1}S_{2n}$$

where we have written P for $(P_{12}P_{21})$ for simplicity in the treatment to follow.

We now have to evaluate the two summations and simplify the result. The individual constituents of the summation $\sum_{n=1}^{\infty} P^{n-1}S_{2n}$ may be expanded in a two-dimensional array

$$\left[2 + \frac{(-2)}{1!}\right]$$
$$+ P[4 + 3(-2)/1! + 2(-2)^2/2! + (-2)^3/3!]$$
$$+ P^2[6 + 5(-2)/1! + 4(-2)^2/2! + 3(-2)^3/3! + 2(-2)^4/4! + 5(-2)^5/5!]$$
$$+ P^3[8 + 7(-2)/1! + 6(-2)^2/2! + 5(-2)^3/3!\cdots\cdots]$$
$$\vdots$$

Adding the columns, we have

$$\sum_{n=1}^{\infty} P^{n-1}S_{2n} = \frac{2}{(1-P)^2} + \frac{(-2)(1+P)}{1!\,(1-P)^2} + \frac{(-2)^2 2P}{2!\,(1-P)^2} + \frac{(-2)^3P(1+P)}{3!\,(1-P)^2} + \frac{(-2)^4 2P^2}{4!\,(1-P^2)} + \cdots$$

$$= \frac{2}{(1-P)^2}\left[1 + \frac{(-2\sqrt{P})^2}{2!} + \frac{(-2\sqrt{P})^4}{4!}\cdots\right] + \frac{1+P}{\sqrt{P}(1-P)^2}\left[\frac{(-2\sqrt{P})}{1!} + \frac{(-2\sqrt{P})^3}{3!}\cdots\right]$$

$$(17) \quad = \frac{2}{(1-P)^2}\cosh 2\sqrt{P} - \frac{1+P}{\sqrt{P}(1-P)^2}\sinh 2\sqrt{P}$$

A similar treatment yields the further relationship

$$(18)\quad \sum_{n=1}^{\infty} P^{n-1} S_{2n+1} = -\frac{1}{P} - \frac{2}{\sqrt{P}(1-P)^2}\sinh 2\sqrt{P} + \frac{1+P}{P(1-P)^2}\cosh 2\sqrt{P}$$

Substituting the results of (17), and (18) in (16) and making use of the relations

$$P_{11} + P_{12} = 1$$
$$P_{21} + P_{22} = 1$$

we have

$$(19)\quad f = \frac{P_{12} - P_{21}}{2P_{12}} + \frac{P_{12} + P_{21}}{2P_{12}}\cosh 2\sqrt{P_{12}P_{21}} - \sqrt{\frac{P_{21}}{P_{12}}}\sinh 2\sqrt{P_{12}P_{21}}$$

which may be rearranged to the form

$$(20)\quad f = \left(\cosh\sqrt{P_{12}P_{21}} - \sqrt{\frac{P_{21}}{P_{12}}}\sinh\sqrt{P_{12}P_{21}}\right)^2$$

It is desirable to be able to express f as a function of the polymer composition rather than the propagation probabilities used in equation (20). This may be accomplished by making use of the relations[9]

$$\frac{P_{21}}{P_{12}} = \frac{m_1}{m_2}$$
$$\sqrt{P_{12}P_{21}} = \frac{1 - \sqrt{1 - 4m_1m_2(1 - r_1r_2)}}{2(1 - r_1r_2)\sqrt{m_1m_2}}$$

Thus we see that f is expressible in terms of the copolymer composition m_2 and the quantity $(1 - r_1r_2)$ which is a measure of the alternation tendency in copolymerization. It is possible, therefore, to plot a family of curves of f against m_2 with (r_1r_2) as parameter (see Fig. 1). In the case $r_2 = 0$ that portion of the curve for m_2 greater than 0.5 is unattainable in practice, as is that portion of the curve for m_2 less than 0.5 in the case $r_1 = 0$. The curve drawn for $r_1r_2 = 0$ may therefore be regarded as a composite of the two extreme cases.

(9) r_1 and r_2 are relative rates of propagation and are characteristic of the monomer pair used. See the references given under (8)

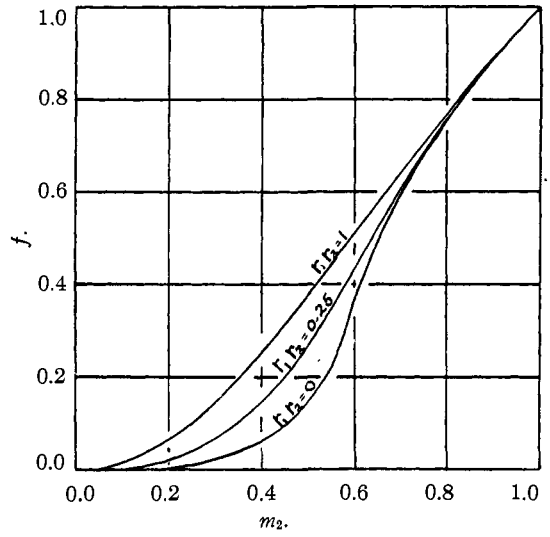


Fig. 1.—Fraction of acid remaining unlactonized as a function of mole fraction of acid in copolymer.

Summary

An expression has been derived for the amount of lactonization to be expected in a copolymer containing hydroxyl and carboxyl groups.

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2-Benzylphenol Derivatives. III.[1] Basic Ethers

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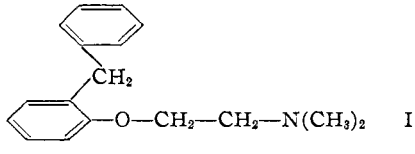
In previous communications the antihistaminic action of 2-benzylphenyl β-dimethylaminoethyl ether (I) and some of its analogs was reported.[1]



I

A number of other β-dimethylaminoethyl ethers related to I have been prepared in this Laboratory and submitted for pharmacological evaluation. More analogs of I are in preparation and will be the subject of a future communication.

The method of synthesis of these ethers is essentially that reported previously.[1b] The C-alkylation of phenols by halides of the benzyl type, according to the method of Claisen,[2] has been extended to heterocyclic systems. Phenol has been alkylated with 2-thenyl and 5-chloro-2-thenyl chloride to give 2-(2′-thenyl)-phenol, and 2-(5′-chloro-2′-thenyl)-phenol, respectively. In the case of alkylation of phenol with 2-thenyl chloride, the isomeric 4-(2′-thenyl)-phenol has been isolated and characterized. Alkylation of 8-hydroxyquinoline with benzyl chloride gave a compound believed to be 7-benzyl-8-hydroxyquinoline. Conversion of the various substituted phenols to the β-dimethylaminoethyl ethers proceeded smoothly via the Williamson ether synthesis.

(1) For preceding papers in this series, see (a) Cheney, Smith and Binkley, THIS JOURNAL, **71**, 60 (1949); (b) Wheatley, Cheney and Binkley, *ibid.*, **71**, 64 (1949).

(2) Claisen, *Ann.*, **420**, 210 (1925).