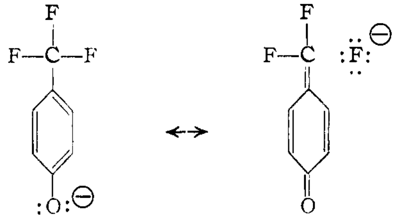
TABLE VI

τ-CONSTANTS OF TRIFLUOROMETHYL GROUP

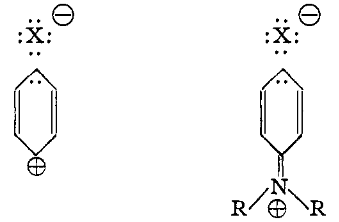
Reaction	Solvent	Temp., °C.	Log $k°$	ρ	log k_{meta}	σ_{meta}	log k_{para}	σ_{para}
Ionization of benzoic acids	50% EtOH	25	-5.71^a	$+1.464^a$	-5.11	0.41	-4.94	0.53
Ionization of benzoic acids	H_2O	24	-4.203^b	$+1.000^b$	-3.788^c	.42	.....	...
Benzoic acids with diphenyldiazomethane	100% EtOH	30	$+0.041^a$	$+0.937^a$	$+0.502$	.53	$+0.461$	.48
Ionization of anilinium ions	H_2O	25	-4.569^b	$+2.730^b$	-3.49	.41	-2.57	.74
Ionization of dimethylanilinium ions	H_2O	25	......	$+2.77^d$	-3.27	.42	-2.67	.64
Ultraviolet absorption characteristics[e]	H_2O	..	......	......	......	(.41)[f]	....	.77[g]

[a] Ref. 13. [b] Ref. 9. [c] Swarts, *Bull. acad. roy. Belg.*, [3] **35**, 395 (1898). [d] Based on values of pK_A of *p* and *m*-nitrodimethylanilines. [e] Doub and Vandenbelt, THIS JOURNAL, 69, 2714 (1947). [f] Assumed. [g] Calculated from $\lambda_{max.}$ of *p*-aminobenzotrifluoride (285 mμ) assuming σ-meta to be 0.41 ($\Delta\sigma$ =0.36) by the procedure of Doub and Vandenbelt.

advanced in favor of I over III. In the first place I should probably be more important from energetic considerations since a negative charge is expected to be more favorably located on fluorine than on carbon as in III. Second, the extraordinarily facile loss of fluoride ion from *o*- and *p*- but not *m*-trifluoromethylphenolate ions[10] indicates a considerable loosening of the C–F bonds in these substances which may be expressed by resonance similar to that represented



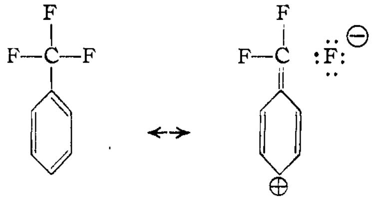
by IV. Finally, if resonance of type III is significant for the trifluoromethyl group, it might be expected to be exhibited to some degree at least by the halogens through contributions of forms such as VI. Actually, the criteria used in the present work give little if any indication of VI. Thus, the degree of interaction between the groups of *p*-amino- and *p*-dimethylaminohalobenzenes is small[7,17] and but one σ-constant is needed to express the influence of *p*-halogen substituents on the reactivity of either anilines or benzoic acid.[9]



VI

Summary

Dipole moment and relative reactivity data have been used to show that an important part of the electrical effect of a trifluoromethyl group located on an aromatic ring may be represented by resonance forms of the following type



CAMBRIDGE 39, MASSACHUSETTS

RECEIVED AUGUST 16, 1949

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Copolymerization Process. I. Integration of the Rate Equations

BY EDWARD H. DEBUTTS*

The idea that many copolymerization reactions proceed by a free radical mechanism is quite well established. The acceptance of the free radical mechanism has been due in some measure to the experimental verification of predictions based on the rate equations derived assuming such a mechanism. It has been shown theoretically by several workers[1,2,3] that the composition of a copolymer should depend upon certain experimentally determinable ratios of propagation reaction rate constants (these being termed "monomer reactivity ratios") and upon the concentrations of the monomers involved. This concept has been subjected to exhaustive experimental tests[4] and has been found to be correct within rather small error. A study of the over-all rates of copolymerization has been made from the theoretical point of view by Melville, Noble and

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* Harvard University Faculty, 1948–.

(1) Wall, THIS JOURNAL, **66**, 2050 (1944).

(2) Mayo and Lewis, *ibid.*, **66**, 1594 (1944).

(3) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

(4) Mayo, Lewis and Walling, THIS JOURNAL, **70**, 1529 (1948); other references will be found here and in (6).

Watson,[5] who show that the rate will depend upon monomer reactivity ratios which involve termination rate constants as well as propagation rate constants. This work has been extended by Walling,[6] who is primarily interested in the experimentally important case for bimolecular termination. There are presented in Walling's paper experimental data which agree reasonably well with the general theory. He also points out methods by which the new type of reactivity ratios can be determined.

To date there have not been published equations which show the manner in which the concentrations of monomers in a copolymerizing mixture vary with time. That is to say, the rate equations have not been integrated.[7] This is probably due, in part at least, to a realization of the fact that the initial concentrations of monomers are arbitrary and there is as yet no *a priori* method available which allows the calculation of individual amounts reacted after a given time interval. One should be able, however, to calculate the variation of the ratios of concentrations. We shall show that this is the case.

If the over-all rate equation is altered so that we have the time derivative of the ratio of the monomer concentrations instead of the derivative of their sum, the equation becomes easily integrable. Moreover, under certain special conditions the general rate equation can be simplified and the integrated forms of these approximations are, as one might expect, somewhat simpler than in the general case.

Derivation of the Equations.—The accepted mechanism for free-radical copolymerizations involves four second order propagation reactions. In addition to these, there are three termination reactions which apparently should be bimolecular if high molecular weights are to be attained.[8] Finally there are some initiation processes whose nature will not concern us here.

If one focuses his attention on the propagation phase of the process then it can be shown that the composition of copolymer which forms is given by[1,2,3]

$$\frac{\mathrm{d}[M_1]}{\mathrm{d}[M_2]} = \frac{[M_1]}{[M_2]}\,\frac{r_1[M_1] + [\mathrm{M}_2]}{[M_1] + r_2[M_2]} \qquad (1)$$

Here the notation is that suggested by Alfrey, Mayo and Wall[9] with the [M]'s designating the concentration of monomers and the *r*'s monomer reactivity ratios. Walling[6] has shown that for the case of bi-molecular termination the over-all rate of a copolymerization reaction is depicted by

$$\frac{-\mathrm{d}([M_1] + [M_2])}{\mathrm{d}t} = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)I^{1/2}}{(\delta_1{}^2r_1{}^2[M_1]^2 + 2\phi\delta_1\delta_2r_1r_2[M_1][M_2] + \delta_2{}^2r_2{}^2[M_2]^2)^{1/2}} \qquad (2)$$

Here

$$\delta_1{}^2 = k_{t11}/k_{11}{}^2,\ \delta_2{}^2 = k_{t22}/k_{22}{}^2,\ \phi^2 = k_{t12}/k_{t11}k_{t22}$$

The subscript *tij* indicates that we are dealing with a termination reaction rate constant. When no *t* is present, propagation rate constants are designated. The symbol *I* represents the rate at which kinetic chains are started. Throughout the treatment below it will be assumed that *I* is constant.

If we set

$$y = [M_2]/[M_1] \qquad (3)$$

then (1) can be written

$$\frac{\mathrm{d}[M_1]}{\mathrm{d}t} = \frac{1}{y}\,\frac{r_1 + y}{1 + r_2y}\,\frac{\mathrm{d}[M_2]}{\mathrm{d}t} \qquad (4)$$

On differentiation of (3) we have

$$\frac{\mathrm{d}[M_2]}{\mathrm{d}t} = y\,\frac{\mathrm{d}[M_1]}{\mathrm{d}t} + [M_1]\,\frac{\mathrm{d}y}{\mathrm{d}t} \qquad (5)$$

If now we solve (4) and (5) simultaneously for the time derivatives of the concentrations and make use of (3), (2) can be transformed to read

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{y[(r_1 - 1) - y(r_2 - 1)]I^{1/2}}{(r_1{}^2\,\delta_1{}^2 + 2\phi\,\delta_1\,\delta_2r_1r_2y + r_2{}^2\delta\,{}_2{}^2y^2)^{1/2}} \qquad (6)$$

To simplify the notation in that which follows it is convenient to define some new symbols; let $a_1 = r_1\delta_1$, $a_2 = r_2\delta_2$, $b_1 = (r_1 - 1)$, and $b_2 = (r_2 - 1)$. Further let us designate the denominator of (6) by

$$D' = (a_1{}^2 + 2\phi a_1a_2y + a_2{}^2y^2)^{1/2} \qquad (7')$$

and put

$$D = D'[M_1] \qquad (7)$$

Making these substitutions we obtain our final expression for the rate of a copolymerization reaction.[10]

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{y(b_1 - b_2y)I^{1/2}}{D'} \qquad (8)$$

Equation (8) is clearly equivalent to

$$D'\left(\frac{1}{y} + \frac{b_2/b_1}{1 - b_2y/b_1}\right)\mathrm{d}y = b_1I^{1/2}\,\mathrm{d}t \qquad (9)$$

The first factor of the left-hand side of this equation is of a form which can be integrated by formula 187 of Pierce.[11] The second factor can be put into the same form by changing the concentration variable according to

$$w = b_2y/b_1 - 1 \qquad (10)$$

There are two solutions to this general rate equation. The first arises when the product b_1b_2 is greater than zero; the other must be used

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(5) Melville, Noble and Watson, *J. Polymer Sci.*, **2**, 229 (1947).

(6) Walling, THIS JOURNAL, **71**, 1930 (1949).

(7) Melville, Noble and Watson, ref. 5, give an integrated form for one of their equations. Their result is, however, quite different from any presented in this article.

(8) Bartlett and Altschul, THIS JOURNAL, **67**, 812, 816 (1945).

(9) Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

(10) In the manuscript originally submitted, this equation was derived by a more cumbersome method. The derivation presented here was suggested by Dr. Cheves Walling of the United States Rubber Company and the author would like to thank him for allowing it to be used in this article.

(11) Pierce, "A Short Table of Integrals," 3rd revised ed., Ginn and Company, Boston, Mass., 1929.

when this product is negative. When $b_1b_2 > 0$, the concentrations vary with time according to[12]

$$a_1b_2 \ln \frac{[M_2](D^0 + a_1[M_1]^0 + \phi a_2[M_2]^0)}{[M_2]^0\,(D + a_1[M_1] + \phi a_2[M_2])} + a_2b_1 \ln \frac{[M_1]\,(D^0 + a_2[M_2]^0 + \phi a_1[M_1]^0)}{[M_1]^0\,(D + a_2[M_2] + \phi a_1[M_1])} + A \ln \frac{(b_1[M_1]^0 - b_2[M_2]^0)(AD + Ba_1[M_1] + Ca_2[M_2])}{(b_1[M_1] - b_2[M_2])(AD^0 + Ba_1[M_1]^0 + Ca_2[M_2]^0)} = b_1b_2I^{1/2}\,(t - t^0) \quad (11)$$

Here D can be determined by (7) and A, B and C by

$$\begin{aligned} A^2 &= a_1^2b_1^2 + 2\phi a_1a_2b_1b_2 + a_2^2b_1^2 \\ B &= a_1b_2 + \phi a_2b_1 \\ C &= \phi a_1b_2 + a_2b_1 \end{aligned} \quad (12)$$

If, on the other hand, $b_1b_2 < 0$ we have (allowing b_2 to be negative)

$$a_1b_2 \ln \frac{[M_2](D^0 + a_1[M_1]^0 + \phi a_2[M_2]^0)}{[M_2]^0\,(D + a_1[M_1] + \phi a_2[M_2])} + a_2b_1 \ln \frac{[M_1]\,(D^0 + a_2[M_2]^0 + \phi a_1[M_1]^0)}{[M_1]^0\,(D + a_2[M_2] + \phi a_1[M_1])} + (-A^2)^{1/2} \sin^{-1} \left[\frac{-(A^2)^{1/2}}{a_2^2a_1^2(\phi^2 - 1)}\right] \left[\frac{B(D^0a_1[M_1] - Da_1[M_1]^0) + C(D^0a_2[M_2] - Da_2[M_2]^0)}{(b_1[M_1] - b_2[M_2])(b_1[M_1]^0 - b_2[M_2]^0)}\right] = I^{1/2}\,(t - t^0) \quad (13)$$

These solutions to the over-all rate equation need not always be used. Two special cases arise if we factor D'. Consider

$$D' = (a_1 + a_2y)\left[1 + \frac{2a_1a_2y}{(a_1 + a_2y)^2}(\phi - 1)\right]^{1/2} \quad (14)$$

It is seen that if the term

$$\frac{2a_1a_2y}{(a_1 + a_2y)^2}(\phi - 1) \quad (15)$$

is small compared to one, then the reaction velocity is governed by

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{y(b_1 - b_2y)I^{1/2}}{a_1 + a_2y} \quad (16)$$

But if (14) is large the rate equation is

$$\frac{\mathrm{d}y}{\mathrm{d}t} = y^{1/2}\,(b_1 - b_2y)\left(\frac{I}{2a_1a_2(\phi - 1)}\right)^{1/2} \quad (17)$$

In the first case, the time dependence of the concentrations is given by

$$a_1b_2 \ln \frac{[M_2](b_1[M_1]^0 - b_2[M_2]^0)}{[M_2]^0\,(b_1[M_1] - b_2[M_2])} + a_2b_1 \ln \frac{[M_1](b_1[M_1]^0 - b_2[M_2]^0)}{[M_1]^0\,(b_1[M_1] - b_2[M_2])} = b_1b_2I^{1/2}\,(t - t^0) \quad (18)$$

When cross-termination is predominant, *i. e.*, when ϕ is large, we have, as in the general case, two solutions.[13] If the product b_1b_2 is positive the proper solution is

$$\left(\frac{2a_1a_2\,(\phi - 1)}{b_1b_2}\right)^{1/2} \ln \frac{(\sqrt{b_1[M_1]} + \sqrt{b_2[M_2]})(\sqrt{b_1[M_1]^0} - \sqrt{b_2[M_2]^0})}{(\sqrt{b_1[M_1]} - \sqrt{b_2[M_2]})(\sqrt{b_1[M_1]^0} + \sqrt{b_2[M_2]^0})} = I^{1/2}\,(t - t^0) \quad (19)$$

In the second case (allowing b_2 to be negative) we have after integration

$$\left[\frac{8a_1a_2(\phi - 1)}{-b_1b_2}\right]^{1/2} \sin^{-1} \frac{\sqrt{-b_1b_2}(\sqrt{[M_2][M_1]^0} - \sqrt{[M_1][M_2]^0})}{\{(b_1[M_1] - b_2[M_2])(b_1[M_1]^0 - b_2[M_2]^0)\}^{1/2}} = I^{1/2}\,(t - t^0) \quad (20)$$

One could, of course, derive further rate equations by expanding D' by the binomial theorem. These approximations would contribute little to our present discussion and are omitted for this reason.

Discussion.—There are encountered in the study of the copolymerization process two major difficulties. The first of these is a variation with time of the rate of initiation of chain-forming fragments, the other is an acceleration of rate after from ten to forty per cent. conversion. This latter cannot be dealt with at the present time. The former would clearly invalidate much of what has been said here. Recently, however, Lewis and Matheson[14] reported that the rate of production of free radicals by 2-azo-bis-isobutyronitrile is constant in several solvents. This indicates that this compound could be used where a constancy of I is necessary. Data presented by Walling[6] substantiate this view.

If some catalyst such as this be used, then the results presented give us a method by which we can predict the composition of a copolymerizing mixture with time. In addition we can gain some knowledge of the gross composition of the copolymer which has been formed at any specified stage of the reaction. When applying the integrated expressions it seems evident that the approximate solutions should be used where possible.

It is quite interesting to note that two solutions to the rate equations sometimes result. The one to be used, it will be recalled, is determined by the algebraic sign of b_1b_2. This same condition determines whether or not a given monomer pair will form an "azeotrope."[1] In addition to showing that b_1b_2 must be greater than zero for azeotropy, Wall[1] predicted that a copolymer whose composition is the same as that of the reaction mixture will form if y is set equal to b_1/b_2. It will be noted that the integrated equation for pairs of this type is discontinuous at the point $y = b_1/b_2$. This is not surprising when we remember that the rate equation becomes $\mathrm{d}y/\mathrm{d}t = 0$ at this composition. Thus the concentration ratio in the reaction mixture will tend asymptotically to that of the azeotrope. If no azeotrope is possible, then there are no points of discontinuity in the plot of y *versus* time. When b_1b_2 is negative a function which is partly trigonometric results. It would be interesting to examine some pair such as sty-

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(12) The superscript zero will be used to indicate evaluation at time t^0. When there is no superscript the integral is evaluated at time t.

(13) Equation (16) can be made integrable by making the substitution $z^2 = y$.

(14) Lewis and Matheson, THIS JOURNAL, **71**, 747 (1949).

rene–vinyl acetate (for which $b_1b_2 < 0$) in the light of the equations herein reported.

Acknowledgment.—The author wishes to thank Dr. Roland E. Florin of the Chemistry Department of the University of Nebraska for his helpful criticisms during the early part of this work.

Summary

The copolymerization rate equation and some approximations to it were integrated. Some of the implications of the results were discussed briefly.

CAMBRIDGE 38, MASSACHUSETTS

RECEIVED SEPTEMBER 7, 1949

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Water Sorption by Synthetic High Polymers

BY MALCOLM DOLE* AND I. LUCILLE FALLER[1]

Introduction

It is the purpose of this paper to describe results obtained in studying the sorption of water vapor by synthetic high polymers in order to discover correlations if any between water sorption and the chemical and physical constitution of the polymers. Systematic studies on synthetic polymers over a complete vapor pressure range and at different temperatures as a function of polymer constitution have not often been carried out. By synthetic high polymers we restrict ourselves to synthetic linear polymers. The sorption of water by three dimensional plastics occurs too slowly for equilibrium to be reached even after months of soaking in liquid water; see, for example, the review by Kline, Martin and Crouse.[2] Bull[3] has investigated drawn and undrawn Nylon at 25 and 40° as well as a number of naturally occurring proteins. Mellon, Korn and Hoover[4] have measured the water sorption of casein as a function of the extent of benzoylation of its free amino groups.

The percentage of water sorbed at 81 and 100% relative humidity by N-methylated polydecamethylene sebacamide (10–10 polyamides) has been determined by Baker and Fuller,[5] who found that the amount of water sorbed gradually increased as a function of the N-methylation up to 55% methylation which was as far as their studies were carried. Other measurements of water sorption at 100% relative humidity by N-alkylated polyamides have been reported by Wittbecker, Houtz and Watkins.[6] Apparently the water sorption is reduced as the size and branching of the substituted alkyl group increases. The degree of disorder introduced into the polymer also affects the properties of the material, as indeed is demonstrated by the data reported below.

In the paper by Hauser and McLaren[7] water sorption isotherms are given at 25° for the following sorbents: polyvinyl alcohol, cellulose acetate, Nylon, polyvinyl butyral, rubber hydrochloride and vinylidene chloride–acrylonitrile copolymer. Mention is also made of measurements at 40°.

Theoretical treatment of water sorption data can be usually classified into one of three points of view; first, application of strict adsorption theory such as that of Brunauer, Emmett and Teller[8] (henceforth referred to as BET); second, application of liquid-mixing equations of Flory[9] and Huggins[10]; and third, introduction into the theory of factors to allow for swelling effects. Application of the BET equation has been made by Bull,[3] Dole and McLaren,[11] Pauling[12] and others. Cutler and McLaren[13] have recently interpreted the sorption of water by proteins in terms of the liquid-mixing theory of Huggins.[10] Even more recently Rowen and Simha[14] also advocate the use of Huggins' equation with parameter, μ. An additional term, suggested by Rowen and Simha to account for the contribution to the entropy resulting from elastic deformation, was dropped by them as being of negligible importance, at least for the sorption of water by cellulose. Mellon, Korn and Hoover[4] find that neither the disorientation nor the application of tension affects appreciably sorption by proteins.

White and Eyring[15] have similarly considered the elastic work of swelling, but have combined their swelling theory with adsorption theory to ob-

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* Harvard University Ph.D., 1928.

[1] University Fellow, 1946–1948; present address, Argonne National Laboratory, Chicago.

[2] G. M. Kline, A. R. Martin and W. A. Crouse, *Modern Plastics*, **18**, No. 2, 119 (1940).

[3] H. B. Bull, THIS JOURNAL, **66**, 1499 (1944).

[4] E. F. Mellon, A. H. Korn and S. R. Hoover, *ibid.*, **69**, 827 (1947). See also Mellon, Korn and Hoover, *ibid.*, **70**, 1144, 3040 (1948); **71**, 2761 (1949).

[5] W. O. Baker and C. S. Fuller, *ibid.*, **65**, 1120 (1943).

[6] E. L. Wittbecker, R. C. Houtz and W. W. Watkins, *Ind. Eng. Chem.*, **40**, 875 (1948).

[7] P. M. Hauser and A. D. McLaren, *ibid.*, **40**, 112 (1948).

[8] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[9] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

[10] M. L. Huggins, *Ind. Eng. Chem.*, **35**, 216 (1943); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

[11] M. Dole and A. D. McLaren, THIS JOURNAL, **69**, 651 (1947).

[12] L. Pauling, *ibid.*, **67**, 555 (1945).

[13] Janice A. Cutler and A. D. McLaren, *J. Polymer Sci.*, **3**, 792 (1948).

[14] J. W. Rowen and R. Simha, *J. Phys. and Colloid Chem.*, **53**, 921 (1949).

[15] H. J. White and H. Eyring, *Textile Research J.*, **17**, 10 (1947); White and Stam, *ibid.*, **19**, 136 (1949).