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COPOLYMERIZATION¹

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I. INTRODUCTION

Although the polymerization of ethylene derivatives such as styrene (179) and vinyl chloride (28) was discovered in the middle of the last century, intensive work in industrial laboratories and practical utilization of the discoveries has occurred largely in the past thirty years. Quantitative understanding of the possible mechanisms and kinetics of the process has begun even more recently and, while not yet complete, has contributed significantly both to technology and to our comprehension of the nature of organic reactions. Although it is now generally recognized that vinyl polymerization may proceed through either free-radical or ionic intermediates, the reaction involving the former has the greater applicability, is technically more important, and has received by far the most study. Here, free radicals are produced by the action of heat or light upon a monomer or an added initiator (e.g., a peroxide). These radicals add to the ethylenic bond of the monomer, generating new radicals at the other end of the bond, and this process of polymerization by successive addition of monomer units continues until the radicals are destroyed. The overall rate of polymerization depends upon the rate with which a radical reacts with monomer and upon the radical concentration, which in turn depends upon the balance between the rates of formation and destruction, so that measurements of overall rates ordinarily give ratios of three rate constants. Similarly, the molecular weight of the polymer formed depends upon the balance between the rate of chain growth and chain interruption, by either radical destruction or chain transfer.³ Quite recently, several workers have been successful in the difficult task of resolving these separate rate constants (22, 38, 121, 122, 195) and it now appears that, in a typical polymerization reaction, radical lives are of the order of seconds (in the course of which several thousand additions of monomer units occur to the growing chain) and radical concentrations lie in the range of 10^{-8} to 10^{-9} molar.

The possibilities of reaction, and variety of products obtainable, are greatly increased when polymerizations are carried out in mixtures of two or more monomers, for now *copolymer* chains may contain various arrays of monomer units. This reaction of *copolymerization* is the subject of this review.

The theory of the composition of copolymers formed in free-radical copolymerization will be taken up first, since it has received the most exhaustive study. This topic will be followed by a consideration of the relation between structure and reactivity of olefins towards hydrocarbon free radicals, in the current picture

³ A comprehensive exposition of these ideas, which underlie many of the arguments of this review, will be found in several recent texts (29, 158).

of which copolymerization data play a most important role. Next, the problem of overall rates of copolymerization (on which much less information is available) will be discussed. Finally, the few available studies of copolymerization by ionic (nonradical) mechanisms will be reviewed. Since the scope of this review is primarily the theory underlying the *reaction* of copolymerization, no attempt will be made to treat the equally important relation between the composition and physical properties of copolymers, on which an extensive although largely empirical literature exists, nor the means of preparing and processing copolymers in industry, except as they bear on our understanding of the reaction. Some of the material of this review has been summarized, although more briefly, in a recent paper by Simha and Wall (178).

II. THE COMPOSITION OF COPOLYMERS

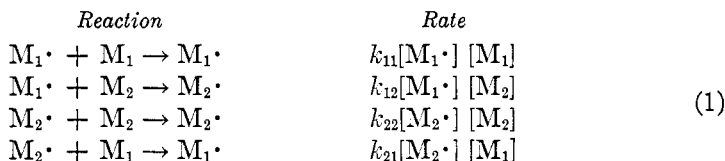
A. EARLY INVESTIGATIONS

According to Meyer (141), the reaction of copolymerization was first described in 1914 by Klatte (99), who carried out the polymerization of a mixture of vinyl esters. Although, in the subsequent period of intensive applied research, interest in copolymerization was spurred by the observation that copolymers (e.g., Vinylite (47), Buna S, Vinyon (170)) frequently had more desirable physical properties than either polymers of single monomers or mixtures of such polymers, investigation of the nature of the copolymerization reaction lagged. Nevertheless, during the 1930's evidence accumulated that striking differences existed in the tendencies of monomers to enter into copolymers. Thus, when Staudinger and Schneiders (191) fractionated a vinyl chloride-vinyl acetate copolymer made from a 1:1 feed, they obtained fractions containing these monomers in the ratio 9:3, 7:3, 5:3, and 5:7, but none in the ratio 1:1. Further, marked differences in the ability of divinyl compounds to enter into copolymerization with styrene or methyl methacrylate were deduced by Norrish and Brookman (150) from the relative tendencies of mixtures to form insoluble gels. Their study also provided one of the first demonstrations that inclusion of two monomer types in the same polymer chain actually occurred. Similarly, in vinyl chloride-acrylic ester copolymers, the acrylate was found to enter the copolymer faster than the chloride, so that the first polymer was rich in acrylate and the last rich in vinyl chloride. Empirically, it was observed that this heterogeneity could be corrected and a uniform composition copolymer obtained by adding the more reactive monomer gradually during the polymerization (58).

Indications of rather specific copolymerization phenomena also arose. Although maleic anhydride and some related compounds were very difficult to polymerize alone, they were capable of copolymerizing readily with polymerizable monomers such as styrene and vinyl chloride (203). Still more surprisingly, the pairs stilbene-maleic anhydride (204) and isobutylene-fumaric ester (84), in which no monomer polymerizes readily by itself under the same conditions, readily gave high-molecular-weight 1:1 copolymers, regardless of which monomer was in excess. Further, although a styrene-vinyl acetate (or styrene-vinyl chloride) mixture would polymerize to give only a mixture of two polymers (141), a copolymer

containing all three monomers could be obtained in the presence of an acrylic or maleic ester.

Any attempt to give quantitative treatment to results of the sort just described and to develop an adequate theory of copolymerization requires the introduction of some sort of model for the reaction, and a number of simplifying assumptions. The first attempt of this nature, and one which foreshadowed subsequent developments to a striking degree, was made by Dostal (50) in 1936. In his treatment, the behavior of an active center depended solely upon the terminal group (i.e., the monomer unit last added to the chain) and was independent of the length or overall composition of the polymer chains. Under these conditions, only two types of active centers will exist in the copolymerization of any two monomers, and for long polymer chains the formation of copolymer is determined by the four reactions:



where M_1 and M_2 represent the two monomers, and $M_1 \cdot$ and $M_2 \cdot$ represent chains ending in M_1 and M_2 units, respectively.⁴ Dostal wrote out correct expressions for the rate of polymerization and the composition of a copolymer in these terms; but, since his expressions involved four or more unknown rate constants, he devised no experimental test of his conclusions.

In 1939, Norrish and Brookman (149) carried out a careful experimental study of the rates of polymerization of styrene, methyl methacrylate, and their mixtures. To the simplification above, they added the assumption that the concentration of free radicals would be the same in all the mixtures at the same catalyst concentration. This assumption was later shown to be unjustified, for copolymer compositions calculated from the parameters obtained from their rates did not agree with those found by analysis (129).

F. T. Wall (206) in 1941 made an important advance in suggesting that absolute rates be neglected in copolymerization, and that the relative reactivities of the monomers be studied by investigating copolymer compositions. Wall's treatment was derived without regard for the four reactions of equation 1 but, in those terms, he made the additional simplifying assumption that $k_{11}/k_{12} = k_{21}/k_{22} = \alpha$, that the relative reactivities of the monomers were the same towards both radicals. From these assumptions,

$$\frac{d[M_1]}{d[M_2]} = \alpha \frac{[M_1]}{[M_2]} \quad \text{or} \quad \log ([M_1]_0/[M_1]) = \alpha \log ([M_2]_0/[M_2]) \quad (2)$$

⁴ Throughout this review, the nomenclature suggested by Alfrey, Mayo, and Wall (17) will be followed. Monomers will be represented by M_i and chains ending in an M_j -type active center by $M_j \cdot$. The rate constant for reaction of $M_j \cdot$ with M_i will be designated by k_{ji} (radical first).

and the composition of the copolymer could be described in terms of the feed and a *single, easily measured* constant. Although early tests of this equation by Marvel and his students (119, 120) appeared to justify Wall's assumptions, it is evident that equation 2 could not be applied to some systems mentioned above, such as stilbene-maleic anhydride. In fact, a careful study of the styrene-methyl methacrylate system, begun in this laboratory in 1942, showed that α varies significantly with the initial monomer ratio, and led to one derivation of the copolymerization equation discussed in the next section.

Starting with the four chain growth steps in copolymerization, Jenckel (88) in 1942 interpreted the formation of mixed, 1:1, and strictly random copolymers in terms of the four rate constants in the above equations, but for the general case he made essentially the same assumptions as Wall. His method for determining the relative reactivities for a pair of monomers, to polymerize a mixture completely, fractionate, and determine the spread in the compositions of the polymers, was tedious and inaccurate. By this method the pairs styrene-methyl methacrylate and vinylpyrrolidine-vinylcarbazole behaved as if they contained equally reactive monomers, styrene-methyl acrylate as if one were about twice as reactive as the other, and styrene-vinyl acetate as if the reactivities were so different that a mixture of two polymers was obtained.

Simha and Branson (177) have made a detailed mathematical analysis of copolymerization, considering the contributions of chain initiation and termination to composition, and assuming that both the rate and the course of the reaction depend either on the terminal groups of the radicals or on their average compositions. Their results are not in general easily susceptible to experimental test.

B. THE COPOLYMERIZATION EQUATION

1. Assumptions and derivation

Although the four reactions of chain growth in copolymerization were first recognized by Dostal in 1936, and the necessity of expressing copolymer compositions in terms of easily measurable parameters was realized by Wall in 1941, a publication of the combination of the two principles did not appear for three more years. In large measure, the slow development of a theory of copolymerization was due to inadequate data. Thus we have found that almost all of the available technical data are unsuitable for quantitative calculation, because they are obtained from experiments run to high conversion, because they do not cover a sufficient range of feeds, or because they lack essential information on feed composition, polymer composition, or conversion. Uncertainty is also introduced by poor or unstated isolation and analytical techniques.

The widespread interest in copolymerization at the time is evidenced by the fact that in 1944, besides the generalized treatment of Simha and Branson (177), three independent developments of what is now generally termed the "copolymerization equation" were published by Alfrey and Goldfinger (7), by Mayo and Lewis (129), and by Wall (207). In every case, the developments assumed, first, that one was dealing with a chain reaction involving long chains so that

consumption of monomer could be discussed solely in terms of chain propagation reactions; second, that these chains had very short lives compared to the duration of the overall reaction, so that steady-state expressions might be set up for the concentrations of active centers; and, finally, that the propagation reactions could be adequately described by equations 1. Under these conditions, the rate of disappearance of the two monomers in a copolymerization is given by

$$-d[M_1]/dt = k_{11}[M_1\cdot] [M_1] + k_{21}[M_2\cdot] [M_1] \quad (3a)$$

$$-d[M_2]/dt = k_{12}[M_1\cdot] [M_2] + k_{22}[M_2\cdot] [M_2] \quad (3b)$$

and the relation between $[M_1\cdot]$ and $[M_2\cdot]$ is given by the steady-state expression:

$$k_{21}[M_2\cdot] [M_1] = k_{12}[M_1\cdot] [M_2] \quad (4)$$

Dividing equation 3a by 3b, eliminating the concentrations of active centers by combining the result with equation 4, and introducing the parameters, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, leads by straightforward algebra to the final copolymerization equation,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] [M_1] + r_2 [M_2]} \quad (5)$$

the validity of which was first established by Mayo and Lewis for the system styrene-methyl methacrylate (129) and has been repeatedly confirmed by subsequent investigations.

A similar development of equation 5 has been subsequently published by Melville, Noble, and Watson (138), while Goldfinger and Kane (75) have obtained the same expression by a rather elegant statistical method which assumes equations 1 and infinitely long chains generated in a monomer mixture of constant composition, but makes no explicit steady-state assumption.

2. Characteristics of monomer reactivity ratios

Equation 5 relates the composition of the copolymer being formed at any instant, $d[M_1]/d[M_2]$, from a polymerizing mixture of two monomers at concentrations $[M_1]$ and $[M_2]$ by means of two parameters, r_1 and r_2 . These parameters are evaluated simultaneously from the indicated experimental quantities of at least two feeds, using some form of equation 5. Relations at other feeds can then be calculated without additional data. Details of the experimental determination are deferred to Section II,C, and the characteristics of the parameters are taken up here. These parameters, *the monomer reactivity ratios*, are each simply the ratio of the two rate constants for the reaction of a chain with a given monomer unit on the growing end with its own type of monomer and with the other type of monomer. It should be noted that a value of $r_1 > 1$ indicates that a radical reacts more readily with a monomer of its own type than with the other, and $r_1 < 1$ that it reacts with its own type less readily. Thus, in a styrene (M_1)-methyl methacrylate (M_2) mixture ($r_1 = 0.52$, $r_2 = 0.46$), each radical reacts about twice as readily with the opposite monomer type. Since rate constants for chain initiation and termination do not appear in equation 5, it predicts no de-

pendence of polymer composition on overall rates of polymerization, nor on the nature of the free-radical source which initiates polymerization. Both these predictions have been confirmed, directly for the styrene-methyl methacrylate system by comparing the composition of the products from the slow thermal polymerization with those from the more rapid one catalyzed by benzoyl peroxide (129), and indirectly for a number of others. On the other hand, as will be discussed in Section V, change in mechanism to a polymerization proceeding through an ionic active center may completely alter the monomer reactivity ratios.

Since, in general, rate constants (and rate constant ratios) refer only to some specified environment, some attention has been paid to the question of the effect of changing medium upon monomer reactivity ratios. Experiments on the styrene-methyl methacrylate system, which has been studied most exhaustively, have shown no change in the monomer reactivity ratios upon the addition of small quantities of water, ethylbenzene, dodecyl mercaptan, or hydroquinone, or the presence or absence of air (except insofar as oxygen absorption in polymerization interfered with polymer analysis) (129) nor by changing the reaction medium from mixtures of pure monomers to monomer solutions (109, 129, 153) in ethyl acetate, benzene, or acetonitrile, or even in methanol, a solvent from which the polymer precipitates as it is formed. Actually, since the customary method of determining monomer reactivity ratios is to demonstrate that single values of r_1 and r_2 exist which predict the compositions of the copolymers obtained from a wide range of monomer ratios (and accordingly a wide range of media), the fact that equation 5 applies at all to actual systems affords a general demonstration of this insensitivity. Finally, although the question of the application of the copolymerization equation to emulsion polymerization will be considered in Section II,E, it may be noted here that direct application of the copolymerization equation even to heterogeneous systems is known to fail only when monomer distribution between the phases preferentially removes one monomer from the polymerization site.

The general conclusion that a single pair of monomer reactivity ratios suffices to describe the copolymerization of a given monomer pair under all conditions at a particular temperature (temperature dependence will be considered in Section III,H) is perhaps not surprising. Change of medium exerts an enormous effect upon polar reactions through such phenomena as solvation and the effect of dielectric constant upon the electrostatic forces between ions. In contrast, the usual organic radicals, except when they react chemically by such processes as chain transfer, show little interaction with the solvent, and the rates of reactions following free-radical paths show little sensitivity to changes in medium.⁵ This conclusion permits simplification of treatment, greatly extends the usefulness of the copolymerization equation, and permits discussion of the significance of

⁵ Thus, e.g., the thermal polymerization of styrene proceeds at identical rates in a variety of solvents (173, 193, 194). Increased rates sometimes noted in polymerizations in highly viscous media apparently arise from the inability of growing polymer chains to diffuse together and undergo mutual termination (37, 152).

monomer reactivity ratios solely in terms of monomer and radical structures. Further, if a given monomer is copolymerized with a series of others, comparison of r 's for the radical derived from that monomer gives the relative reactivities of the whole series of monomers towards the radical in question. The significance of such series will be discussed in Section III, but it should be noted here that, while the copolymerization equation permits the comparison of the relative reactivities of a series of monomers with a single radical type, comparison of the relative rates of reaction of different radicals with a single monomer requires, as well, a knowledge of radical concentrations or, what usually amounts to the same thing, the actual rate constants of chain growth.

3. Types of copolymerization

Since the relation between the composition of a monomer mixture and the copolymer formed from it is of great practical importance, and since this in turn is determined by the monomer reactivity ratios for the particular monomer pair, the manner in which the two are related has been discussed at some length, particularly by Alfrey and Goldfinger (7), by F. T. Wall (207), who has emphasized the formal similarity to distillation, and, more recently, by Gindin, Abkin, and Medvedev (72) and by Simha and L. A. Wall (178).

For the purpose of considering the relation here, it is useful to mention the three extreme types of copolymerization which are theoretically possible. The first and simplest, sometimes called *ideal* (207), is that in which the relative reactivities of the two monomers are the same towards both radicals, $r_1 = 1/r_2$, or simply $r_1 r_2 = 1$, and the copolymerization equation reduces to the simpler form proposed by Wall (equation 2). Here monomer units will be arranged at *random* along the polymer chains in relative amounts determined by the feed and the relative reactivities of the two monomers. In the second case, the *alternating* copolymer, each radical prefers to react exclusively with monomer of the other type; $r_1 = r_2 = 0$, and monomer units alternate regularly along the chains. Although, at first glance, such behavior may seem totally unexpected, it provides the key to the copolymerization of such pairs as maleic anhydride–stilbene, noted earlier. In general, known copolymerizations lie between these extremes; one monomer of a pair is more reactive than the other but there is also a tendency for the monomers to alternate in copolymerization so that $0 < r_1 r_2 < 1$. Finally, the possibility that each type of radical may react preferentially with the corresponding monomer should be mentioned: both r_1 and r_2 would then be greater than 1, and there would be a tendency toward independent and concurrent polymerization. No such *independent* polymerization is known. In fact there are few, if any, cases where the $r_1 r_2$ product is certainly and significantly greater than unity.

4. Relation between feed and instantaneous polymer composition

The relation between feed and the instantaneous composition of the copolymer being formed for the case of the ideal copolymer is illustrated in figure 1 for a number of values of r_1 . The analogy to vapor–liquid composition diagrams for

perfect solutions is plainly evident. Further, it may be seen that, except for monomer pairs of very similar reactivities, only a small range of feeds will yield copolymers containing appreciable amounts of both components.

The change in nature of the copolymer-feed relation as one goes from the case of an ideal polymer to one in which the monomer units show an increasing tendency to alternate is illustrated in figure 2, where, for the case $r_2 = 0.5$, values of r_1 are chosen decreasing from 2.0 to zero. Inspection of figure 2 reveals a rather important, if obvious, generalization: as alternation in copolymerization increases, more and more feeds yield a copolymer containing a good deal of each component. Indeed, it is this tendency to alternate in copolymerization, a property of most monomer pairs, that makes practical the preparation of many known copolymers.

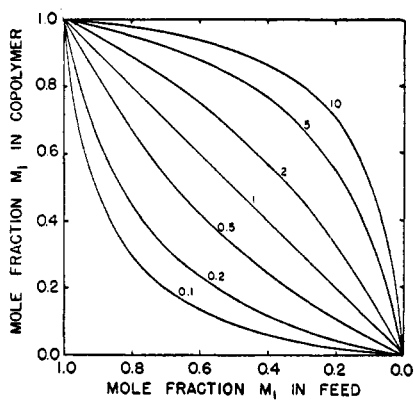


FIG. 1

FIG. 1. Relation between copolymer and feed compositions for "ideal" copolymerizations for indicated values of r_1 ($r_1 r_2 = 1$).

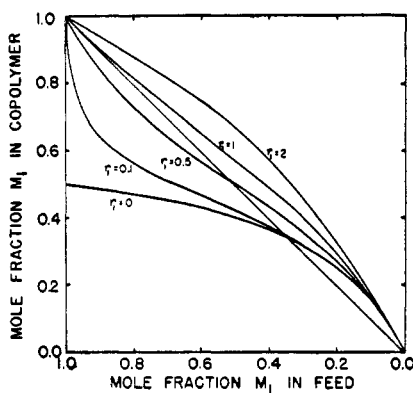


FIG. 2

FIG. 2. Effect of increasing alternation on relation between feed and copolymer composition ($r_2 = 0.5$ for every system).

Figure 2 also illustrates another interesting property of alternating copolymerizations. For values of $r_1 < 1$, the curve of copolymer composition crosses the line representing composition of feed. At this point, feed and copolymer compositions are identical. Wall, again in analogy to distillation, has termed the reaction under such conditions an *azeotropic copolymerization* (207). From equation 5 it may easily be shown (7, 207) that the feed composition at this crossing is given by

$$\frac{[M_1]}{[M_2]} = \frac{(r_2 - 1)}{(r_1 - 1)} \quad (6)$$

Since r_1 and r_2 are both positive, the condition for existence of an azeotropic copolymerization is that both monomer reactivity ratios be simultaneously either larger (no case known) or smaller than unity.

The picture of the copolymerization reaction from which equation 5 is derived also permits analysis of the detailed structure of polymer chains. As mentioned

earlier, the distribution of monomer units along a chain will cover the range from complete randomness in the "ideal" copolymer to strict alternation in the "alternating" copolymer. Expressions for the "ideal" case were developed by Wall (205, 207), and general expressions for any values of the monomer reactivity ratios by Alfrey and Goldfinger (7). As shown by the latter authors, but in the symbols used here, for long chains the probability, P_{11} , of an $M_1\cdot$ radical adding M_1 (and similarly the other possibilities) is given by:

$$\begin{aligned} P_{11} &= r_1[M_1]/(r_1[M_1] + [M_2]) \\ P_{12} &= [M_2]/(r_1[M_1] + [M_2]) \\ P_{22} &= r_2[M_2]/([M_1] + r_2[M_2]) \\ P_{21} &= [M_1]/([M_1] + r_2[M_2]) \end{aligned} \quad (7)$$

From equation 7, the probability of any sequence of M_1 units containing exactly m M_1 units (or the fraction of all M_1 sequences containing that number) is given by

$$N_1(m) = P_{11}^{(m-1)} P_{12} \quad (8a)$$

and, for M_2 sequences

$$N_2(m) = P_{22}^{(m-1)} P_{21} \quad (8b)$$

From equation 8 the average sequence lengths become:

$$\begin{aligned} \bar{m}_1 &= \sum_1^{\infty} m P_{11}^{(m-1)} P_{12} / \sum_1^{\infty} P_{11}^{(m-1)} P_{12} = 1/P_{12} \\ \bar{m}_2 &= \sum_1^{\infty} m P_{22}^{(m-1)} P_{21} / \sum_1^{\infty} P_{22}^{(m-1)} P_{21} = 1/P_{21} \end{aligned} \quad (9)$$

In general, \bar{m}_1 will vary from unity for regular alternation up to the reciprocal of the fraction of M_2 in the copolymer for the "ideal" case.

The problem of the distribution of chain lengths and of polymer compositions between chains has been attacked by Stockmayer (192) by developing simpler approximations to the general equations of Simha and Branson (177). The expressions, while entirely amenable to calculation, are rather complex and the reader is referred to the original paper for details. However, it should be noted that the spread in compositions of chains again increases in going from alternating to ideal copolymers and, even in the latter case, is very small. For example, for an ideal copolymer of chain length 100, formed from an equimolecular mixture of two monomers with $r_1 = r_2 = 1$, only 12 per cent of the polymer will consist of chains containing less than 43 per cent of one monomer unit. For chains of 10,000, 88 per cent will lie between 49.3 and 50.7 per cent. The question of molecular weight distribution has also been discussed recently by Melville, Noble, and Watson (139).

5. Effect of conversion on copolymer composition

Our consideration of copolymer compositions and distributions has so far considered only the instantaneous relation between copolymer and feed. On the

other hand, since composition of copolymer and feed always differ, except for the case of an "azeotropic" copolymer, this relation is constantly changing. Further, since it is essential in practice to carry polymerizations to high conversions, the manner in which copolymer compositions vary as reaction proceeds is of great importance.

This relation was first obtained by Mayo and Lewis (129) by integration of equation 5 to yield

$$\log \frac{[M_2]}{[M_2]_0} = \frac{r_2}{1 - r_2} \log \frac{[M_2]_0[M_1]}{[M_1]_0[M_2]} - \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \log \frac{(r_1 - 1)[M_1]/[M_2] - r_2 + 1}{(r_1 - 1)[M_1]_0/[M_2]_0 - r_2 + 1} \quad (10)$$

Although computation may be simplified by putting equation 10 in the form

$$[M_1]/[M_1]_0 = k^{1/(1-r_2)} \{ ([M_2]_0/[M_1]_0 - p) / ([M_2]_0/[M_1]_0 - pk) \}^{(pr_2+1)/(1-r_1)} \quad (11)$$

where $p = (1 - r_1)/(1 - r_2)$ and $k = [M_2]_0[M_1]/[M_1]_0[M_2]$, and calculating $[M_1]/[M_1]_0$ for chosen values of k (213), the operation is time consuming.

Approximations to equation 10 have been obtained (213) by a power series expansion of equation 5, the first term of which is

$$\frac{\log ([M_1]/[M_1]_0)}{\log ([M_2]/[M_2]_0)} = \frac{r_1[M_1]_0 + [M_2]_0}{[M_1]_0 + r_2[M_2]_0} \quad (12)$$

Although such an approximation correctly predicts polymer composition at 0 and 100 per cent reaction, it is increasingly in error for intermediate compositions as the copolymer departs from ideality, and as the feed departs from the azeotrope, if such exists.

In the writers' experience, the most convenient method for determining copolymer compositions and distributions is the method of graphical or numerical integration developed by Skeist (180). Equation 5 may be expressed in the form

$$\frac{d[M_1]}{d([M_1] + [M_2])} = F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (13)$$

where f_1 and f_2 are now mole fractions of monomers in the feed. Considering now a mixture such that the polymer being formed contains more of monomer M_1 than the feed, i.e., $F_1 > f_1$, if there are a total of M moles of monomers present, when dM moles have polymerized the polymer will contain $F_1 dM$ moles of M_1 . At the same time, the number of moles of M_1 in the feed will have been reduced to $(M - dM)(f_1 - df_1)$. Consequently the material balance of M_1 gives

$$f_1 M - (M - dM)(f_1 - df_1) = F_1 dM \quad (14)$$

whence

$$dM/M = df_1/(F_1 - f_1) \quad (15)$$

or

$$\ln M/M_0 = \int_{(f_1)_0}^{(f_1)} \frac{df_1}{F_1 - f_1} \quad (16)$$

If the quantities F_1 and $1/(F_1 - f_1)$ are now computed from equation 5 at suitable intervals for $0 < f_1 < 1$, the fraction of total monomers which must react to change the composition of residual monomers from any value to any other value may quickly be obtained by determining $\ln (M/M_0)$ by graphical or numerical integration of equation 16 between the desired values of f_1 , and the corresponding value of F_1 (the composition of the polymer being formed at that point in the reaction) determined as well. The average composition of the total polymer formed at that point follows by graphical integration of a plot of F_1

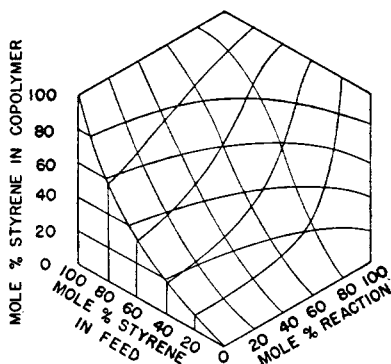


FIG. 3

FIG. 3. Styrene-2-vinylthiophene: variation in instantaneous composition of copolymer being formed with initial feed and per cent reaction.

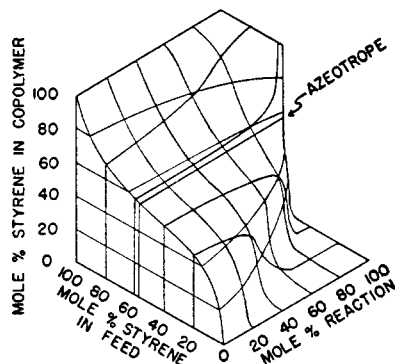


FIG. 4

FIG. 4. Styrene-diethyl fumarate: variation in instantaneous composition of copolymer being formed with initial feed and per cent reaction.

vs. M_1 or as the difference between the composition and amount of residual monomers and those originally present.

The variation of these compositions with extent of reaction for various feeds can conveniently be represented by block diagrams. Figures 3 to 8 are examples for two actual cases taken from table 1: styrene-2-vinylthiophene, which form an almost ideal copolymer but differ threefold in reactivity ($r_1 = 0.35$, $r_2 = 3.10$), and styrene-diethyl fumarate, which show a strong tendency to alternate ($r_1 = 0.30$, $r_2 = 0.07$). For the styrene-vinylthiophene system the surfaces are relatively simple, the greater reactivity of the vinylthiophene causing both unreacted monomers and polymer being formed to approach pure styrene in composition as the reaction nears completion. The styrene-diethyl fumarate system presents a much more complicated picture, since these monomers yield an azeotropic copolymer containing 57 mole per cent styrene. Feeds near the azeotropic composition give almost constant copolymer compositions to high extents of conversion, although all feeds containing over 57 per cent styrene

yield eventually pure polystyrene and those containing under 57 per cent, eventually pure polydiethyl fumarate.

Although the instantaneous polymer composition diagrams indicate how polymer compositions vary with conversion, a more useful picture is obtained by

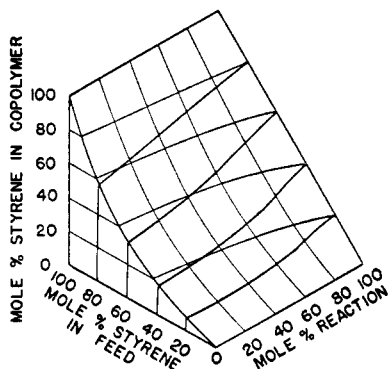


FIG. 5

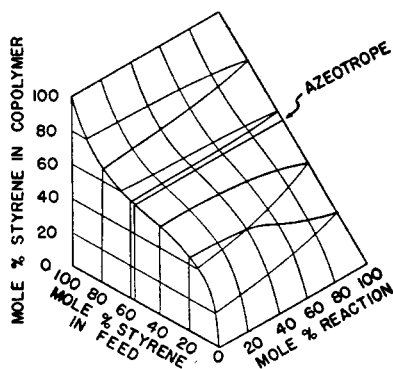


FIG. 6

FIG. 5. Styrene-2-vinylthiophene: variation with initial feed of composition of total polymer formed up to indicated per cent reaction.

FIG. 6. Styrene-diethyl fumarate: variation with initial feed of composition of total polymer formed up to indicated per cent reaction.

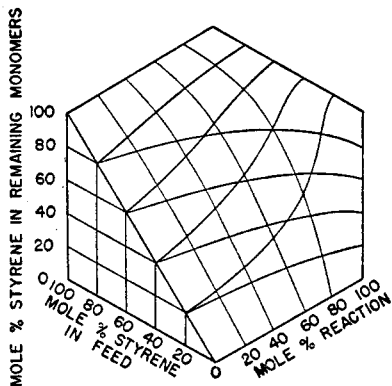


FIG. 7

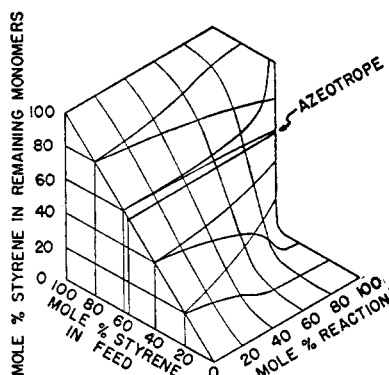


FIG. 8

FIG. 7. Styrene-2-vinylthiophene: variation in composition of remaining monomers with initial feed and per cent reaction.

FIG. 8. Styrene-diethyl fumarate: variation in composition of remaining monomers with initial feed and per cent reaction.

considering polymer composition distributions.⁶ The form of such distributions for ideal copolymers has been considered by Wall (206) and the general case by

⁶ In this discussion, the small instantaneous distribution of compositions is necessarily neglected. However, it is generally small compared to the distribution arising from changes in feed composition with conversion.

Skeist (180). Only for the ideal case has the distribution function been obtained in explicit form, but, since the amount of polymer formed of composition lying between F_1 and $F_1 + dF_1$ is given by dM/dF_1 at that value, the distribution arising from polymerization of any feed may be obtained by graphical differentiation of a conversion-instantaneous polymer plot (180). The results, rather than being represented as curves, may be better visualized as bar-charts. Examples illustrating polymer distributions for the styrene-2-vinylthiophene and styrene-diethyl fumarate systems for several initial feeds appear in figures 9 and 10. Each block represents a 5 per cent range of polymer composition, the height

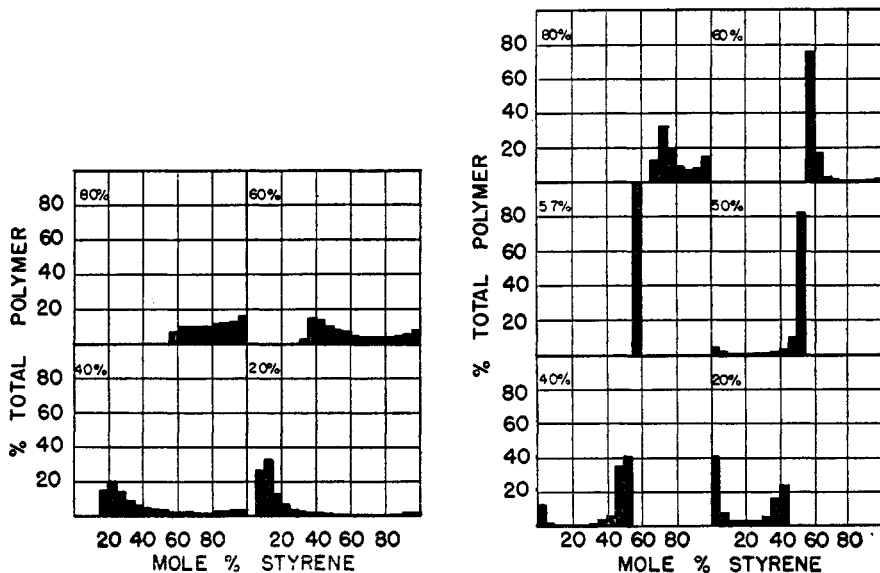


FIG. 9

FIG. 10

FIG. 9. Styrene-2-vinylthiophene: distribution of copolymer compositions in completely polymerized sample for indicated per cent styrene in total polymer (and initial feed).

FIG. 10. Styrene-diethyl fumarate: distribution of copolymer compositions in completely polymerized sample for indicated per cent styrene in total polymer (and initial feed).

corresponding to the per cent present in the completely polymerized system, with 95-100 per cent styrene on the right of each figure.

The distribution diagrams show clearly that, for some feeds in these systems, not only are a wide variety of polymer compositions produced, but appreciable quantities of two distinct compositions appear, with little material of intermediate composition. For an ideal copolymer, it can be shown that this U-shaped distribution arises whenever an r is less than 0.5 or greater than 2 (206); empirically, the same rule appears to hold true for the general case (180).

Technically, it is frequently desirable to prepare homogeneous copolymers rather than those having a wide distribution of compositions. In the case that this composition does not correspond to an azeotrope, two methods are available: either the polymerization may be interrupted at a point somewhat short of

complete conversion (i.e., a styrene–diethyl fumarate copolymer prepared from a 40 mole per cent styrene feed and interrupted at 75 per cent reaction should yield only polymer containing 44–52 per cent styrene) or the polymerization may be begun with a feed yielding the proper polymer and its composition maintained by continuous or portionwise addition of the faster reacting monomer. Both methods of producing homogeneous copolymers appear to have found considerable technical use. For example, the latter was patented in 1937 by Finkentscher and Hengstenberg (58) and is reported to be employed at present in the manufacture of Vinyon N (170).

C. EXPERIMENTAL DETERMINATION OF MONOMER REACTIVITY RATIOS

1. *Experimental methods*

The application of the principles developed in the preceding section to actual monomer systems requires the experimental determination of monomer reactivity ratios. In practice, this has always been done by the determination of the relation between feed and copolymer compositions for a given monomer pair for two (or more) feeds, but the application of studies of monomer distribution along the polymer chain has been suggested by Merz, Alfrey, and Goldfinger (140), whose calculations have recently been revised and extended (16, 102). The usual experimental procedure has been to fill suitable reaction vessels with known quantities of monomers plus initiator (commonly benzoyl peroxide), heat them in a thermostat until partially polymerized, isolate the polymer by some sort of precipitation and drying technique, and determine its composition. In this laboratory it has been found convenient to employ 0.05–0.1 mole of total monomers and carry out the reaction in sealed tubes from which air has been removed by pumping and degassing on a high-vacuum line. Although it is desirable to remove most of the air to eliminate induction periods and to prevent polymer contamination by reaction of the polymerizing radicals with oxygen, such rigorous precautions are not necessary. In the case that the polymer being formed is insoluble in the monomer mixture, it is frequently advantageous to add a suitable solvent to eliminate the possible complications of phase separation. Thus, for example, consistent results for the system vinyl chloride–vinyl acetate (133) were only obtained when experiments with a high proportion of vinyl chloride were carried out in the presence of chlorobenzene so that the reaction mixture remained homogeneous.

In polymer isolation, the chief problem is that of quantitative separation of the polymer from unreacted monomer and from solvent. This is usually accomplished by multiple precipitations from a solvent by a nonsolvent for the polymer (but a solvent for the monomer, e.g., from benzene with methanol or petroleum ether), followed by drying under vacuum. The effectiveness of various isolation techniques for styrene–methyl methacrylate copolymers has been discussed by Mayo and Lewis (129), and a convenient method of isolating benzene-soluble copolymers by sublimation of benzene from frozen solutions has been described by the same authors (105). However, the most effective techniques

vary from system to system, and the quantitative isolation of pure polymer is particularly difficult from systems in which the polymer is benzene-insoluble or where one monomer is relatively nonvolatile (e.g., diethyl fumarate). In fact, the retention of unreacted monomer, which may polymerize in the drying step, by the polymer can be the major source of error in the determination of monomer reactivity ratios. Accordingly, it is not unwise to check the efficacy of a doubtful technique, as by adding a polymer of known composition to a model reaction mixture and reisolating and reanalyzing it (109).

For the determination of monomer reactivity ratios in emulsion polymerizations, customary emulsion recipes have been carried to low extents of reaction, and the polymer separated from monomer by stripping the latex by steam distillation or by repeated precipitation after coagulation.

Copolymer compositions have most commonly been determined by elementary analysis. Since it is difficult to obtain agreement between calculated and found results for certain polymers by conventional analytical procedures (e.g., Kjeldahl nitrogen on polyacrylonitrile is commonly low), in some cases empirical values for the compositions of the monomers have been used as a basis of calculation (109, 153, 217). Analysis for characteristic groups has also been employed, in particular the determination of acetoxy in vinyl acetate copolymers, since vinyl acetate differs little in elementary composition from a number of other common monomers (133). The application of a physical method of copolymer analysis to the determination of monomer reactivity ratios has been made in the analysis of styrene-butadiene (83, 110) and styrene-isoprene (83) copolymers by index of refraction measurements; physical methods in general (e.g., ultraviolet or infrared absorption spectra) appear capable of quite general application and have been suggested by Simha and Wall (178). Determination of copolymer compositions by ultraviolet absorption spectra has recently been reported by Marvel and coworkers (117).

2. Analysis of data

Since by equation 5 the relation between the compositions of feed and copolymer for a monomer pair is determined by the monomer reactivity ratios, the reverse of the procedure used in drawing figures 1 and 2 can be used in determining monomer reactivity ratios. Thus, the results of two or more experiments (carried to low conversion so that the differential form of equation 5 will apply) may be located on a feed-copolymer composition plot and the choice of r_1 and r_2 which gives the best fit of equation 5 determined by trial and error. This technique is entirely feasible and has been employed by a number of investigators. On the other hand, it becomes increasingly tedious the better the experimental data, and the final choice of a "best fit" for a sigmoid curve determined by two parameters is largely a matter of individual judgment, unless rather cumbersome methods of curve fitting are employed. In our experience, a much more expeditious method is as follows. Solving equation 5 for r_2 gives:

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{d[M_2]}{d[M_1]} \left(1 + \frac{[M_1]}{[M_2]} r_1 \right) - 1 \right] \quad (17)$$

From equation 17 it is evident that the results of any one experiment (i.e., particular values of $[M_1]/[M_2]$ and $d[M_1]/d[M_2]$) may be represented as a straight line on a graph with r_1 as ordinate and r_2 as abscissa. The point of intersection of the lines corresponding to two experiments gives the values of r_1 and r_2 for that system, while the area encompassing the intersections of a number of experiments covering a range of feeds serves as a check of the validity of the copolymerization equation. An example of such a graphical solution for the system styrene-methyl methacrylate, taken from the first paper of Mayo and Lewis (129), is shown in figure 11.

The method of determining monomer reactivity ratios from a feed-copolymer composition plot is limited to low-yield experiments, although it can be extended somewhat by using average rather than initial feed compositions. However, even

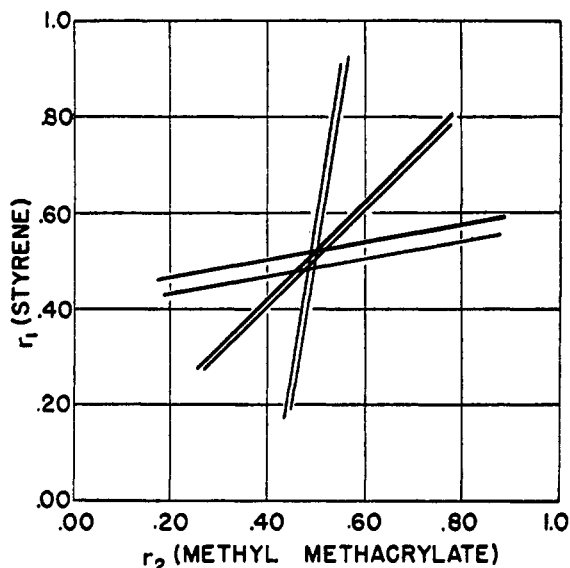


FIG. 11. Graphical solution of copolymerization equation for styrene-methyl methacrylate (six experiments).

this technique may introduce serious errors when the extent of reaction exceeds 10–20 per cent. The r_1 vs. r_2 plot method, however, can be used on data obtained at any extent of reaction at which the residual monomers still contain significant amounts of both reactants, by employing the integrated form of equation 5. For this purpose, a transformation of equation 10 to the form

$$r_2 = \frac{\log ([M_2]_0/[M_2]) - \frac{1}{p} \log \frac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0}}{\log ([M_1]_0/[M_1]) + \log \frac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0}} \quad (18)$$

where $p = (1 - r_1)/(1 - r_2)$, developed by Dr. Mooney of this Laboratory (129), greatly simplifies the computation. For each experiment, equation 18 is

solved for selected values of p (see below), yielding r_2 -values, each of which is related to a corresponding r_1 -value through the selected value of p . A plot of r_2 against r_1 then yields a curve for each experiment. Since equation 18 has been used in treating the data obtained from most of the experiments carried out in this Laboratory, the nature of the $r_1 - r_2$ relation which it describes has been analyzed in some detail, and some of the results seem worth describing for the benefit of other investigators.

It has been found that equation 18 describes a single-valued function which, for positive values of r_1 and r_2 , closely approximates a straight line of slope $(1/[M_1] - 1/[M_1]_0)/(1/[M_2] - 1/[M_2]_0)$. For negative values of r_1 , however, it may curve sharply and becomes discontinuous between the points $r_1 = -[M_2]_0/[M_1]_0$, $r_2 = -[M_1]_0/[M_2]_0$, and $r_1 = -[M_2]/[M_1]$, $r_2 = -[M_1]/[M_2]$.⁷ The generally linear nature of the function in the region of physically significant intersections greatly simplifies calculation, since three points are usually adequate for drawing

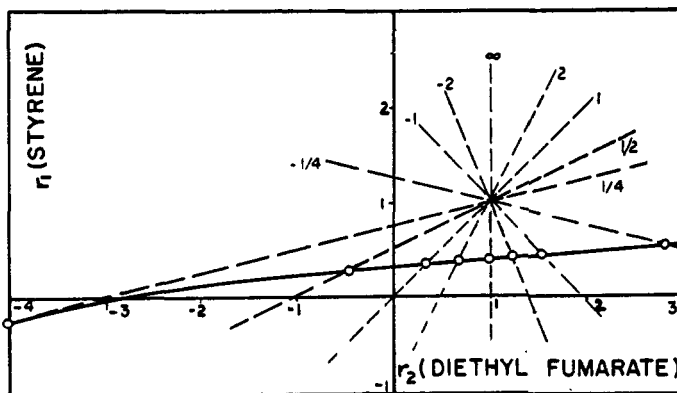


FIG. 12. Example of r_1 - r_2 plot using integrated form of the copolymerization equation. Dashed lines are loci of points with indicated values of p .

and checking calculations on a line corresponding to a given experiment. The labor required to carry out a calculation depends largely upon the computer's success in choosing suitable values of p for calculating r_1 . Here an estimate of the expected values of r_1 and r_2 for the monomer pair, and the realization that the locus of all points with a given value of p lie on a line of slope p passing through $r_1 = r_2 = 1$, may save much time. An example of the results of such a calculation for a (hypothetical) experiment on the system styrene (M_1)-diethyl fumarate (M_2) ($r_1 = 0.30$, $r_2 = 0.07$), in which $[M_1]_0 = 0.80$, $[M_2]_0 = 0.20$, $[M_1] = 0.3735$, $[M_2] = 0.0415$, is shown in figure 12.

An alternative method of determining monomer reactivity ratios from high-conversion experiments, amounting essentially to determining copolymer compositions at several conversions for each feed and extrapolating back to zero

⁷ Cases of significant curvature in positive regions have been observed for some high-conversion experiments.

conversion, has been employed by Wall (209). However, it requires considerably more experimental data than the method described here.

3. Experimental errors

The magnitude and effect of experimental errors in determining monomer reactivity ratios is of importance in judging the validity of tests of the copolymerization equation and of interpretations of the effect of structure on reactivity in radical reactions based upon monomer reactivity ratios. Experience with the many systems investigated in this Laboratory has been summarized by Lewis, Walling, Cummings, Briggs, and Mayo (109) and has led to the conclusion that, with proper techniques of polymer isolation, the major experimental error arises from errors in polymer analysis. The problem thus becomes one of estimating this error and determining its effect upon the accuracy of the determination of the monomer reactivity ratios. This determination is particularly simple in the case that the monomer reactivity ratios are determined from pairs (or pairs of groups) of experiments at high and low $[M_1]/[M_2]$ ratios (4:1 and 1:4 being convenient). Here the error in r_1 is determined almost entirely by the error in analysis in the high $[M_1]$ experiment, and the error in r_2 by the other, since for high M_1 , the plot of equation 17 or 18 will be almost horizontal. If the probable error in analysis is known, new values of $[M_1]$ and $[M_2]$ (or $d[M_1]/d[M_2]$ if equation 17 is used) representing the possible range may be calculated and pairs of new solutions of the equation plotted for each experiment. The size of the parallelogram formed by intersection of these lines now gives the probable error. An example of such a treatment for four monomer pairs is shown in figure 13 (217). Here experimental errors have been taken as 0.2 per cent bromine in the styrene-*p*-bromostyrene system, and 0.2 per cent carbon in the methyl methacrylate-*m*-methyl styrene system, and 0.1 per cent nitrogen in the others. For most pairs, it will be seen that the spread between duplicate experiments is smaller than the analytical uncertainty, a good indication that other sources of error have been eliminated.

In some cases, it is possible to make a good estimate of analytical error, or errors from other sources may be suspected. Further, a test of the validity of the copolymerization equation requires experiments at more than two feeds, and here the procedure based on analytical error is difficult to apply. Accordingly, some system for estimating uncertainty for such cases must be set up, based upon the size of the region in which the lines intersect. A typical example of data gathered at a variety of feeds is the results of six experiments on the copolymerization of ethyl methacrylate-vinylidene chloride at 68°C., reported by Agron, Alfrey, Bohrer, Haas, and Wechsler (1); in figure 14 these are represented on an r_1 - r_2 plot. Although the lines corresponding to the separate experiments do not meet at a point, all are touched by a circle of radius 0.07 with a center at $r_1 = 2.01$, $r_2 = 0.28$. Since this is the smallest circle touching all the lines, one procedure is to take its center as the "best" value and ± 0.07 as the experimental error. However, if a single experiment (the line of lowest slope) is neglected, a new best point ($r_1 = 2.13 \pm 0.03$, $r_2 = 0.33 \pm 0.03$) is obtained lying outside the original circle. A more conservative treatment is to take the spread in intersections as

the experimental uncertainty, and this has been done in estimating experimental error in many of the determinations made in this laboratory. Here, neglecting intersections of nearly parallel lines, this treatment would indicate $r_1 = 2.04 \pm 0.12$, $r_2 = 0.28 \pm 0.08$. Alfrey *et al.* have chosen $r_1 = 2.2$, $r_2 = 0.35$ for this pair by means of a feed-copolymer composition plot, and curves corresponding to the two choices are illustrated in figure 15. The difficulty in choosing the "best fit" from such a diagram is plainly evident, as is the fact that copolymer com-

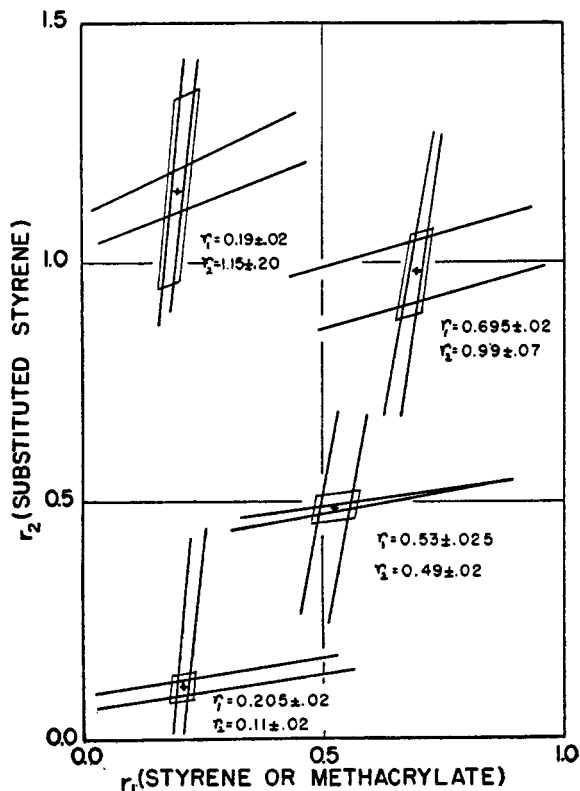


FIG. 13. Determination of experimental errors from analytical uncertainty. Upper right, styrene-*p*-bromostyrene; upper left, styrene-*p*-nitrostyrene; lower left, methyl methacrylate-*p*-dimethylaminostyrene; lower right, methyl methacrylate-*m*-methylstyrene.

positions are not usually very sensitive to small changes in r 's. This in turn emphasizes the necessity of good data for any accurate determination of monomer reactivity ratios.

D. COLLECTED VALUES OF MONOMER REACTIVITY RATIOS

Table 1 summarizes available data on monomer reactivity ratios. We have tried to make this table as comprehensive as possible and have included (1) all published values, (2) our calculations from data in other papers where ratios

were not calculated, and (β) our calculations of ratios from some patents when data were adequate. However, no attempt has been made to cover the patent literature thoroughly. r_1r_2 products are given whenever the values of r_1 and r_2 are known with sufficient accuracy.

Systems are grouped in the order of the amount of study the monomers have received. Thus, all copolymerizations of styrene, which has been studied in the most combinations, are given first, with the second monomers listed in alphabetical order. Copolymerizations of methyl or alkyl methacrylates (except with styrene) are given next, followed by vinyl acetate, acrylonitrile, vinylidene chloride, methyl acrylate, vinyl chloride, butadiene, and other monomers, in that order. Tables 6 and 7 together serve as a convenient index to monomer combinations which have been studied.

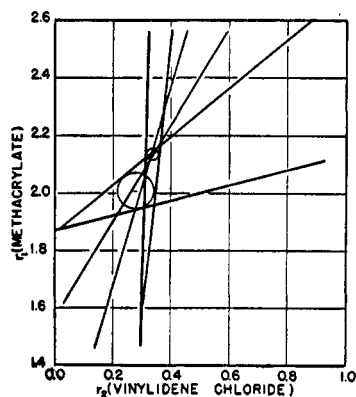


FIG. 14

FIG. 14. Ethyl methacrylate-vinylidene chloride: graphical solution of the copolymerization equation.

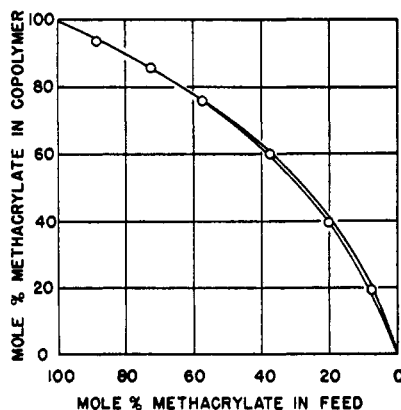


FIG. 15

FIG. 15. Ethyl methacrylate-vinylidene chloride: feed-copolymer composition diagram.

Experimental errors of monomer reactivity ratios determined in this laboratory were estimated as described in the preceding section: in early work by the size of the intersection obtained on graphical solution of the copolymerization equation; more recently by whichever was the larger, the size of the intersection or the error arising from analytical uncertainty. Experimental errors have only occasionally been given by other workers, and in some cases we have made estimates of these errors by plotting the data and employing the size of the resulting intersection.

In connection with the Government-supported research on synthetic rubber, Professor C. S. Marvel and his associates at the University of Illinois (69, 117, 118) have made a large number of copolymers in emulsion at 50°C. from feeds containing 75 per cent by weight of butadiene and 25 per cent of various substituted styrenes to replace the unsubstituted styrene used in GR-S. The available data on reactivities are summarized in table 2 as α -values (equation 2). Butadiene was

TABLE I
Monomer reactivity ratios in oil-phase and emulsion copolymerizations

r_1	M_1	r_2	$r_1 r_2$	r_1^2	r_2^2	T	REFERENCES
Styrene = M_1							
± 0.01	Acrylic acid	0.25	± 0.02	0.04	0.04	60	(43)
0.41	Acrylonitrile	0.04	0.04	0.03	0.03	60	(107)
0.41		0.03	0.03	0.05	0.02	75	(64)
0.37		0.05	0.02	0.03(α)	0.03	50	(83)
0.52 ^a		0.00(α)	0.02	0.05	0.02	67-80	(63)
0.33 ^a		0.02	0.02	0.02	0.02	50	(83)
0.38		0.05	0.02	0.02	0.02	41.5	(76)
0.45		0.02	0.02	0.02	0.02	65	
0.47		0.02	0.02	0.02	0.02	86.5	(131)
90	Allyl acetate	0.0	0.016	0.0	0.016	60	
31.5	Allyl chloride	1.05	0.21	0.05	0.016	70	(217)
0.55	<i>m</i> -Bromostyrene	0.99	0.07	0.39	0.03	60	(217)
0.695	<i>p</i> -Bromostyrene	1.39	0.03	1.48	0.08	60	(110)
0.78	Butadiene	1.48	0.08	1.35(b, s)	0.34	50	(83)
0.23		0.07	0.12	1.4(α)	0.78	50	(83)
0.58(b, s)		0.15	0.2	1.59(α)	0.7	50	(137)
0.5(α)		0.1	0.05	1.8(α)	0.7	50	(83)
0.44(α)		0.03	0.4	1.8(α)	1.1	45	(143)
0.6(α)		0.1	0.32	1.83(α, b)	1.2	45	(143)
0.65(α, b)	2-Chloroallyl acetate	0(b, d)	0.01	0(b, d)	0.01	50	(90)
4.1(b, c)	2-Chloroallyl alcohol	0(b, d)	0.01	0(b, d)	0.01	40	(90)
12.5(b, e)	2-Chloroallyl chloride	0(b, d)	0.06	0(b, d)	0.06	70	(13)
5.0		7	2	0(b, d)	0.3	40	(90)
2.5(b, e)		0.8	0.64	5.22(α)	0.3	70	(6)
0.05	2-Chloro-1,3-butadiene	0.02	0.1	0.00(α)	0.64	50	(83)
0.00(α)		0.02	0.1	0.00(α)	0.1	50	(83)
0.00		0.02	0.1	0.00(α)	0.1	50	(83)

0.052	±0.10	2-Chloro-1,3-butadiene	8.11	±0.34	0.42	60	(49)
0.59	0.03	β -Chloroethyl acrylate	0.08	0.01	0.047	60	(49)
0.64	0.05	<i>m</i> -Chlorostyrene	1.09	0.23	0.70	60	(217)
0.56	0.03	<i>o</i> -Chlorostyrene	1.64	0.07	0.92	60	(216)
0.74	0.03	<i>p</i> -Chlorostyrene	1.025	0.05	0.76	60	(109)
0.816	0.03	<i>p</i> -Chlorostyrene	1.042	0.05	0.85	131	(109)
0.15	0.02	Citraconic anhydride	0.01	0.01		60	(43)
20(e)		Crotonic acid	0(d)			60	(49)
0.28	0.025	<i>p</i> -Cyanostyrene	1.16	0.13	0.33	60	(217)
0.041	0.012	2,3-Dichloro-1,3-butadiene	10.8	1.2	0.46	60	(49)
1.6(a, b)		1,1-Dichloro-2,2-difluoroeth-ylene	0(a, b, d)			45	(135)
210	15	<i>cis</i> -Dichloroethylene	0(d)			60	(106)
75	25	<i>trans</i> -Dichloroethylene	0			68	(10)
37	3		0(d)			60	(106)
~10			0			68	(10)
0.20	0.07	2,5-Dichlorostyrene	0.8	0.09	0.16	70	(18)
0.18	0.06		0.25	0.05	0.05	41.5	}
0.32	0.06		0.08	0.05	0.03	65	
0.40	0.03		0.05	0.03	0.02	86.5	
2.5	0.02	Diethyl chloromaleate	0(d)			70	(18)
0.30	0.02	Diethyl fumarate	0.070	0.007	0.021	60	(108)
0.400	0.02		0.0905	0.007	0.036	131	(109)
6.52	0.50	Diethyl maleate	0.005	0.01	<0.1	60	(109)
5.48	0.56		0(d)			131	(109)
5.0	1.5		0.0	0.1		70	(18)
1.02	0.06	Dimethylaminostyrene	0.84	0.05	0.85	60	(217)
0.21	0.02	Dimethyl fumarate	0.025	0.015	0.005	60	(106)
8.5	0.2	Dimethyl maleate	0.03	0.01	0.3	60	(106)
0.19	0.03	Fumaronitrile	0.0			60	(106)
0.3(b)	0.3		0(b)			50-70	(146)
0.62	0.05	<i>p</i> -Iodostyrene	1.25	0.30	0.76	60	(217)
1.38	0.054	Isoprene	2.05	0.45	2.8	50	(83)
0.80	0.00		1.68(a)	0.00	1.3	50	(83)

TABLE 1—Continued

r_1	M_2	r_2	$r_1 r_2$	$r_1 r_2$	T	REFERENCES
	Styrene = M_1 —Continued					
0.30	Itaconic acid	0.20		0.06	°C.	(66)
0.04	Maleic anhydride	~0			70	(14)
0.19	Maleonitrile	0.0		<0.002	80	(106)
0.15	Methacrylic acid	0.7	±0.05	0.10	60	(43)
0.30	Methacrylonitrile	0.16	0.06	0.05	60	(110)
0.25		0.25	0.02	0.06	80	(65)
71	Methyl acetate	0			60	(131)
22 ^(e)	Methyl chloride	0 ^(d)			60	(131)
1.16	<i>p</i> -Methoxystyrene	0.82	0.07	0.95	60	(217)
0.75	Methyl acrylate	0.18	0.02	0.14	60	(109)
0.825		0.238	0.02	0.20	131	(109)
0.75	Methyl cinnamate	0.2	0.05	0.15	70	(18)
1.9	Methyl methacrylate	0 ^(d)			60	(49)
0.520		0.460	0.026	0.24	60	(109)
0.590		0.536	0.026	0.32	131	(109)
0.50		0.44		0.22	35	(208)
0.56 ^(e)		0.49 ^(e)		0.27	35	(208)
5.1	Methyl vinyl sulfide	0.12	0.05	0.61	60	(162)
2.0	Methyl vinyl sulfone	0.01	0.01		60	(162)
2.4		0.0	0.02	<0.05	60	(49)
0.29	Methyl vinyl ketone	0.35	0.02	0.10	60	(110)
0.18	Monoethyl fumarate	0.25	0.10	0.045	60	(106)
0.13	Monoethyl maleate	0.035	0.01	0.005	60	(106)
0.19	<i>p</i> -Nitrostyrene	1.15	0.20		60	(217)
0.45 ^(e)	<i>m</i> -Nitrostyrene	0.85 ^(e)	0.1	0.38	75	(180a)
1.31	Pentachlorostyrene	0.10	0.02	0.13	70	(5)
185	Tetrachloroethylene	0 ^(d)			60	(48)
16	Trichloroethylene	0.0			60	(48)
6.9	3,3,3-Trichloropropene	0.0	0.02	<0.2	60	(49)

		Methyl (or alkyl) methacrylate = M ₁					
55	±10	Vinyl acetate	0.01	0.01			(133)
5.5	0.8	Vinylcarbazole	0.012	0.002		±0.07	(13)
17	3	Vinyl chloride	0.02			0.34	(48)
35			0.067			2.3	(42)
35 ^(a)			0.077 ^(a)			2.7	(42)
90	20	Vinyl ethyl ether	0 ^(d)				(110)
1.85	0.05	Vinylidene chloride	0.085	0.010		0.16	(48)
0.55	0.025	2-Vinylpyridine	1.14	0.08		0.63	(216)
0.62	0.02	4-Vinylpyridine	0.52	0.06		0.32	(70)
0.35	0.025	2-Vinylthiophene	3.10	0.45		1.09	(216)
Methyl (or alkyl) methacrylate = M ₁							
1.35	0.1	Acrylonitrile	0.18	0.10		0.24	(107)
23		Allyl acetate	0 ^(d)				(131)
41 ^(e)		Allyl chloride	0 ^(d)				(131)
50		Allyl chloroacetate	0 ^(d)				(44)
0.48	0.02	<i>m</i> -Bromostyrene	1.17	0.25		0.56	(217)
0.395	0.02	<i>p</i> -Bromostyrene	1.10	0.25		0.44	(217)
0.25	0.03	Butadiene	0.75	0.05		0.19	(110)
0.06 ^(a)	0.03		0.53 ^(a)	0.05		0.032	(218)
1.0 ^(b,e)		2-Chloroallyl acetate	0 ^(d)				(90)
4.4 ^(b,e)		2-Chloroallyl alcohol	0 ^(d)				(90)
5.5	0.8	2-Chloroallyl chloride	0.017	0.003		0.09	(13)
0.5 ^(b,e)			0 ^(d)				(90)
0.083	0.007	2-Chloro-1,3-butadiene	6.12	0.2		0.51	(49)
0.47	0.075	<i>m</i> -Chlorostyrene	0.91	0.11		0.43	(217)
0.50	0.03	<i>o</i> -Chlorostyrene	1.37	0.10		0.69	(216)
0.415	0.02	<i>p</i> -Chlorostyrene	0.89	0.05		0.37	(217)
0.4	0.2		0.8 ^(b)	0.4		0.3	(120)
0.22	0.02	<i>p</i> -Cyanostyrene	1.41	0.13		0.31	(217)
0.075	0.015	2,3-Dichloro-1,3-butadiene	10.3	1.5		0.69	(49)
0.44		2,5-Dichlorostyrene	2.25			1.0	(1)

TABLE I—Continued

r_1	M_1	r_2	$r_1 r_2$	T	REFERENCES
Methyl (or alkyl) methacrylate = M_1 —Continued					
20(e)	Diethyl maleate	0 ^(d)		60	(131)
0.205	<i>p</i> -Dimethylaminostyrene	0.11	±0.02	60	(217)
0.36	<i>p</i> -Iodostyrene	0.95	0.20	60	(217)
30	Isopropenyl acetate	0.017		75	(80)
6.7	Maleic anhydride	0.02		75	(228)
0.67	Methacrylonitrile	0.65	0.06	60	(110)
10(e)	Methallyl acetate	0 ^(d)		60	(131)
7.5(e)	Methallyl chloride	0 ^(d)		60	(131)
0.29	<i>p</i> -Methoxystyrene	0.32	0.05	60	(217)
0.50	α -Methylstyrene	0.14	0.01	60	(216)
0.53	<i>m</i> -Methylstyrene	0.49	0.02	60	(217)
0.405	<i>p</i> -Methylstyrene	0.44	0.02	60	(217)
14	Methyl vinyl sulfone	0 ^(d)		60	(49)
0.35(e)	<i>m</i> -Nitrostyrene	0.85 ^(e)	0.2	75	(180a)
4.0	Pentachlorostyrene	0.35	0.05	70	(5)
81(e)	Trichloroethylene	0 ^(d)		60	(131)
20	Vinyl acetate	0.015	0.015	60	(133)
2.0	Vinylcarbazole	0.20	0.03	70	(13)
13(e)	Vinyl chloride	0 ^(d)		60	(131)
2.53	Vinylidene chloride	0.24	0.03	60	(107)
2.2 (butyl ester)		0.35	0.77	68	(1)
2.2 (ethyl ester)		0.35	0.77	68	(1)
0.395	2-Vinylpyridine	0.86	0.06	60	(216)
Vinyl acetate = M_1					
0.061	Acrylonitrile	4.05	0.3	60	(133)
0.02		6	2	60	(65)
0.60	Allyl acetate	0.45	0.15	60	(110)

0.7	Allyl chloride	0.67	0.47	68	(1)
0.3	Crotonic acid	0.01	±0.01	68	(43)
6.3	<i>cis</i> -Dichloroethylene	0.018	0.003	60	(106)
2.8		0	0.11	68	(10)
0.99	<i>trans</i> -Dichloroethylene	0.086	0.010	60	(106)
0.85		0	0.085	68	(10)
0.011	Diethyl fumarate	0.444	0.003	60	(106)
0.17	Diethyl maleate	0.043	0.007	60	(106)
1.0	Isopropenyl acetate	1.0	1.0	75	(80)
0.055	Maleic anhydride	0.003	0.00016	75	(228)
0.01	Methacrylonitrile	12	<0.24	70	(65)
0.13 ^(b)	Methyl chloride	0 ^(d)	2	73-90	(144)
0.1	Methyl acrylate	9	2.5	60	(133)
0.3	Methyl vinyl sulfone	0.4	0.1	60	(162)
0.0		0.40	0.08	60	(49)
6.8	Tetrachloroethylene	0	<0.005	60	(48)
5		0		68	(1)
0.66	Trichloroethylene	0.01	<0.014	60	(138)
0.67		0		68	(10)
0.19	3,3,3-Trichloropropene	0.19	0.036	60	(49)
0.35	Vinyl bromide	4.5	1.6	60	(138)
0.23	Vinyl chloride	1.68	0.08	60	(133)
0.6 ^(b)		1.8 ^(b)	0.38	40	(119)
0.3		2.1	0.63	68	(1)
0.3		2.1	0.63	75	(80)
3.0	Vinyl ethyl ether	0 ^(d)		60	(138)
0 ^(d)	Vinylidene chloride	3.6	<0.12	60	(48)
0.1		6	0.6	68	(1)
Acrylonitrile = M ₁					
0.08	α -Acetoxystyrene	0.4	0.05	75	(43)
3.0	Allyl chloride	0.05	0.15	60	(43)
0.014	1,1-Bis(<i>p</i> -anisyl)ethylene	0 ^(d)	0.01	60	(49)

TABLE 1—Continued

η	M_n	r_1	r_2	r_{12}	T	REFERENCES
Acrylonitrile = M_1 —Continued						
0.024	0.003		0 ^(d)		60	(49)
0.00	± 0.04	± 0.08			50	(83)
0.05 ^(a)	0.01	0.01		<0.016	50	(83)
0 ^(a)		0.46 ^(a)		0.02	50	(209)
0.25		0.33			60	(218)
0.005	0.011	6.07	0.53		50	(83)
0.034 ^(a)	0.00	6.93 ^(a)	0.23	0.24	50	(83)
0.045	0.004	5.35	0.20	0.24	60	(49)
21	10	0 ^(d)			60	(49)
8 ^(e)		0 ^(d)			60	(131)
12 ^(e)		0 ^(d)			60	(131)
13.6	1.0	0 ^(d)			60	(49)
0.028	0.003	0 ^(d)			60	(49)
0.26	0.02	0.09	0.02	0.023	41.5	(76)
0.22	0.05	0.07	0.05	0.02	65	
0.25	0.11	0.07	0.06	0.02	86.5	(49)
12.2	2.4	0 ^(d)			60	
5.4	0.5	0 ^(d)			60	(49)
0.03	0.03	0.45	0.05		50	(83)
0.05 ^(a)	0.02	0.29 ^(a)	.02	0.015	50	(83)
6 ^(e)		0 ^(d)			60	(131)
6	2	0 ^(d)			60	(49)
0.06	0.02	0.1	0.02	0.006	75	(65)
0.61	0.04	1.78	0.22	1.1	60	(110)
0.26	0.03	0.33	0.05	0.09	60	(49)
470 ^(e)		0 ^(d)			60	(48)
67 ^(e)		0 ^(d)			60	(131)

12.2	± 1.2	3,3,3-Trichloropropene	0.100	± 0.015	1.2	60	(49)
5.0	0.05	Vinyl benzoate	0.05	0.005	0.25	75	(43)
3.28	0.06	Vinyl chloride	0.02	0.02	<0.13	60	(110)
3.7			0.074		0.27	50	(42)
2.8 ^(b)	0.5		0.04 ^(b)	0.02	0.1	40	(170)
5 ^(e)		Vinyl ethyl ether	0 ^(d)			60	(131)
12	2	Vinyl 2-ethylhexanoate	0.01	0.01		30	(43)
3.0	0.05	Vinyl formate	0.04	0.005	0.12	60	(43)
0.91	0.10	Vinylidene chloride	0.37	0.10	0.34	60	(107)
Vinylidene chloride = M ₁							
6 ^(e)		Allyl acetate	0 ^(d)			60	(131)
3.8		Allyl chloride	0.26		0.99	68	(1)
<0.05 ^(a)		Butadiene	1.9 ^(a)	0.2	0.1	5	(218)
35	5	Crotonic acid	0.065	0.005	2.3	60	(43)
12.2	2.0	Diethyl fumarate	0.046	0.015	0.56	60	(48)
40	8	Diethyl maleate	0.0	0.04	<0.2	60	(49)
4.8 ^(b, d)	0.2	Dimethyl oxalate	0.16 ^(b)	0.01	0.8	40	(34)
1.5 ^(e)		Isobutylene	0 ^(d)			60	(131)
10 ^(e)		Maleic anhydride	0 ^(d)			60	(131)
2.4 ^(e)		Methyl acetate	0 ^(d)			60	(131)
1.1 ^(e)		Methyl allyl chloride	0 ^(d)			60	(131)
0.99	0.10	Methyl acrylate	0.84	0.06	0.83	60	(49)
0.15	0.02	Methyl isopropenyl ketone	4.5	0.1	0.7	60	(43)
7.0	1	Vinyl benzoate	0.1	0.02	0.7	60	(43)
1.8 ^(b)	0.5	Vinyl chloride	0.2 ^(b)	0.2		45	(165)
3 ^(e)		Vinyl ethyl ether	0 ^(d)			60	(131)
0.1		Phenylacetylene	1.4		0.14	60	(49)
Methyl acrylate = M ₁							
5 ^(e)		Allyl acetate	0 ^(d)			60	(131)
0.049	0.005	1,1-Bis(<i>p</i> -anisyl)ethylene	0 ^(d)			60	(49)

TABLE I—Continued

η_1	M_2	η_2	η_{12}	T	REFERENCES
Methyl acrylate = M_1 —Continued					
0.092	± 0.006	0(d)		°C.	(49)
0.05(°)	0.02	0.76(°)	± 0.04	5	(218)
0.08(°)	0.02 (butyl ester)	0.99(°)	0.07	5	(218)
0.7(b, °)		0(d)		100	(90)
0.081	0.015	11.1	1.4	60	(49)
0.92	0.05	0.95	0.03	60	(49)
55	5	0(d)		60	(49)
0.15		4		70	(101)
0.15(b)	0.03	3.4(b)	1.4	70	(101)
0.102	0.006	0(d)		60	(49)
8.5	2	0(d)		60	(49)
11.2	2	0(d)		60	(49)
2.8	0.05	0.02		75	(228)
0.35	0.04	0.05	0.03	60	(162)
0.62	0.03	0.027	0.04	60	(49)
35(°)		0(d)		60	(131)
830(°)		0(d)		60	(49)
9.0		0.083		50	(42)
3(°)		0(d)		60	(131)
Vinyl chloride = M_1					
1.16(b, °)		0(d)		40	(144)
0.7(b, °)		0(d)		100	(90)
0.12	0.01	0.47	0.05	60	(106)
0.77	0.03	0.009	0.003	60	(106)
2.05	0.3	0.08	0.1	60	(110)
		n(d)		65	(73)

2.2	Isopropenyl acetate	0.25		±0.55	65	(80)
0.29	Maleic anhydride	0.008		0.0023	75	(228)
0.31 ^(b, c)	Methylal chloride	0 ^(d)			45	(144)
2.0	Vinyl isobutyl ether	0.02	0.01	0.04	50	(43)
Butadiene = M ₁						
0.059	2-Chloro-1,3-butadiene	3.41	0.07	0.2	50	(83)
0.00 ^(a)		2.86 ^(a)			50	(83)
1.07 ^(a)	<i>p</i> -Chlorostyrene	0.42 ^(a)		0.5	50	(209)
~0 ^(a)	1-Cyano-1,3-butadiene	1.70 ^(a)			50	(209)
0.46 ^(a)	2,5-Dichlorostyrene	0.46 ^(a)	0.01	0.2	50	(209)
0.25 ^(a, b)	Ethyl α -cyanocinnamate	0 ^(a, d)			35	(145)
0.36 ^(a)	Methacrylonitrile	0.04 ^(a)	0.04	0.014	5	(218)
<i>p</i> -Chlorostyrene = M ₁						
1.48	α -Methylstyrene	0.25	0.05	0.37	74	(76a)
0.86	<i>p</i> -Methoxystyrene	0.58	0.03	0.50	60	(217)
1.15	<i>p</i> -Methylstyrene	0.61	0.03	0.70	60	(217)
0.25	<i>m</i> -Nitrostyrene	1.3	0.1	0.32	75	(180a)
0.70	<i>p</i> -Nitrostyrene	0.91	0.37	0.64	60	(217)
β -Chloroethyl acrylate = M ₁						
5.5	Allyl acetate	0 ^(d)			60	(110)
4	Methylal acetate	0 ^(d)			60	(110)
2-Chloro-1,3-butadiene = M ₁						
6.65	Diethyl fumarate	0.025	0.010	0.17	60	(49)
3.17	1,1-Diphenylethylene	0.00	0.07	<0.2	60	(49)
2.82 ^(a)	Isoprene	0.063 ^(a)	0.051	0.2	50	(83)
3.65		0.133	0.025	0.5	50	(83)

TABLE I—Concluded

r_1	M_1	r_2	r_3	$r_1 r_2$	T	REFERENCES
Maleic anhydride = M_1						
<0.13 0 ^(d)	Allyl acetate	<0.0075		<0.001	°C.	(26)
0.03	2-Chloroallyl acetate	0 ^(b, c)			35	(90)
±0.03	Stilbene	0.03	±0.03		120	(106)
0.002	Isopropenyl acetate	0.032	0.005	0.000064	60	(228)
0.08	Isostilbene	0.07	0.07		75	(106)
Tetrafluoroethylene = M_1						
0.85 ^(a, b, c)	Ethylene	0.15 ^(a, b, c)			80	(87)
<0.3 ^(a, b, c)	Isobutylene	0.0 ^(a, d)			80	(87)
1.0 ^(a, b, c)	Chlorotrifluoroethylene	1.0 ^(a, b, c)			60	(51)
REFERENCES						
M_1	r_1	M_2	r_2	$r_1 r_2$	T	REFERENCES
2-Chloroallyl acetate	0 ^(d)	Acrylic acid	1.0 ^(b, c)		°C.	(90)
2-Chloroallyl alcohol	0 ^(d)	Methacrylic acid	4.5 ^(b, c)		100	(90)
2-Chloroallyl chloride	0 ^(d)	Methacrylic acid	4.0 ^(b, c)		100	(90)
<i>o</i> -Chlorostyrene	22 ± 8	Anethole	0 ± 0.01		70	(4)
Chlorotrifluoroethylene	1.2 ^(a, b, c)	Vinyl fluoride	0.8 ^(a, b, c)		80	(51)
2,3-Dichloro-1,3-butadiene	4.35 ± 0.45	1,1-Diphenylethylene	0 ^(d)		60	(49)
Diethyl fumarate	1.10 ± 0.10	3,3,3-Trichloropropene	1.46 ± 0.35	1.6	60	(49)
α -Methylstyrene	0.1 ± 0.02	Methacrylonitrile	0.06 ± 0.02	0.006	75	(65)

(a) Emulsion polymerization.

(b) Calculated by present authors from original data.

(c) Corrected for *m*-nitrostyrene consumed in chain termination.

(d) Assumed.

(e) Value from single experiment.

(f) Assuming that only one dimethylallyl group reacts.

(g) $T_{\text{crit}} = 230^\circ$ for *o*-chlorostyrene as 1.5143 (110)

the reference monomer in all cases, and an α -value of 1.5, for example, means that the substituted styrene was entering the copolymer 1.5 times as fast as butadiene, after allowing for their relative concentrations in the feed. The results suffer from several limitations: data are available for only a single feed (or a narrow range), so that no account can be taken of alternation tendencies, and a high α -value may indicate either a high average activity or a high tendency to alternate with butadiene; since conversions were high (70–80 per cent) and polymer analyses were not very reliable (particularly those based on absorption

TABLE 2

Relative reactivities of substituted styrenes in copolymerization at 50°C. with feeds containing 75 per cent butadiene by weight

STYRENE	RELATIVE REACTIVITY	STYRENE	RELATIVE REACTIVITY
3,4-Dimethylstyrene	1.7	2,4-Dichlorostyrene	0.80
2-Vinylthiophene	1.65, 1.3 ^(a)	<i>m</i> -Methoxystyrene	0.76
2,5-Dichlorostyrene	1.6	6-Methoxy-3-methyl-	
<i>o</i> -Fluorostyrene	1.4	styrene	0.70
3,4-Dichlorostyrene	1.4	<i>p</i> -Benzylstyrene	0.69
3,5-Dichlorostyrene	1.3	<i>p</i> -Chlorostyrene	0.69 ^(b)
2,3-Dichlorostyrene	1.3	3,4-Dimethoxysty-	
<i>o</i> -Bromostyrene	1.3	rene	0.61
<i>m</i> -Trifluoromethylsty-		<i>Styrene</i>	0.61
rene	1.2	<i>m</i> -Methylstyrene	0.60 ^(c) , 0.54 ^(d) , 1.31
<i>m</i> -Bromostyrene	1.2	4-Methoxy-3-methyl-	
2,5-Dimethylstyrene	1.2	styrene	0.58
<i>p</i> -Cyanostyrene	1.1	3,5-Dimethylstyrene	0.56
<i>m</i> -Chlorostyrene	1.0	2,4-Dimethylstyrene	0.53
(<i>Butadiene</i>)	1.00	<i>m</i> - <i>tert</i> -Butylstyrene	0.53
<i>o</i> -Methoxystyrene	0.98	<i>p</i> -Phenoxystyrene	0.50, 0.36 ^(e)
<i>m</i> -Fluorostyrene	0.93	2,6-Dichlorostyrene	0.31
<i>o</i> -Chlorostyrene	0.85	<i>m</i> - <i>sec</i> -Butylstyrene	0.11
<i>p</i> -Bromostyrene	0.84	Anethole ^(f)	0.054

^(a) By sulfur analysis and ultraviolet absorption spectrum, respectively.

^(b), ^(c), ^(d), ^(e) Feeds contained 69, 72.5, 85, and 61.5 per cent by weight of butadiene, respectively.

^(f) β -Methyl-*p*-methoxystyrene.

spectra), the all-important composition of unreacted monomer mixture is often subject to great uncertainty.

In spite of their limitations, the data in table 2 are included in this review because they cover many monomers which have not been tested otherwise. Using α -values for single experiments at 1:1 feeds together with literature data, Nozaki (153) has estimated relative reactivities in copolymerization for fourteen monomers. Those data are not included here because monomer reactivity ratios for most of his pairs are now known, and in any event cannot be obtained from his data, but his discussion will be referred to later. Nozaki's paper also contains some α -values calculated from data in a series of patents assigned to the Dow

Chemical Company (34-36, 164, 229-230). The patent data are of some use in comparing relative reactivities of quite a number of monomers with vinylidene chloride, but of little use in accurate estimation of monomer reactivity ratios, because of the use of only a narrow range of feeds, bifunctional monomers, or changing temperatures, because the fraction of one monomer which reacted was so low or so high that it was not known accurately, or because of a few obvious analytical difficulties.

E. COPOLYMERIZATION IN HETEROGENEOUS SYSTEMS

Practically, many copolymerizations are carried out in nonhomogeneous media. For example, copolymerizations involving acrylonitrile or the vinyl halides frequently yield insoluble polymers which separate from solution in the course of the reaction. Although it has been shown (109) that the monomer reactivity ratios for styrene-methyl methacrylate are the same when the reaction is carried out in methanol (from which the polymer precipitates) as those determined in homogeneous solution, for some systems studied in our laboratories (e.g., vinyl chloride-vinyl acetate) rather inconsistent and irreproducible results accompany phase separation, but disappear when a suitable solvent for the polymer is added. A reasonable explanation is that, in the absence of solvent, polymerization may occur independently in each phase but the ratios of polymerizable monomers may be different in the two phases. Thus, in a hypothetical system in which M_1 and initiator are selectively absorbed by polymer while M_2 constitutes a separate phase, the result, regardless of the monomer reactivity ratios, would be a copolymer consisting chiefly of M_1 units.

A particularly important case of copolymerization in a nonhomogeneous medium is that of copolymerization in emulsion. Here, at various times in the reaction, some four phases are present: water, soap micelles, emulsified monomer droplets, and polymer particles swollen with monomer. Although there has been controversy as to the locus of the polymerization reaction, the work of Harkins appears to leave little doubt that, except at the very start of the reaction, the actual chain-growth steps occur within the swollen polymer particles, the monomer droplets serving simply as reservoirs to replenish them with monomer (79).⁸ The compositions of copolymers formed in homogeneous systems and in emulsion have been compared by several workers. Although W. V. Smith obtained indirect evidence of identical behavior of styrene-methyl methacrylate in emulsion and homogeneous-phase copolymerizations by chain-transfer measurements (181), the first direct comparison was made by Fordyce and Chapin, employing low-conversion experiments with the styrene-acrylonitrile system at 75°C. (64). Copolymers prepared in emulsion consistently contained 1-3 per cent less acrylonitrile than those prepared in oil-phase copolymerization, a result attributed by the authors to removal of acrylonitrile from the site of reaction by

⁸ This statement is consistent with the possibility that chain initiation may occur in the aqueous phase, as shown by Smith for the persulfate-initiated polymerization of styrene (183).

solution in the aqueous phase. Fordyce (63) has subsequently shown that monomer reactivity ratios for this pair determined in emulsion at low, 12–17 per cent, and 42–52 per cent conversion are in agreement within experimental error, while Smith (182), by measuring the actual distribution ratio of acrylonitrile between styrene and water, has verified the supposition of Fordyce and Chapin as to the origin of differences in results in emulsion and in oil-phase copolymerizations. When monomer reactivity ratios are recalculated from the latter's data, correcting to the actual styrene-acrylonitrile ratio in the nonaqueous phase, results are in agreement with those obtained in oil-phase experiments. More recently, Fordyce and Ham have verified the agreement over a wide range of water-monomer ratios, using a variety of emulsifying agents (67). A case where water solubility of one monomer leads to even more striking differences in emulsion and homogeneous copolymerization has been uncovered by Fordyce and Ham in the system styrene-itaconic acid (66). In dioxane at 70°C. the monomer reactivity ratios are 0.30 for the styrene radical and 0.20 for itaconic acid. In emulsion, copolymers contain only traces of itaconic acid, which is apparently almost completely extracted from the emulsion particles by the water, in which it has a solubility of 72.6 g./100 g. at 70°C.

Comparisons of emulsion and oil-phase copolymerizations with dienes have been made by Hennery-Logan and Nicholls (83). Results are listed in table 1, but since there is some uncertainty as to experimental error, it is questionable if the apparent differences are real, particularly since, except for acrylonitrile, none of the monomers show appreciable water-solubility. Fordyce and coworkers (62, 63, 66, 67) have used the agreement between copolymerization results in emulsion and in homogeneous media as proof that the locus of emulsion polymerization is in the oil phase. Actually, as pointed out by Smith (181) and Wall (209), it need only be assumed that the monomer ratios in the oil phase and at the site of reaction be the same to account for such agreement. Thus, if the relative monomer concentrations are the same in the emulsified droplets and the swollen polymer particles, the data are equally in agreement with the Harkins model of emulsion polymerization (79), which has been strongly supported by the recent interpretation of the kinetics of emulsion polymerization of Smith and Ewart (183, 184).

F. COPOLYMERIZATION IN SYSTEMS OF MORE THAN TWO MONOMERS

The treatment of the problem of copolymer compositions formed from systems containing three monomers was first carried out by Alfrey and Goldfinger (8), and the solution has subsequently been extended to n monomers by Walling and Briggs (213). For such systems, expressions for rates of monomer disappearance are given by

$$\begin{aligned}
 -\frac{d[M_1]}{dt} &= k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] + \cdots + k_{n1}[M_n\cdot][M_1] \\
 &\quad \vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \\
 -\frac{d[M_n]}{dt} &= k_{1n}[M_1\cdot][M_n] + k_{2n}[M_2\cdot][M_n] + \cdots + k_{nn}[M_n\cdot][M_n]
 \end{aligned} \tag{19}$$

TABLE 3
Three- and four-component polymerizations of styrene (S), methyl methacrylate (M), acrylonitrile (A), and vinylidene chloride (V) at 60°C. (213)

EXPT. NO.	FEED		POLYMER	
	Mole per cent	Monomers	Found <i>mole per cent</i>	Calculated <i>mole per cent</i>
1.....	31.24	S	43.4	44.3
	31.12	M	39.4	41.2
	37.64	V	17.2	14.5
2.....	35.10	M	50.8	54.3
	28.24	A	28.3	29.7
	36.66	V	20.9	16.0
3.....	34.03	S	52.8	52.4
	34.49	A	36.7	40.5
	31.48	V	10.5	7.1
4.....	35.92	S	44.7	43.6
	36.03	M	26.1	29.2
	28.05	A	29.2	27.2
5.....	53.23	S	52.6	52.9
	26.51	M	20.2	23.2
	20.26	A	27.2	23.9
6.....	28.32	S	38.4	41.4
	28.24	M	23.0	22.7
	43.44	A	38.6	35.9
7.....	27.76	S	36.4	36.8
	52.06	M	40.6	43.8
	20.18	A	23.0	19.4
8.....	25.21	S	40.7	41.0
	25.48	M	25.5	27.3
	23.91	V	8.0	6.9
	25.40	A	25.8	24.8

and application of the conventional steady-state assumption to each radical yields the auxiliary equations:

$$\begin{aligned}
 k_{11}[M_1\cdot][M_1] + \cdots + k_{1n}[M_1\cdot][M_n] &= k_{11}[M_1\cdot][M_1] + \cdots + k_{n1}[M_n\cdot][M_1] \\
 k_{n1}[M_n\cdot][M_1] + \cdots + k_{nn}[M_n\cdot][M_n] &= k_{1n}[M_1\cdot][M_n] + \cdots + k_{nn}[M_n\cdot][M_n]
 \end{aligned}
 \tag{20}$$

Elimination of the n radical concentrations $[M_1\cdot], \dots, [M_n\cdot]$ between equations 19 and 20 is best accomplished by solution of equation 20 by the method of determinants and, in fact, the final solution is conveniently left in that form. However, since the final expressions are lengthy, the reader is referred to the

original literature (213). Expansion of the result for the case of three monomers gives the relation,

$$\begin{aligned} & \frac{d[M_1]}{[M_1]([M_1]/r_{21}r_{31} + [M_2]/r_{21}r_{32} + [M_3]/r_{23}r_{31})([M_1] + [M_2]/r_{12} + [M_3]/r_{13})} \\ &= \frac{d[M_2]}{[M_2]([M_1]/r_{12}r_{31} + [M_2]/r_{13}r_{32} + [M_3]/r_{13}r_{32})([M_1]/r_{21} + [M_2] + [M_3]/r_{23})} \\ &= \frac{d[M_3]}{[M_3]([M_1]/r_{13}r_{21} + [M_2]/r_{12}r_{23} + [M_3]/r_{13}r_{23})([M_1]/r_{31} + [M_2]/r_{32} + [M_3])} \quad (21) \end{aligned}$$

where $r_{ij} = k_{ii}/k_{ij}$, equivalent to that derived by Alfrey and Goldfinger (8). Since equation 21 and similar forms for greater numbers of monomers express

TABLE 4

Three-component polymerizations of styrene (S), methyl acrylate (M), vinyl chloride (V), and acrylonitrile (A) at 50°C. (42)

EXPT. NO.	WEIGHT PER CENT	MONOMERS	POLYMER	
			Found	Calculated
			<i>weight per cent</i>	<i>weight per cent</i>
1.	20	S	46.5	45.2
	60	M	52.0	53.7
	20	V	1.5	1.1
2.	60	S	76.1	75.7
	20	M	22.8	23.6
	20	V	1.1	0.7
3.	32.0	S	67.1	66.1
	48.8	A	32.5	33.4
	19.2	V	0.4	0.5
4.	30.2	S	70.4	71.0
	15.4	A	26.2	26.8
	54.4	V	3.4	2.2

the composition of a copolymer in terms of monomer concentrations and monomer reactivity ratios, they present the possibility of calculating copolymer compositions for systems of n monomers from data gained from studies on monomer pairs. Experimental verification of equation 21 was first made by Walling and Briggs for the four possible three-component and the one four-component systems of styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride, with the results shown in table 3. Similar verification has recently been obtained by Chapin, Ham, and Fordyce for the systems styrene-vinyl chloride-methyl acrylate and styrene-vinyl chloride-acrylonitrile (42) (table 4).

Integration of equation 21 or the more general case to describe the variation of copolymer composition with feed has not been achieved. However, Walling and

Briggs have discussed a power series approximation to the integral (213), and Skeist has described a means of numerical approximation which, in principle, can be extended to any desired degree of accuracy, and has used it to plot an instantaneous copolymer composition *vs.* conversion diagram for the styrene-methyl methacrylate-acrylonitrile system (180).

The question of azeotropic copolymer formation in *n*-component systems has been discussed by Walling and Briggs, who have shown that, for any system, only one azeotrope is possible, and have expressed its composition, in terms of monomer reactivity ratios, in determinant form (213).

The distribution of units along the chain of copolymers containing more than two components has been considered by Alfrey and Goldfinger (8), who have obtained an expression analogous to equation 7, i.e., the fraction of sequences of monomer M_i having a length *m* is given by

$$N_i(m) = \left(\frac{[M_i]}{[M_1]/r_{i1} + \cdots + [M_i] + \cdots} \right)^{m-1} \left(1 - \frac{[M_i]}{[M_1]/r_{i1} + \cdots + [M_i] + \cdots} \right) \quad (22)$$

In the case that one monomer in a terpolymerization has a negligible self-propagation rate, or shows a strong tendency to alternate with the other two, equation 21 breaks down. This problem, which may arise in practice with monomers such as maleic anhydride, α -methylstyrene, or isobutylene, has been discussed by Alfrey and Goldfinger (9). Taking M_3 as the alternating monomer, so that r_{31} and r_{32} approach zero, equation 21 becomes

$$\begin{aligned} & \frac{d[M_1]}{[M_1](R[M_1]/r_{21} + [M_2]/r_{21} + R[M_3]/r_{23})([M_1] + [M_2]/r_{13} + [M_3]/r_{13})} \\ &= \frac{d[M_2]}{[M_2](R[M_1]/r_{12} + [M_3]/r_{13})([M_1]/r_{23} + [M_2] + [M_3]/r_{23})} \\ &= \frac{d[M_3]}{[M_3]([M_1]/r_{13}r_{21} + [M_3]/r_{12}r_{23} + [M_2]/r_{12}r_{23})(R[M_1] + [M_2])} \quad (23) \end{aligned}$$

where $R = k_{13}/k_{23}$, the ratio of rate constants for reaction of a chain ending in M_3 with M_1 and M_2 . From equation 23 it is not possible to calculate a terpolymer composition for such a system from monomer reactivity ratios alone, but a single terpolymerization experiment will be required to determine *R*. The expression for the further case of r_{23} and r_{21} also vanishing is also treated, and here the further ratio k_{12}/k_{32} must be obtained from terpolymerization data. Finally, the system where all rate constants but k_{12} , k_{13} , k_{21} , and k_{31} are negligible so that

$$\frac{d[M_2]}{d[M_3]} = \frac{k_{12}}{k_{13}} \frac{[M_2]}{[M_3]} \quad (24)$$

has been considered by Walling, Seymour, and Wolfstirn (221) and used in treating the case of the terpolymerization of maleic anhydride, and two α -

methylstyrenes where polymer chains consist almost exclusively of alternating units of maleic anhydride and one or the other styrene.

Actually, for systems of this sort, where a monomer always alternates with a series of other monomers, terpolymerization studies provide the only key to the determination of relative reactivities towards the alternating radical, and it may be hoped that more extensive studies of such systems will appear in the future.

G. CHAIN TRANSFER IN COPOLYMERIZING SYSTEMS

The reaction of chain transfer, in which an atom or group on a solvent molecule undergoes a radical displacement reaction with a growing polymer molecule to terminate the polymer molecule but not the kinetic chain, was first defined by Flory in 1937 (60). Expressions for the effect of chain transfer on polymer molecular weight in one-monomer systems were derived and tested independently by Mayo (125), by Hulburt, Harman, Tobolsky, and Eyring (86), and by Medvedev, Koritzkaya, and Alexeyeva (135a). It is of interest to note that the general equation relating disappearance of monomer (M) to disappearance of solvent (S) (126)

$$\frac{d[M]}{d[S]} = \frac{[M]}{C[S]} + 1 \quad (25)$$

is identical in form and derivation to the special case of the copolymerization equation where $r_2 = 0$ and the transfer constant $C = 1/r_1$.

The application of chain-transfer theory to copolymerizing systems was first made by W. V. Smith (181), who has shown that the relative rates of disappearance of monomer and solvent are given by the equation

$$\frac{d \ln [S]}{d \ln ([M_1] + [M_2])} = \frac{r_1 C_1 [M_1] + r_2 C_2 [M_2]}{r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2} \quad (26)$$

where C_1 and C_2 are the transfer constants for monomers M_1 and M_2 , respectively, with S, and where concentrations are expressed in mole fractions. Defining the "transfer function", C (i.e., the effective transfer constant), for such a system by

$$C = d \ln [S] / d \ln ([M_1] + [M_2]) \quad (27)$$

Smith has verified equation 26 for the case of emulsion copolymerization of styrene-methyl methacrylate in the presence of *n*-amyl mercaptan. Here C_1 (styrene) = 21, $C_2 = 0.72$. The agreement between theory and experiment is shown in figure 16. Chain transfer in copolymerization has been discussed more recently by Alfrey and Hardy, who have defined a quantity K , equivalent to C above, and obtained the related expressions for degree of polymerization (11).

H. EFFECT OF NEXT-TO-LAST MONOMER UNIT

The possibility that the reactivity of a polymer chain in copolymerization might depend upon the next-to-last, as well as the last, monomer unit has been

considered by Merz, Alfrey, and Goldfinger (140). Here the reactions determining the rates of monomer consumption are given by

$$\left. \begin{aligned} \frac{-d[M_1]}{dt} &= k_{11}[M_1][M_1M_1\cdot] + k'_{11}[M_1][M_2M_1\cdot] \\ &\quad + k_{21}[M_1][M_2M_2\cdot] + k'_{21}[M_1][M_1M_2\cdot] \\ \frac{-d[M_2]}{dt} &= k_{12}[M_2][M_1M_1\cdot] + k'_{12}[M_2][M_2M_1\cdot] \\ &\quad + k_{22}[M_2][M_2M_2\cdot] + k'_{22}[M_2][M_1M_2\cdot] \end{aligned} \right\} (28)$$

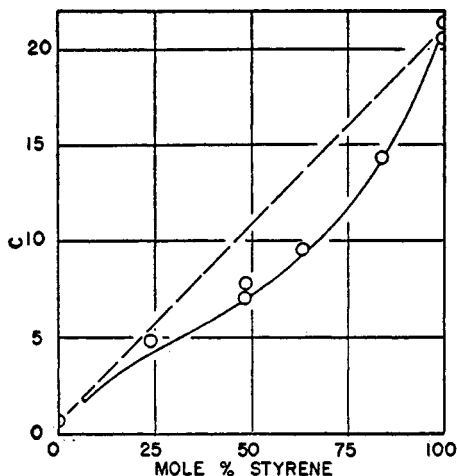


Fig. 16. Agreement between theory (solid line) and experiment (circles) in chain transfer of copolymerizing styrene-methyl methacrylate with *n*-amyl mercaptan.

By introducing the usual steady-state approximation for each radical the following relation results

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + \frac{r'_1[M_1]}{[M_2]} \frac{[M_2] + r_1[M_1]}{[M_2] + r'_1[M_1]}}{1 + \frac{r'_2[M_2]}{[M_1]} \frac{r_2[M_2] + [M_1]}{r'_2[M_2] + [M_1]}} \quad (29)$$

where $r_1 = k_{11}/k_{21}$, $r'_1 = k'_{11}/k'_{21}$, etc.

From the assumptions underlying equations 28 and 29 expressions may also be derived for the distribution of sequence lengths for each monomer along the chain. Merz, Alfrey, and Goldfinger have suggested dechlorination studies on vinyl chloride copolymers or lactonization studies on copolymers of vinyl acetate and acrylic esters as means of investigating any effect of the preceding unit on the nature of $M\cdot$, but no experimental work has been reported (140).

The possibility of such an effect was suggested by study of Fisher-Hirsch-

felder models in this laboratory in 1945 and equation 29 was derived (108). However, since in none of several cases investigated did insertion of plausible values of r 's into equation 29 give consistent solutions for systems for which r_1 , r_2 plots of the usual copolymerization equation gave poor intersections, and since such poor intersections in general improved with improvements in experimental technique, it was concluded that equation 29 had little experimental justification, and the effect, if any, of change of the next-to-last monomer unit on polymer compositions must be too small to be detected by present experimental techniques.

III. STRUCTURE AND REACTIVITY IN COPOLYMERIZATION

Although earlier discussions of radical addition reactions (132, 227) had always assumed (at least tacitly) that the order of reactivity of olefins in radical reactions would be independent of the nature of the attacking radical, the first measurements of monomer reactivity ratios (107, 129) showed clearly that in copolymerization this order is complicated by the tendency of most monomer pairs to enter alternately into the copolymer chain, and it was early suggested (107) that these two phenomena, general reactivity and alternating tendency, are the major factors in determining the behavior of monomers in copolymerization. In this discussion, the empirical picture (based upon data from table 1) will first be presented, beginning with the evidence for the alternating tendency, and then considering data indicating the order of general monomer reactivities. Theoretical correlation of these data will then be considered, followed finally by the implications of this work for other free-radical reactions.

A. *The alternating effect*

Since, if the order of reactivity of monomers towards all radicals were the same, all copolymerizations should approach Wall's "ideal" case of $r_1 = 1/r_2$, or $r_1 r_2 = 1$, the $r_1 r_2$ product provides a convenient measure of the alternating tendency of a monomer pair.⁹ When $r_1 r_2$ products for monomer pairs are compared, it becomes evident that monomers can be arranged in an order such that increasing separation of a pair parallels increasing tendency to alternate ($r_1 r_2 \rightarrow 0$). Such a series, running from the hydrocarbon monomers and vinyl acetate at one end to carbonyl- and nitrile-conjugated monomers at the other, is illustrated in table 5. In general, $r_1 r_2$ products decrease regularly from right to left of rows and from top to bottom of columns, but there are enough inconsistencies to indicate that some interactions between monomers are fairly specific: for example, vinyl acetate alternates more than styrene with vinylidene chloride and diethyl fumarate, and less with vinyl chloride and acrylonitrile and the differences in $r_1 r_2$'s appear to be beyond experimental doubt.¹⁰ On the other hand, where experimental errors are larger, table 5 can be used to evaluate some of the

⁹ Actually, for the "ideal" case, not only the general order, but the quantitative relative reactivities of monomers towards all radicals must be the same. In practice the range of relative reactivities of monomers may vary somewhat from radical to radical.

¹⁰ There is some evidence that this effect is steric in origin; cf. Section III, I.

data in table 1. For example, table 1 gives the monomer reactivity ratios: vinyl acetate, 0.1 ± 0.1 ; methyl acrylate, 9 ± 2.5 . Since the ratio for vinyl acetate is known only to be small, and since the product of the two, from table 5, should be about 0.3, a more accurate ratio for the vinyl acetate radical is probably nearer 0.03 than 0.1.

In the first discussion by Lewis, Mayo, and Hulse (107), the alternating effect was suggested as arising sometimes from steric effects, and sometimes from dipolar interaction or compound formation between monomers. The role of polar phenomena has been amplified by Price (157), primarily in terms of electrostatic interaction between permanent charges, and by Bartlett and Nozaki in terms of donor and acceptor properties of the monomers involved (27). Although the question will be considered in more detail in a later section, it should be noted that the monomer order of table 5 closely parallels the expected order of tendencies of the substituents to donate electrons to, or withdraw electrons from, the double bond (i.e., hydrocarbon or acetoxy groups supplying electrons, carbonyl or cyano groups withdrawing them) and there is little doubt that the phenomenon of alternation is primarily of "polar" origin. Subsequent work has indicated that compound formation between monomers is probably of little direct significance (*cf.* Section III,E,2), although steric phenomena may be important (*cf.* Section III,I).

Alfrey and Lewis have published a theoretical consideration of the relation between heats of copolymerization and copolymer composition (15).

B. RELATIVE GENERAL REACTIVITIES OF MONOMERS

In Section II,B,2 it was pointed out that the relative reactivities of a series of monomers with a given radical may be determined by comparing the reciprocals of the monomer reactivity ratios for that radical observed in a series of copolymerizations. Table 6 summarizes available data. Each column gives the reactivities of the monomers at the left toward the radical at the top, the reactivity of the monomer corresponding to the radical at the top being taken as one in each column. Since a different standard (the reactivity of the radical with its own monomer) is taken in each column, quantities in one column cannot be compared with those in another. Since table 6 is a convenient index to systems on which data are available in table 1, and since a few monomers have been omitted from table 6 when they have been tested in few combinations, table 7 lists combinations appearing in table 1 but not in table 6. Comparisons of *m*- and *p*-substituted styrenes and α -methylstyrenes appear in table 9.

The monomers have been arranged in order of decreasing average reactivity. The 1- and 1,2-substituted ethylenes are listed separately and the latter group will be considered in Section III,I. The radicals are listed in order of decreasing tendency of the substituents to donate electrons, as in table 5. If it were not for the existence of the alternating effect in copolymerization, the numbers would decrease uniformly in each column and the relative reactivities of the monomers would be nearly independent of the attacking radical. However, wherever an alternating tendency occurs, the reactivity of each monomer of a pair toward the

TABLE 6
Relative reactivities of monomers with polymer radicals

MONOMER	RADICAL	BUTADIENE ^(a)	STYRENE	ISOPROPENYL ACETATE	VINYL ACETATE	ALLYL ACETATE	ALLYL CHLORIDE	VINYL CHLORIDE	CHLOROPRENE	2,5-DICHLORO-STYRENE	METHYL METH-ACRYLATE	VINYLBENE CHLORIDE	METHYL ACRYLATE	β -CHLORO-METHYL ACRYLATE	METHACRYLO-NITRILE	ACRYLO-NITRILE	DIBENYL FUMARATE	MALIC ANHYDRIDE
Chloroprene		16	19						1.0		12		12		22	40		
1,1-Diphenylethylene									0.32		10		10		36			
2,5-Dichlorostyrene		2.2	5						1.0	2.3	7		7		5			
Buladiene ^(a)		1.0	1.3						0.3	4.0	20		20		20			
α -Methylstyrene		0.7	1.0						0.12	2.0			5.5		17			
Styrene									0.12	1.3	12		12		6			
Phenylacetylene									0.16	0.44	10		1.6		4			
Methyl methacrylate		1.3	1.9	60							4				1.5			
Methyl vinyl ketone		3.5	3.5												5.5			
Methacrylonitrile		2.8	4												1.6			
Acrylonitrile		3	2.4						0.19	1.5					1.0			
β -Chloroethyl acrylate									0.19	0.74					1.0			
Methyl acrylate		1.3	1.3						0.09	0.3					1.1			
Vinylidene chloride		0.5	0.54												1.0			
Methyl vinyl sulfone															1.2			
Methyl vinyl sulfide															1.2			
Methallyl chloride															1.1			
Isobutylene															3			
Methallyl acetate		0.014													0.18			
Vinyl chloride		0.05		4											0.25			
Allyl chloride		0.03													0.11			
Vinyl acetate		0.02		1.0											0.30			
Allyl acetate		0.01		1.0											0.33			
Isopropenyl acetate				1.0											0.2			
Vinyl ethyl ether				0.3											0.08			
3,3,3-Trichloropropene				0.14											0.2			
															0.082			
															0.90			

other type of radical is always increased, and the significant discrepancies in table 6 can thus be accounted for: whenever a monomer lower in the table is more reactive than one above it toward the reference radical at the top of the

TABLE 7

Monomer combinations which appear in table 1 but not in table 6

α -Acetoxystyrene with acrylonitrile
Acrylic acid with styrene, 2-chloroallyl acetate
Allyl chloracetate with methyl methacrylate
1,1-Bis(<i>p</i> -anisyl)ethylene and 1,1-bis(<i>p</i> -chlorophenyl)ethylene with acrylonitrile and methyl acrylate
Butyl acrylate with butadiene
Butyl methacrylate with vinylidene chloride
2-Chloroallyl acetate, alcohol, chloride with styrene, methyl methacrylate; acetate with acrylic acid, methyl acrylate, maleic anhydride; chloride, alcohol with methacrylic acid
<i>o</i> -Chlorostyrene with styrene, methyl methacrylate, anethole
<i>p</i> -Chlorostyrene with butadiene, α -methylstyrene, <i>m</i> -nitrostyrene
Citraconic anhydride with styrene
1-Cyanobutadiene with butadiene
1,1-Dichloro-2,2-difluoroethylene with styrene
2,3-Dichloro-1,3-butadiene with styrene, methyl methacrylate, 1,1-diphenylethylene
Diethyl chloromaleate with styrene
Dimethyl allyl oxalate with vinylidene chloride
Dimethyl fumarate, maleate with styrene
Diphenylacetylene with acrylonitrile, methyl acrylate
1,1-Diphenylethylene with 2,3-dichlorobutadiene
Ethyl α -cyanocinnamate with butadiene
Ethyl methacrylate with vinylidene chloride
Fumaronitrile, maleonitrile with styrene
1-Hexene and 1-hexyne with acrylonitrile, methyl acrylate
Itaconic acid with styrene
Methacrylic acid with styrene
Methyl cinnamate with styrene, acrylonitrile
Methyl isopropenyl ketone with vinylidene chloride
Monoethyl fumarate, maleate with styrene
Pentachlorostyrene with styrene and methyl methacrylate
Stilbene, isostilbene with maleic anhydride
Tetrafluoroethylene with ethylene, isobutylene, chlorotrifluoroethylene
Vinyl bromide with vinyl acetate
Vinyl benzoate with acrylonitrile, vinylidene chloride
Vinylcarbazole with styrene, methyl methacrylate
Vinyl fluoride with chlorotrifluoroethylene
Vinyl formate, 2-ethylhexanoate with acrylonitrile
α -Vinylpyridine with styrene, methyl methacrylate
4-Vinylpyridine with styrene
α -Vinylthiophene with styrene

column, the lower monomer has the greater tendency to alternate in copolymerization with the reference monomer. Considering the experimental errors involved, there seem to be no exceptions which are certainly significant, although the data indicate that isobutylene is less active with the vinyl chloride radical, and that

vinylidene chloride is more reactive with the diethyl fumarate radical, than would be expected.

The origin of orders of reactivity in radical reactions such as appear in table 6 appears to lie in resonance stabilization of the transition states by structures related to those stabilizing the resulting radical: the greater the resonance stabilization of the radical which results, the higher is the general reactivity of a monomer. This relation will be considered at greater length in Section III,F.

C. PREDICTION OF MONOMER REACTIVITY RATIOS

Aside from any question of the origin of the general reactivities and alternating tendencies of monomers, tables such as 5 and 6 are of great utility in estimating monomer reactivity ratios for monomer pairs on which data are not available; they make possible quite satisfactory guesses of unknown monomer reactivities on the basis of structural analogy. For example, table 5 shows that in the copolymerization of methyl vinyl ketone with styrene the alternation tendency of the ketone is slightly greater than that for methyl acrylate, and table 6 shows that the average activity of the ketone is about 2.5 times that of the ester (2.7 with styrene before allowing for greater alternating effect with ketone). From the monomer reactivity ratios for the copolymerization of any monomer with methyl acrylate (e.g., vinyl acetate, 0.03, methyl acrylate, 9, from table 1 and discussion of table 5), we estimate that the monomer reactivity ratios for the ketone and vinyl acetate will be: methyl vinyl ketone, 9×2.5 or 23, and vinyl acetate, $0.03/2.5$ or 0.01. An equivalent method substitutes the use of relative reactivities in table 6 for use of monomer reactivity ratios in table 1: The relative reactivity of vinyl acetate with the methyl vinyl ketone radical will be 0.4 that with the acrylate radical, or 0.044. The relative reactivity of the ketone with the vinyl acetate radical, will be 2.5 times that of the acrylate radical (some number larger than 5, here about 30) or around 75. The respective monomer reactivity ratios are the reciprocals of 0.044 and 75: methyl vinyl ketone 23, vinyl acetate ~ 0.01 .

D. THE ALFREY-PRICE EQUATION

1. Derivation and assumptions

An interesting attempt to express monomer reactivity ratios quantitatively in terms of concepts similar to those discussed in the two preceding sections has been made by Alfrey and Price (19). According to these authors, the monomer reactivity ratios for a monomer pair are given by the equations

$$r_1 = \frac{Q_1}{Q_2} e^{-e_1(e_1-e_2)} \quad (30a)$$

$$r_2 = \frac{Q_2}{Q_1} e^{-e_2(e_2-e_1)} \quad (30b)$$

where Q_1 and Q_2 are measures of the general reactivities of monomers M_1 and M_2 , respectively, and e_1 and e_2 describe their polar properties.

The derivation of equation 30 is based upon the suggestion, earlier made by Price (157), that the alternating tendency in copolymerization arises from the electrostatic interaction of permanent charges arising from polarization of radicals and double bonds, and closely parallels that used by Ri and Eyring in the treatment of aromatic nitration (166). In the Alfrey-Price treatment, the rate constant for reaction of an $M_1\cdot$ radical with M_2 is taken as a function of four independent terms

$$k_{12} = P_1 Q_2 e^{-e_1 e_2} \quad (31)$$

where P_1 is related to the reactivity of $M_1\cdot$, Q_2 to the reactivity of M_2 , and e_1 and e_2 are quantities describing the charges on $M_1\cdot$ and M_2 , respectively, by the relation

$$e_1 = C_1 / \sqrt{r D k T} \quad (32)$$

where C_1 is the actual charge on $M_1\cdot$, r the separation of charges in the transition state, D the "effective" dielectric constant, k the Boltzmann constant, and T the absolute temperature. If it is further assumed that the charge on a monomer and the radical derived from it are identical, the rate constant for reaction of $M_1\cdot$ with M_1 becomes

$$k_{11} = P_1 Q_1 e^{-e_1^2} \quad (33)$$

and division of equation 33 by equation 31 yields equation 30a.¹¹

Application of the Alfrey-Price equation to the treatment of copolymerization presents attractive possibilities. From the theoretical point of view, it should permit clean separation and quantitative measurement of general reactivities and alternating tendencies. On the practical side, the determination of monomer reactivity ratios for the copolymerization of a single monomer with all other members of a set of n should permit calculation of monomer reactivity ratios for all $n(n-1)/2$ possible combinations. On the other hand, both the derivation and the applicability of the equation have received some criticism (see below).

Application of the Q and e concept to systems of n monomers has been made by Fordyce, Chapin, and Ham (65), who find that the relative amounts of M_1 and M_n entering a copolymer may be expressed as

$$\frac{d[M_1]}{d[M_n]} = \frac{[M_1]^2 Q_1^2 e^{-e_1^2} + [M_1][M_2] Q_1 Q_2 e^{-e_1 e_2} + \dots + [M_1][M_n] Q_1 Q_n e^{-e_1 e_n}}{[M_1][M_n] Q_1 Q_n e^{-e_1 e_n} + [M_2][M_n] Q_2 Q_n e^{-e_2 e_n} + \dots + [M_n]^2 e^{-e_n^2}} \quad (34)$$

and show that a good check is obtained between theory and experiment using Q 's and e 's from Alfrey and Price (19) and the data of Walling and Briggs (213).

¹¹ The original derivation assumed, as well, similar entropies of activation for all copolymerization reactions, this factor being included somehow in the quantity P . Actually, the only necessary assumption is that the entropies of activation for all reactions of one radical be the same, the validity of which is discussed in Section III, H and I.

However, since Q 's and e 's were already calculated from copolymerizations of the same monomers and since these polycomponent systems obey the copolymerization equation (*cf.* tables 3 and 4), the agreement is not unexpected.

2. *Applicability*

The most serious attempt to demonstrate the applicability of the equation and to show that it correlates known monomer reactivity ratios has been made in a recent paper by Price (161), although earlier attempts, employing fewer data, were made by Alfrey and Price in their original paper (19), by Price (160), and by Fordyce, Chapin, and Ham (65). Price has assembled data for sixty-four copolymerizations involving thirty-one monomers and from them has calculated values of Q and e for each monomer. The results, reproduced with original footnotes in table 8, have been used by Price to construct a "monomer map" by locating each monomer on a Q vs. e plot, which, in effect, combines the conclusions of tables 5 and 6 given in the two previous sections. However, Price has not stated exactly what values of Q and e he has now selected for each monomer from the rather wide ranges given in the table, and the Q -values cannot be obtained accurately from his map because the logarithmic scale is distorted. Therefore, he has not yet presented a definite set of values with which anyone else can make a quantitative test of his theory. On the other hand, the present authors are of the opinion that the Alfrey-Price equation, with properly selected values for Q and e , provides as good a means as any for predicting monomer reactivity ratios. As last used by Price, it is essentially the qualitative method of the previous section, using styrene as the principal standard for measuring alternation tendencies, and e -values, then weighting available results to determine general reactivity, or Q -values. The qualitative method requires the exercise of judgment and permits weighting of results in every prediction. In the use of the Alfrey-Price equation, there is an equal amount of latitude in the choice of Q - and e -values; once these have been chosen for a pair of monomers, the Price-Alfrey equation has the advantage of yielding an unequivocal result.

3. *Theoretical considerations*

With regard to substantiating theoretical concepts, for the seventeen monomers for which more than one copolymerization is available, the median deviation of e from the average for that monomer is 0.15 unit, and of Q about 15 per cent of its measured value. To obtain this modest agreement by selection of 60 arbitrary parameters to fit 128 points, some arbitrary selections of monomer reactivity ratios were made, as indicated by the original footnotes to table 8. Further, certain features of calculating Q and e should be pointed out which weaken Price's theoretical claims. The first is that equations 30 permit the calculation of only relative, not absolute, values of Q and e from monomer reactivity ratio data, because the $n(n - 1)$ equations describing the monomer reactivity ratios for all combinations of n monomers are not independent, but are actually

TABLE 8
 Monomer reactivity factors (after Price (161))^(a)

MONOMER ₁	e	Q	MONOMER ₂	REFERENCES
1. α -Methylstyrene.....	-1.2	0.70	Methyl methacrylate	(216)
	-1.1	0.55	Acrylonitrile	(65)
	-0.8	0.50	Methacrylonitrile	(65)
2. p -Dimethylaminostyrene.....	-1.2	1.35	Styrene	(217)
	-1.55	1.66	Methyl methacrylate	(217)
3. Isobutylene.....	-1.1	0.2	Vinyl chloride	(110)
4. p -Methoxystyrene.....	-1.0	1.0	Styrene	(217)
	-1.1	1.22	Methyl methacrylate	(217)
5. p -Methylstyrene.....	-1.1	1.23	p -Chlorostyrene (A)	(217)
	-0.9	1.05	Methyl methacrylate	(217)
	-0.9	0.92	p -Chlorostyrene (A)	(217)
6. m -Methylstyrene.....	-0.8	0.95	Methyl methacrylate	(217)
7. α -Vinylthiophene.....	-0.8	3.0	Styrene	(216)
8. Styrene.....	(-0.8)	(1.0)		
9. Butadiene.....	-0.8	1.33	Styrene	(110)
10. p -Chlorostyrene (A).....	-0.3	0.88	Styrene	(217)
	-0.6	1.20	Methyl methacrylate	(217)
11. p -Iodostyrene.....	-0.3	1.08	Styrene	(217)
	-0.6	1.28	Methyl methacrylate	(217)
12. m -Chlorostyrene.....	-0.2	0.96	Styrene	(217)
	-0.5	1.05	Methyl methacrylate	(217)
13. o -Chlorostyrene.....	-0.5	1.41	Styrene	(216)
	-0.2	1.15	Methyl methacrylate	(216)
14. p -Bromostyrene.....	-0.2	0.88	Styrene	(217)
	-0.5	1.27	Methyl methacrylate	(217)
15. m -Bromostyrene.....	-0.1	0.98	Styrene	(217)
	-0.4	1.20	Methyl methacrylate	(217)
16. α -Vinylpyridine.....	-0.1	1.07	Styrene	(216)
	-0.6	1.09	Methyl methacrylate	(216)
17. Vinyl acetate (A).....	-0.1	0.022	Vinylidene chloride	(1)
	-0.3	0.028	Methyl acrylate ^(a)	(133)
	-0.4	0.026	Methyl methacrylate ^(b)	(133)
	-0.3	0.047	Allyl chloride	(1)
	-0.5	0.010	Vinyl chloride (A)	(1)
	-0.8	0.015	Vinyl chloride	(133)
	-0.9	0.022	Vinylidene chloride	(48)
18. Vinyl bromide.....	0.1	0.1	Vinyl acetate (B)	(133)
19. Vinyl chloride (A).....	0.2	0.024	Styrene	(48)
	0.0	0.035	Methyl acrylate	(42)
	0.4	0.074	Methyl methacrylate	(1)
20. p -Cyanostyrene.....	0.3	1.61	Styrene	(217)
	(-0.7?)	(2.26?)	Methyl methacrylate	(217)
21. p -Nitrostyrene.....	0.4	1.86	Styrene	(217)
	0.4	1.06	p -Chlorostyrene (A)	(217)
22. 2,5-Dichlorostyrene.....	0.4	1.67	Methyl methacrylate	(1)
23. Methyl methacrylate.....	0.4	0.74	Styrene	(109)
24. Vinylidene chloride.....	0.6	0.2	Styrene	(48)
25. Allyl chloride.....	0.6	0.052	Vinylidene chloride	(1)
26. Methyl acrylate.....	0.6	0.42	Styrene	(109)

TABLE 8—Concluded

MONOMER ₁	<i>e</i>	<i>Q</i>	MONOMER ₂	REFERENCES
27. Methyl vinyl ketone.....	0.7	1.0	Styrene	(110)
28. β-Chloroethyl acrylate.....	0.9	0.46	Styrene	(110)
29. Methacrylonitrile (A).....	1.0	1.0	Styrene	(110)
	0.9	1.15	Styrene	(65)
	0.9	1.06	Vinyl acetate ^(c)	(65)
	1.3	1.5	Methyl methacrylate	(110)
30. Acrylonitrile (A).....	0.9	0.68	Methyl vinyl ketone ^(d)	(110)
Acrylonitrile (B).....	0.9	0.37	Vinyl acetate (B)	(133)
Acrylonitrile (C).....	1.0	0.67	Vinyl acetate (B) ^(e)	(65)
	1.2	0.44	Styrene	(107)
	1.3	0.37	Vinyl chloride	(42)
	1.6	0.9	Vinylidene chloride	(48)
	1.6	0.75	Vinyl chloride ^(f)	(48)
31. Diethyl fumarate.....	1.2	0.77	Styrene	(109)
	1.4	0.028	Vinylidene chloride	(48)
	1.9	0.28	Vinyl chloride	(48)

(a) The value for r_2 is given as 0.1 ± 0.1 ; the value used for the calculations was chosen as 0.05.

(b) The value for r_2 is given as 0.015 ± 0.015 ; the value used for the calculations of Q and e in the table was 0.025. Using $r_2 = 0.015$, $e = -0.7$ and $Q = 0.022$.

(c) Using $r_1 = 12.0$ and $r_2 = 0.02$.

(d) The values for r_1 and r_2 , 1.78 ± 0.22 and 0.61 ± 0.04 , respectively, give a product greater than the theoretical maximum of unity. The lower limits in each case were therefore used in the calculation of Q and e .

(e) Using $r_1 = 6.0$ and $r_2 = 0.03$.

(f) The value for r_1 is given as 0.02 ± 0.02 ; the value used for the calculations was chosen as 0.04.

(g) Explanation by present authors: $Q = 1.0$ and $e = -0.8$ were assigned to styrene. Q - and e -values for other reference monomers in M_2 column were then calculated by equations 30 (as shown in table) and used to calculate Q and e for other monomers from the indicated experimental data.

combinations of only $2(n - 1)$ independent equations (19, 160).¹² Since $2n$ variables must be determined, two must be given arbitrary values (in table 8

¹² The proof of this statement for three monomers may be given as follows: Designating the monomer reactivity ratio for the reaction of an M_i radical with M_i and M_j as r_{ij} , multiplying equations 30a and 30b together and taking logarithms we obtain:

$$\sqrt{-\ln r_{12}r_{21}} = e_1 - e_2$$

Similarly from the copolymerization of M_2 and M_3 :

$$\sqrt{-\ln r_{23}r_{32}} = e_2 - e_3$$

Adding,

$$\sqrt{-\ln r_{12}r_{21}} + \sqrt{-\ln r_{23}r_{32}} = e_1 - e_3$$

But

$$e_1 - e_3 = \sqrt{-\ln r_{13}r_{31}}$$

the relation arising from the copolymerization of M_1 and M_3 . Since two of the equations are thus combinations of the other four, only four independent equations exist.

$Q = 1.0$ and $e = -0.8$ have been chosen for styrene).¹³ Although the necessity of selecting arbitrary base points for scales of Q and e has no effect on the usefulness of equations 30 in predicting monomer reactivity ratios (i.e., if values of Q_1 and e_1 for M_1 are selected, values for M_2 calculated from the results of copolymerizing M_1 and M_2 , and values for M_3 obtained from the copolymerization of M_1 and M_3 , lead to the same calculated values of the monomer reactivity ratios for the copolymerization of M_2 and M_3 , regardless of the original choice of Q_1 and e_1), it introduces uncertainty into any discussion of the significance of the resulting Q . The reason is that relative values of Q depend upon the base point of the e scale, changes resulting in skewing of the Q coordinate (3). As an example, from table 8, data from the copolymerization of styrene with acrylonitrile indicate a Q -value for the latter of 0.44. Had e for styrene been chosen as -0.2 , Q for acrylonitrile would have increased to 1.47. This point has been recognized and discussed by Price (160), and his recent choice of $e = -0.8$ for styrene is apparently intended to afford a scale of Q -values for monomers in accord with his expectations. On the other hand, it should be plain from the relation, $-\ln r_1 r_2 = (e_1 - e_2)^2$, that any choice of either scale gives an identical difference between e -values and points up the relation between e differences and the monomer reactivity ratio product, $r_1 r_2$, used in Section III,A as a criterion of "alternating tendency." From the same relation, a choice of signs is always necessary for the difference, $e_1 - e_2$. This choice corresponds to deciding, in the qualitative treatment, whether the monomer under investigation is an electron donor or electron acceptor with respect to the reference monomer.

Another difficulty in setting up a series of Q - and e -values similar to table 8 arises from the fact that, for many pairs, one monomer reactivity ratio is so near zero that the relative accuracy with which it is known is low. Since both must be known accurately to make any significant calculation of Q and e , some of the assignments of the table are really arbitrary,—e.g., vinyl acetate and vinyl chloride. In short, it is not really possible at present to obtain Q - and e -values for these monomers and styrene on the same scale. On the other hand, a fairly arbitrary choice of Q and e may be perfectly usable for estimating monomer reactivity ratios, since whether the resulting calculated monomer reactivity ratio is 0.02 or 0.002 is of no practical importance in calculating polymer compositions.

A possible weakness in the derivation of the Alfrey-Price equation lies in the assumption of identical values for e for monomer and radical. A similar equation in which different values are permitted has been suggested by L. A. Wall (210),

$$\begin{aligned} r_1 &= \frac{Q_1}{Q_2} e^{-e_1^*(e_1 - e_2)} \\ r_2 &= \frac{Q_2}{Q_1} e^{-e_2^*(e_2 - e_1)} \end{aligned} \quad (35)$$

¹³ Since this is a change from Alfrey and Price's earlier base, Q 's and e 's for all monomers previously considered (19) have been changed. Further, the values should not be compared with those of Fordyce, Chapin, and Ham (65), who also use the earlier base.

in which starred e 's now refer to radical charges. Although Wall has shown that equation 35 gives reasonable results with combinations of styrene, acrylonitrile, isoprene, butadiene, and chloroprene, it has never received extensive test, and the introduction of yet another parameter makes it even harder to validate experimentally.

The validity of the derivation of the Alfrey-Price equation has recently been questioned by the authors of this review because of the failure of monomer reactivity ratios to show a sensitivity to dielectric constant of the reaction medium (220). From equation 32 the quantity e for a monomer bears an inverse relation to the "effective" dielectric constant of the medium, and accordingly the alternating tendency, i.e., $r_1 r_2$, for a monomer pair should vary in some manner with the bulk dielectric constant of the medium. That the "effective" dielectric constant should not be taken as identical with that of the medium is evident for the reason pointed out by Kirkwood and Westheimer (98, 225) in their treatment of the ionization constants of aliphatic acids,—that some of the lines of force between charges must pass through the reactants as well as through the medium. Walling and Mayo have made an attempt to estimate this "effective" dielectric constant, and on the basis of a reasonable model find that it should be approximately the average of the dielectric constants of polymer and solvent.¹⁴

Experimentally, monomer reactivity ratios for styrene-methyl methacrylate have been measured in benzene ($D = 2.28$), methanol ($D = 33.7$), and acetonitrile ($D = 38.8$) and found to be identical (109). On the other hand, calculation shows that the value of $r_1 r_2 = 0.24$ observed in benzene should become indistinguishable from unity in the other two solvents. Actually, the introduction of solvents is not necessary to test the effect of dielectric constant on monomer reactivity ratios. From equations 30 and 32 copolymerization of any two monomers of markedly different dielectric constant should lead to inconsistent solutions of the copolymerization equation.

Although this failure of monomer reactivity ratios to show a sensitivity to medium is in contradiction to the basis of the Alfrey-Price equation, that alternation in copolymerization arises from the interaction of any *fixed* electrostatic charges, it does not necessarily detract from the equation's empirical usefulness, nor upset the concept, which is generally recognized, that some *polar* phenomenon is the major source of the alternation tendency. Rather, it indicates that this tendency must arise from some polarization or rearrangement of electric charge which has not occurred in radical and monomer in their normal states, but which takes place as they come together and approach the transition state.

¹⁴ The large role of the dielectric constant of the solvent may appear surprising, in view of the small separation of charges in the transition state. However, it should be recalled that the electrostatic work involved is actually

$$\int_r^{\infty} \frac{C_1 C_2}{Dx^2} dx$$

where x is the separation between charges and r the separation in the transition state.

E. THE EFFECT OF NUCLEAR SUBSTITUENTS ON THE REACTIVITY OF STYRENE

1. *Substituents and reactivity*

A suggestion as to the nature of this rearrangement of charge has been made by Walling, Briggs, Wolfstirn, and Mayo (217) on the basis of their study of the effect of nuclear substitution on the reactivity of styrene in copolymerization. This particular choice for intensive study was made, first because nuclear substitution in the meta and para position, in general, does not change the entropy of activation for side-chain reactions of benzene (or else produces a change proportional to that in the heat of activation), and, second, because the theory of the effect of such substitution is relatively well understood. In particular, Hammett, who has surveyed available data on a wide variety of such side-chain reactions of benzene, has found that, in general, the effect of meta- or para-substituents can be expressed by the relation $\log K_0/K = \sigma\rho$, where K_0 and K are the rate or equilibrium constants for the reaction of the unsubstituted and substituted compound, σ a parameter having a single value for each substituent, and ρ a constant for any particular reaction (78). The parameters σ and ρ are probably best interpreted as measures, respectively, of the ability of the substituent to withdraw electrons or make them available at the site of reaction, and the effect of such electron-availability on the reaction considered. The technique employed was essentially that chosen in collecting the data of table 6, i.e., to carry out copolymerizations of a series of substituted styrenes with a selected monomer and, from the data obtained, to calculate the relative reactivities of the styrenes towards the radical from the reference monomer. Such series of relative reactivities towards *different* reference monomers were then to be compared, and compared also with Hammett's collected data on polar reactions.

Some of the results are summarized in table 9 and figures 17 and 18, where the logarithm of the relative reactivity of each substituted styrene is plotted against the Hammett constant for the substituent. Figure 17 shows a nearly linear correspondence between σ -values and reactivities of substituted styrenes toward the unsubstituted styrene radical. On the other hand, reactivities of the substituted styrenes in figure 17 towards the methyl methacrylate and maleic anhydride radicals suggest that, while there may be a similar relation between reactivity and positive σ -values, there is no consistent relation between reactivity and negative σ -values. These inconsistencies parallel the strongest alternating effects and bring out the most striking and significant results of the work on the substituted styrenes. They will be considered first, and the superficially regular relations will be considered subsequently.

2. *Reactivities toward acceptor radicals*

In an effort to explain this paradox, that relative reactivities show the poorest correlation with polar reactions where polar phenomena should be most important, Walling, Briggs, Wolfstirn, and Mayo (217) have proposed that the major driving force for strong alternation tendencies is not simple polarization, but *arises from contributions to the transition state of forms in which actual electron*

TABLE 9

Relative reactivities of substituted styrenes towards indicated radicals

SUBSTITUENT	STYRENE	RELATIVE REACTIVITY ^(a)	
		Methyl methacrylate	Maleic anhydride ^(b)
<i>p</i> -OCH ₃	0.86 ± 0.08 (0.95) ^(a)	1.59 ± 0.16 (0.093) ^(a)	18.5 ± 0.4
<i>p</i> -N(CH ₃) ₂	0.98 ± 0.06 (0.85)	2.24 ± 0.22 (0.023)	300
<i>p</i> -CH ₃		1.14 ± 0.06 (0.178)	1.72 ± 0.12
<i>m</i> -CH ₃		0.87 ± 0.04 (0.26)	
None.....	1.00 (1.00)	1.00 (0.24)	1.00
<i>p</i> -F.....			0.72 ± 0.10
<i>p</i> -Cl.....	1.35 ± 0.06 (0.76)	1.11 ± 0.05 (0.37)	0.79 ± 0.02
<i>p</i> -Br.....	1.44 ± 0.04 (0.69)	1.16 ± 0.05 (0.44)	0.73 ± 0.15
<i>p</i> -I.....	1.61 ± 0.13 (0.76)	1.28 ± 0.10 (0.34)	
<i>m</i> -Cl.....	1.56 ± 0.13 (0.70)	0.98 ± 0.15 (0.43)	
<i>m</i> -Br.....	1.82 ± 0.10 (0.58)	0.96 ± 0.04 (0.56)	0.96 ± 0.14
<i>m</i> -NO ₂ ^(c)	2.22 ± 0.25 (0.38)	1.3 ± 0.2 (0.30)	
<i>p</i> -CN.....	3.57 ± 0.35 (0.325)	2.09 ± 0.20 (0.31)	0.96 ± 0.57
<i>p</i> -NO ₂	5.26 ± 0.5 (0.218)		

^(a) Quantities given in parentheses under relative reactivities are monomer reactivity ratio products.

^(b) Relative reactivities for substituted α -methylstyrenes against α -methylstyrene.

^(c) Data on this monomer are too recent to be included in the graphs (180a).

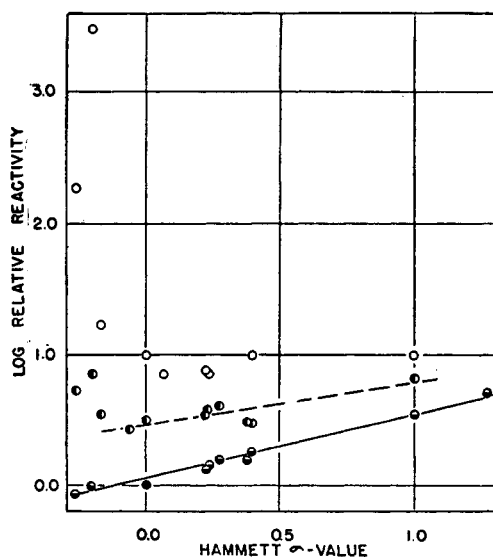


FIG. 17. Plot of log relative reactivity towards indicated radical vs. Hammett σ -value for various substituted styrenes. \bullet , styrene radical; \bullet , methyl methacrylate radical; \circ , maleic anhydride radical (for α -methylstyrenes).

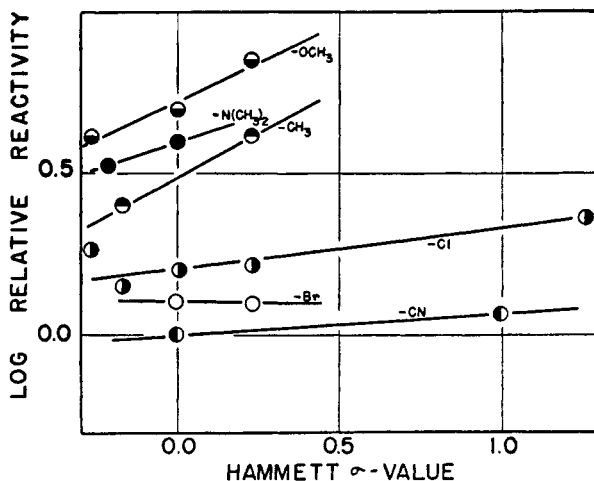
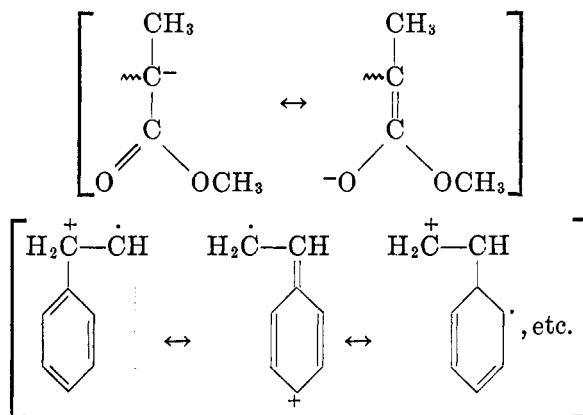


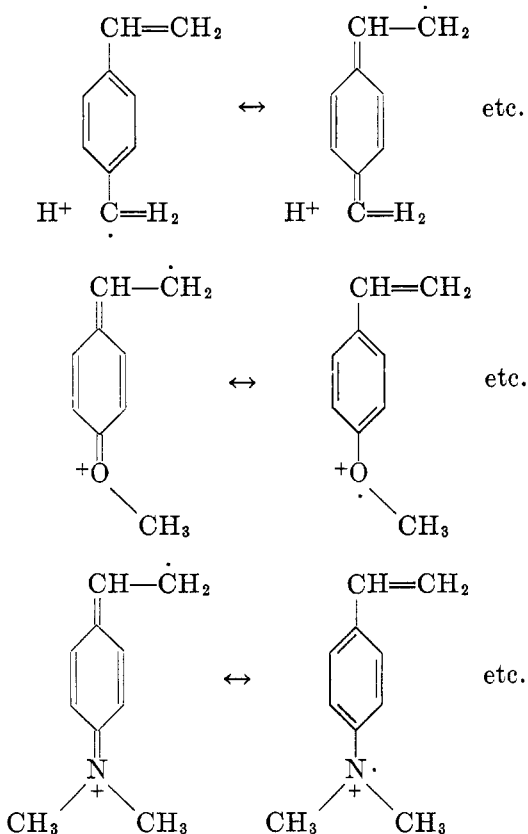
FIG. 18. Plot of log relative reactivities towards para-substituted styrene radicals *vs.* Hammett σ -values for various substituted styrenes. Height of ordinate scale is arbitrary.

transfer between radical and monomer (or vice versa) has taken place. For example, for the case of addition of the methacrylate radical to styrene (where the radical would be expected to be the electron acceptor), structures of this sort would be involved:

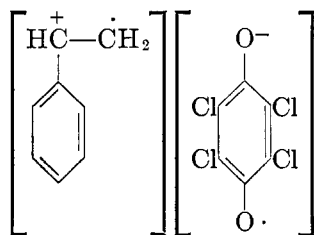


In the conjugate reaction of a styrene radical with methacrylate, structures corresponding to a negative methacrylate ion-radical and a benzyl carbonium ion would contribute. Since electron transfer transforms the methacrylate radical to a relatively stable enolate ion, and the styrene carbonium ion-radical may resonate between twenty-six more or less equivalent forms, and since the resonance stabilization of the activated complex necessary to account for the observed alternation tendency is only 450 cal. (or factor of two at 60°C.), the suggestion has some plausibility. However, the chief requirement of such an interpretation is that it account for the increased effect of *p*-methyl, *p*-methoxy, and *p*-

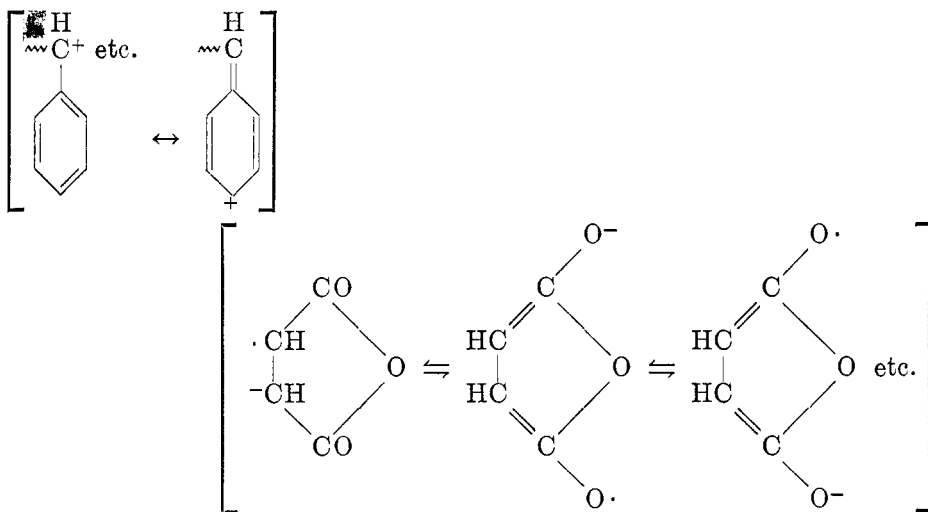
dimethylamino groups on reactivity. Here arguments in favor of such structures proceed on two grounds. First, a number of additional resonance structures do become available on such substitution, i.e.,



and the additional stabilization in the methacrylate–dimethylaminostyrene reaction needs to be only about 1250 cal. in each step. Second, there is a close parallel between the tendency of substituents to increase the reactivity of styrene towards carbonyl conjugated radicals and their effect upon the stability of complexes of styrene with maleic anhydride, trinitrobenzene, and chloranil as judged by the intensity and wave length of color absorption of the complexes (217). Since radical-ion structures (223) in which an electron has been donated by the hydrocarbon to the carbonyl derivative,



e.g., for styrene-chloranil, have been proposed for these complexes, and since structures proposed for the styrene-maleic anhydride complex¹⁵ have the same structure for the anhydride portion as in the addition of a styrene radical to the anhydride (219),



a close relation between structures of molecular and activated complexes is most reasonable. These last formulas suggest, incidentally, why maleic anhydride, with two carbonyl groups over which to distribute its charge and an electron, shows a greater tendency to alternate with styrene than methyl methacrylate with one.

The fact that maleic anhydride both forms a 1:1 molecular complex with styrene and alternates with it in copolymerization attracted the attention of Bartlett and Nozaki (26) who, prior to the publication of Walling, Briggs, Wolfstirn, and Mayo, suggested a relation between the two. It also presents the possibility that alternation in copolymerization may actually proceed through addition of 1:1 molecular complexes to the growing chain. In such a case, while the general forces producing alternation would remain the same, the detailed picture, notably the kinetics, would be quite changed. Nozaki (153), from the small effects of dilution on the copolymerization of styrene and methyl methacrylate, concluded that the role of molecular complexes was small in this reaction. Subsequently, a review of the available evidence (219) (no evidence of physical association in some mixtures of monomers showing high or moderate alternation (103, 217), no change of monomer reactivity ratios on dilution (109, 153, 217), and no unequivocal kinetic evidence in alternating systems (103)) led to the conclusion that growth of copolymers by addition of *molecular complexes* could either be excluded or could not be demonstrated in any of a number of strongly alternating systems. Similar interaction between *radicals* and *monomers*, however, accounts for alternation tendencies.

¹⁵ A relation between the structure of molecular compounds and the transition state of the Diels-Alder reaction has already been proposed by Woodward (232) (cf. Section IV, C).

3. Related phenomena in nonradical reactions

The concept just discussed, that the deviations from a regular Hammett series in the effects of substituents on the reactivity of styrene towards "acceptor" radicals arise from the presence of "special," i.e., additional, resonance forms in the transition state, has actually several parallels in polar reactions. Thus, for example, it has been found necessary to assign a second, larger σ -value to the *p*-nitro group when considering reactions of amines and phenols (78), presumably because of additional contributions from resonance structures of the type:

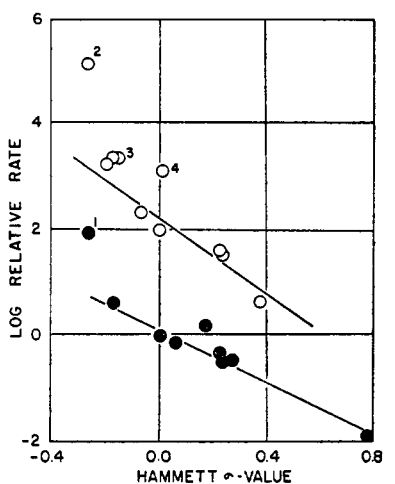
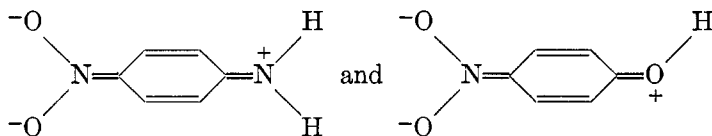
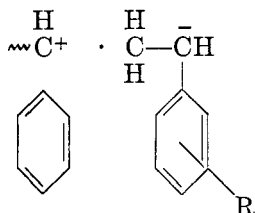


FIG. 19. Log relative rates of solvolysis *vs.* Hammett σ -value. O, substituted benzhydryl chlorides; ●, substituted triphenylmethyl chlorides.

In fact, a survey of some of the series considered by Hammett affords additional evidence as to the nature of the resonance forms in the radical reaction. The solvolysis of benzhydryl and triphenylmethyl halides is generally considered to involve formation of a benzyl carbonium ion, similar in structure to the one involved in the transition state of the reaction of the styrene radical and resembling somewhat the radical ion proposed for the reaction of styrene monomer. When the effect of substituents on these solvolyses is represented on a Hammett plot, using the data of Norris and Banta (148) and Hughes, Ingold, and Taher (85) for benzhydryl chlorides and of Branch and Nixon (147) for triphenylmethyl chlorides (figure 19), the point (1) for *p*-OCH₃ lies well above the best line through the remainder of the data for the latter, while points (2) for *p*-OCH₃, the group of points (3) for various *p*-alkyl groups, and the point (4) for *p*-phenyl all lie above the best line for the former. The parallel to the case of the alternating radicals seems evident.

4. Reactivities toward styrene radicals

Having considered in some detail the deviations from the Hammett relation between reactivity and σ -values, let us now consider the apparent remarkable agreement between reactivity of substituted styrenes toward the unsubstituted styrene radical and the σ -values of the substituents in figure 17. One interpretation is that differences in reactivity may be due primarily to electrostatic interaction between radical and double bond arising from a simple polarization. Since monomeric styrene has a small dipole moment with the negative end toward the side chain (154) and since reactivity increases with the introduction of electron-withdrawing groups, this scheme implies that there is also a negative charge on the trivalent carbon of the styrene radical as it approaches the transition state. A second interpretation is that the reactivities arise from electron donation from the styrene radical to the substituted monomer being attacked, e.g.,



and that reactivity increases with the ability of the monomer to accept an electron.

A more complicated but more correct view is that the two interpretations above are oversimplifications, accounting for only part of the observations. In the first place, the good fit obtained in figure 17 results from using the σ -values for *p*-nitro and *p*-cyano groups applicable to the reactions of *phenols*. The original choice was made partly because this value for the *p*-nitro group gave a better fit than the 0.78 value applicable to most other compounds, and partly because no other value was then available for the *p*-cyano group (although a value of 0.656 has recently (167a) been proposed). The choice may now be defended on the ground that similar resonance structures might be expected to stabilize *p*-nitro- and *p*-cyano-phenoxide ions and the corresponding benzyl carbanion-radicals. Although the choice is reasonable, and although no less arbitrary choice is now possible, it may nevertheless be attacked on the ground that we are using an analogy to *predict* a σ -value under circumstances where Hammett's scheme is *known* to be least reliable. In the second place, we must consider the effects of substituents on general reactivity as well as on polarity, since substituents such as halogen and cyano groups affect both general reactivity and alternation tendency when attached directly to double bonds.

That general reactivity effects alone can account for the reactivities observed towards the styrene radical seems unlikely, since it is hard to see how a *m*-halogen could have a greater stabilizing effect than a *p*-halogen on the resulting radical, or how *p*-methoxy or *p*-dimethylamino groups could result in *destabilization*. On the other hand, some influence of general reactivity changes is suggested by

several observations. First, in figure 17 the (solid black) point for styrene (from which all other points are measured) lies significantly below the best line, a result which could arise from increased general reactivity of all the substituted styrenes, particularly those containing cyano and nitro groups. Second, halo- and cyano-styrenes still show increased reactivities towards the methacrylate radical, although this radical could hardly exhibit *donor* properties. Third, consideration of figure 18 shows that, in contrast to the radicals from styrene and styrene containing donor groups, styrene radicals with acceptor groups show little sensitivity to substituents in the styrenes which they attack. Such lack of selectivity seems more plausible as a balance between alternating and general activity effects, here opposed, than to a complete neutrality for these radicals, since the same substituents, introduced at the double bond, produce radicals capable of strong alternation.

In summary, these studies of the reactivities of the nuclear substituted styrenes have been chiefly successful in dealing with the polar effect in strongly alternating systems, and there suggest the importance of actual electron transfer in the transition state rather than simple polarization as a driving force. Since the magnitude of the alternating effect between many common monomers is quite as large as that observed here, and the order of effect of substituents is at least qualitatively the same (*cf.* table 5), it appears probable that this driving force is quite general. On the other hand, when the alternating effect is small ($r_1 r_2 > 0.2$), its origin is less definite. Further, in the systems studied it is obscured by changes in general reactivity which are roughly parallel and of comparable magnitude.

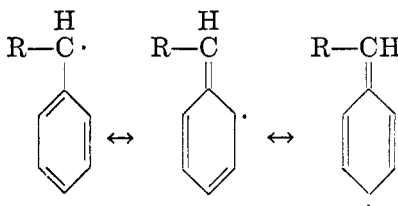
F. GENERAL ACTIVITY AND RESONANCE STABILIZATION OF MONOMERS AND RADICALS

The study of radical addition reactions, notably the direction of addition of radicals to double bonds,¹⁶ early led to the generalization that that radical addition reaction occurs most readily which leads to the most stable radical as product (132). On the other hand, neglecting entropy of activation differences, rates of reaction are determined actually by heats of activation, i.e., the difference in energy content of the reactants and the transition state. These two generalizations have been reconciled by Wheland (226) on the basis that resonance structures which stabilize the resulting radical may contribute appreciably to the stabilization of the transition state as well. From table 6 the effects of 1-substituents in increasing the reactivity of monomers towards attacking radicals are in the order, $-\text{C}_6\text{H}_5 > -\text{CH}=\text{CH}_2 > -\text{COCH}_3 > -\text{CN} > -\text{COOR} > -\text{Cl} > -\text{CH}_2\text{X} > -\text{OCOCH}_3 > -\text{OR}$. The effect of a second 1-substituent is roughly additive. 2-Chlorobutadiene (table 6) and 2,3-dichlorobutadiene (table 7) are the most reactive monomers examined. A methyl group usually increases reactivity (methyl methacrylate $>$ methyl acrylate, methacrylonitrile $>$ acrylonitrile, methallyl $>$ allyl derivatives) and two chlorine atoms are nearly as effective as a

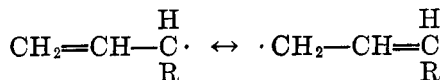
¹⁶ In the light of copolymerization data, some of the conclusions drawn from direction of addition may need revision (*cf.* Section III,J).

carbalkoxy group. Some of these conclusions were first published by Nozaki (153) from single experiments at 1:1 feeds.

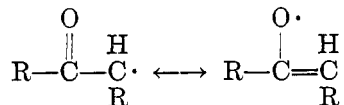
This order is in good accord with the order of stability of the resulting radicals which would be expected on the basis of the number and importance of contributing resonance structures, and with known bond strengths. We may now use these results to correlate radical stabilities with the number and probable contributions of the resonance structures which can be written for them. Thus, considering only the contribution of nonpolar forms, the benzyl radical can be written with four structures with the free valence on the α , ortho, or para carbon atoms,



However, as pointed out by Alfrey and Ebelke (5), when steric hindrance prevents the side chain from lying in the plane of the benzene ring, these resonance possibilities are severely restricted. While a single *o*-chlorine atom *increases* the reactivity of styrene (*o*-chlorostyrene with styrene and methyl methacrylate in table 1, with butadiene in table 2), a second *o*-chlorine atom considerably *reduces* reactivity (2,6-dichlorostyrene with butadiene in table 2; pentachlorostyrene with styrene and methyl methacrylate in table 1). The allyl radicals formed from butadiene derivatives have two nearly equivalent forms and resonance stabilization is large:

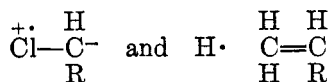


Radicals with conjugated carbonyl or nitrile groups are less stable with only two structures



of which the second, where a carbon atom has acquired an electron at the expense of oxygen or nitrogen, apparently makes the smaller contribution.

Halogen atoms and alkyl groups introduce smaller contributions from structures such as



Stabilization by acetoxy and ether groups appears smaller still, the stabilizing effect of the acetoxy group in vinyl acetate having been estimated by Flory and Leutner as about 1250 cal./mole (61) (*cf.* Section III,J).

Although Paton and Williams stated that the copolymerization of ethylene and acetylene yields a drying oil (155), the only quantitative data known to us on the copolymerization of acetylenes are those obtained by Doak in this Laboratory (49). The results in general (tables 6 and 7) indicate that phenylacetylene, diphenylacetylene, and 1-hexyne have the same order of reactivity toward free radicals as the corresponding ethylenes. The radicals formed from the acetylenes, however, are unreactive, so that poor polymer yields result.

The main section of table 6 brings out clearly the striking effects of conjugated unsaturated groups in activating monomers and stabilizing the radicals which result: except that the two chlorine atoms in vinylidene chloride are nearly equal to a single carbomethoxy group, all the conjugated monomers are considerably more reactive than any of the unconjugated monomers. On the other hand, conjugation with phenyl, vinyl, or carbonyl groups is known to stabilize

TABLE 10

Absolute rate constants for chain growth at 60°C. (in liters per mole per second)

MONOMER	RADICAL			
	Styrene	Methyl methacrylate	Methyl acrylate	Vinyl acetate
Styrene	176	789	11,500	~370,000
Methyl methacrylate	338	367		~250,000
Methyl acrylate	235		2,100	~37,000
Vinyl acetate	3.2	18.3	233	3,700

the reactant monomer as well, a phenomenon which should *reduce* reactivity. However, measurements of heats of hydrogenation (226) indicate that this stabilization amounts to only 2-4 kcal./mole, compared with perhaps 15 kcal. for the allyl radical (39), presumably because, in contrast to the radical structures just discussed, stabilization of the double bond involves structures with either charge separation or fewer numbers of bonds. Since the activated complex contains contributions from resonance forms of both the initial monomer and the new radical to be formed, it is entirely reasonable that resonance stabilization of this complex should be intermediate between the two.

Table 10 provides some quantitative support for this conclusion. This table gives absolute rate constants at 60°C. (in terms of moles per liter per second) for the reactions of four radicals with four monomers. The rate for each monomer with the radical from which it was derived is taken from measurements by Matheson, Auer, Bevilacqua, and Hart (121-124) in this Laboratory, and the remaining rates were then calculated from table 1. In this discussion, styrene will be taken as a representative monomer with high resonance stabilization;

vinyl acetate will be taken as a monomer without such stabilization; the other monomers occupy intermediate positions. Except for the alternating effect, the table shows that the conjugated styrene is 50–100 times as reactive as the unconjugated vinyl acetate toward any chosen radical. On the other hand, the unconjugated vinyl acetate radical is about 1000 times as reactive as the conjugated styrene radical with any one monomer. The effect of resonance in deactivating the radical is considerably greater than its effect in activating the monomer, as also follows from the fact that the rate constant for chain propagation in vinyl acetate alone is about twenty times that in styrene alone.

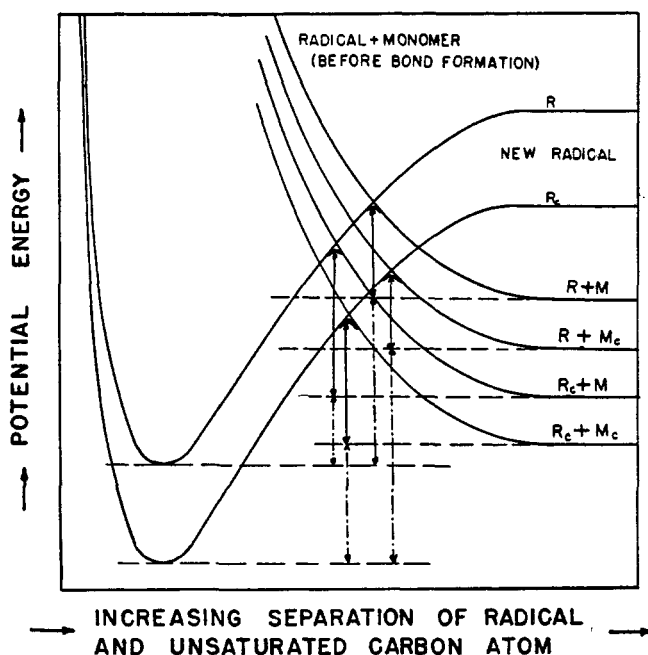
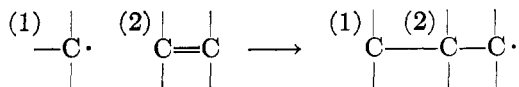


FIG. 20. Potential energy of system, monomer plus radical, as a function of separation of radical and unsaturated carbon atom. Subscript *c* indicates conjugation in monomer (*M*) or radical (*R*). Arrows with solid lines indicate energies of activation; broken lines indicate heats of reaction.

An illuminating discussion of the effect of resonance structures of radicals, monomers, and transition states on reaction rates has been given by Evans in terms of potential energy diagrams (54, 55). His treatment is based upon a model illustrated in figure 20. Here the potential energy changes accompanying attack of a free radical on a double bond are plotted as a function of the separation of carbon atoms 1 and 2:



The two sets of curves represent repulsion between the unbonded carbon atoms 1 and 2 and the extension energy of the final bond formed. At the intersection of the curves, the bonded and unbonded states are equally stable and the transition of one state to another may be facilitated by contributions of resonance to the activated complex, represented by curves below the intersections. When the necessary activation energy is made available, the unbonded reactants in their normal states are converted to the new normal bonded state with evolution of the heat of reaction. The heat of polymerization or copolymerization of a substituted ethylene differs from that of ethylene (taken as standard) because of loss of the resonance energies of the initial radical (R_A) and monomer (R_M), and gain of the resonance energy of the radical formed (R_F). Changes in the activation energy (E) accompanying changes in the heat of reaction (H) are then given by

$$\Delta E = \alpha \Delta H = \alpha(R_A + R_M - R_F) \quad (36)$$

where α is a factor less than unity, and the largest amount of heat liberated accompanies the lowest activation energy.

In order to confine our attention to resonance effects, in figure 20 each set of curves has arbitrarily been drawn parallel and the resonance stabilization of a monomer (if any) taken as one-half that in the resulting radical. From this figure and equation 36 it now follows that, of the initial *radicals*, those with the most resonance stabilization have the highest activation energy and slowest reaction because they lose their resonance energy (R_A) when they react; of the initial *monomers*, the conjugated have the lower activation energy because they gain some resonance energy (less the smaller resonance energy of the monomer) in conversion to a radical. These conclusions are consistent with the results in table 10, i.e.:

	—→ Decreasing heats ¹⁷ and rates of reaction —→			
Radical	Unconjugated	Unconjugated	Conjugated	Conjugated
Monomer	Conjugated	Unconjugated	Conjugated	Unconjugated
	—→ Increasing activation energy for reaction			

It is instructive to consider as well the representation of the alternating effect on a potential energy diagram (figure 21). If the potential curves for the reaction of a monomer and radical in the absence of polar effects are represented by a_1 and b , such electrostatic attraction between fixed charges on monomer and radical as occurs will lower the repulsion curve by an amount inversely proportional to the charge separation (assuming for simplicity a constant effective dielectric constant) to the curve a_2 . Mutual polarization, increasing as radical approaches monomer, will result in a further lowering to a_3 , while actual electron transfer will lead to a final marked rounding off in the region of the transition state (a_4).

¹⁷ In many actual systems, steric considerations also appear to influence heats; cf. Section III, I.

Evans, Gergely, and Seaman (55) have attempted to put the treatment of radical reactions in terms of potential energy diagrams on a quantitative basis. They have calculated activation energies for a number of radical addition and displacement reactions. Taking $\alpha = 0.4$ in equation 36 and assigning certain values to the resonance energies of the radicals and monomers, they have also calculated changes in heats of activation of the various reactions of ethylene, styrene, and butadiene. Their results are listed in table 11, together with the relative rates to be expected at 60°C. in the absence of changes in entropies of activation. The only point at which calculation may be compared with experiment is in the copolymerization of styrene-butadiene, where the respective monomer reactivity ratios are 0.4-0.8 and 1.4, in some agreement (considering the approximations involved) with the calculated values of 0.32 and 0.25, respectively. On the other hand, there is reason to doubt the values of R_M and R_A assigned.¹⁸ Unfortunately, as far as giving this sort of treatment a more general

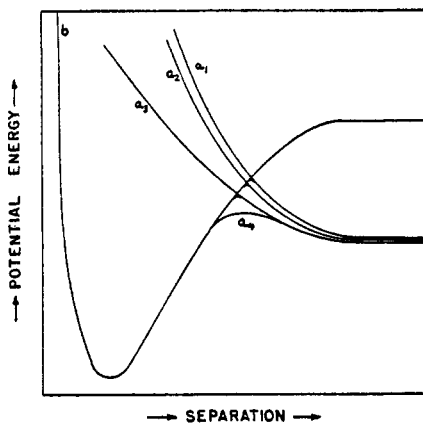


Fig. 21. Potential energy diagram of the alternating effect

test, there seems to be no reliable method, at present, of making independent determinations of resonance stabilization of the radicals derived from most common monomers.

All the foregoing discussion has emphasized the importance of resonance stabilization of the transition state in determining the behavior of monomers. A particularly interesting phenomenon, apparently involving steric inhibition of such resonance, is considered in the next section.

G. DIFFERENCES BETWEEN *cis* AND *trans* ISOMERS

Marvel and Schertz (120) were the first to point out that dimethyl fumarate has considerably more tendency to enter a copolymer with *p*-chlorostyrene than

¹⁸ Heats of hydrogenation indicate values of R_M for styrene and butadiene of 0.7 and 3.5 kcal. (226). The corresponding values of R_A may be estimated as 11.4 and 15 kcal. from pyrolysis rates of methyl, benzyl, and allyl iodides (39).

has dimethyl maleate. To determine the generality and significance of this difference, copolymerizations of a series of geometrical isomers with several monomers were carried out by Lewis and Mayo (106). The essential results are summarized in table 12. If it is assumed that a free radical has either a planar or an easily reversible pyramidal configuration, the addition of a reference radical

TABLE 11

Calculated changes in activation energies and rates in some copolymerizations

(Relative rates at 60°C. given in parentheses*)

MONOMER (R_M)	RADICAL		
	Ethylene ($R_A = 0$)	Styrene ($R_A = 21.2$)	Butadiene ($R_A = 19.1$)
Ethylene (0).....	0 (1)	12.4 (9×10^{-3})	12.0 (1.6×10^{-3})
Styrene (9.7).....	-4.60 (370)	3.91 (1.6×10^{-3})	2.99 (5.6×10^{-3})
Butadiene (10.8).....	-3.22 (125)	5.06 (5×10^{-4})	4.37 (1.4×10^{-3})

* A statistical factor of 2 has been introduced for the two symmetrical monomers. Resonance energies of monomers (R_M), radicals (R_A), and activation energies are expressed in kcal./mole.

TABLE 12

Comparison of *cis* and *trans* isomers in copolymerization

REFERENCE RADICAL	ISOMER PAIR R IN RHC=CHR	MORE REACTIVE ISOMER ^(a)	LESS STABLE ISOMER	PLANAR <i>cis</i> FORM HINDERED
Styrene.....	-COOC ₂ H ₅	<i>trans</i> (21)	<i>cis</i>	+
Styrene.....	-COOCH ₃	<i>trans</i> (20-40)	<i>cis</i>	+
Styrene.....	-COOC ₂ H ₅ , -COOH ^(b)	No significant differ- ence	<i>cis</i>	-
Styrene.....	-CN		<i>cis</i>	-
Styrene.....	-Cl	<i>trans</i> (6)	<i>trans</i>	-
Vinyl chloride.....	-COOC ₂ H ₅	<i>trans</i> (6.5)	<i>cis</i>	+
Vinyl acetate.....	-COOC ₂ H ₅	<i>trans</i> (15)	<i>cis</i>	+
Vinyl acetate.....	-Cl	<i>trans</i> (6.5)	<i>trans</i>	-
Maleic anhydride.....	-C ₆ H ₅	<i>trans</i> (1.5-2.0) ^(c)	<i>cis</i>	+

(a) Ratio of activities of two isomers toward reference radical.

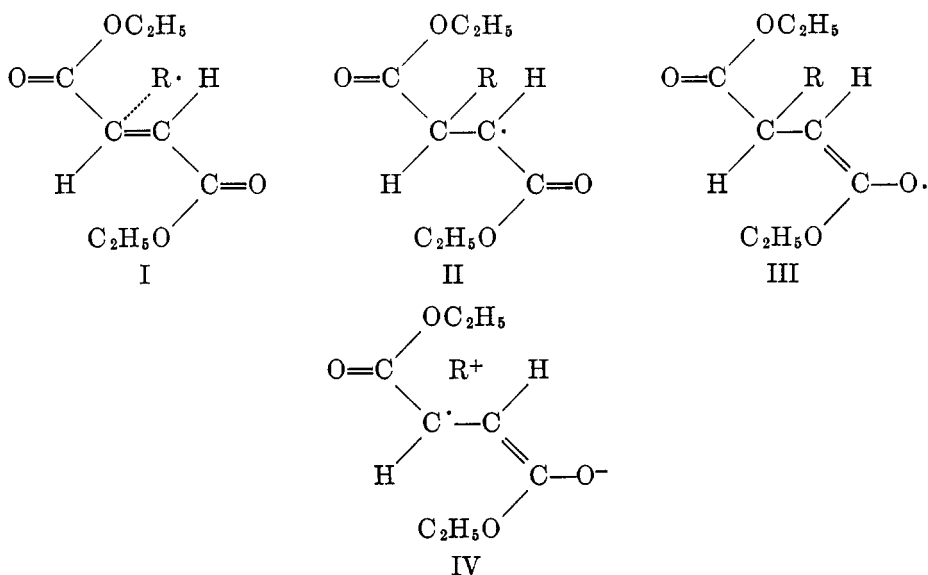
(b) Half-esters of maleic and fumaric acids.

(c) From rates of polymerization.

to either geometric isomer of a pair should lead eventually to the same free radical, a conclusion supported by evidence that vinyl acetate-1,2-dichloroethylene copolymers made from the *cis* and *trans* isomers have the same steric configuration (134). If this conversion occurs simultaneously with addition, the discussion of the previous section suggests that in general the less stable, energy-rich isomer of a pair should be the more reactive. For the dichloroethylenes, of

which the *cis* isomer is the more stable, this expectation is realized. On the other hand, although the ratio of fumaronitrile to maleonitrile in their equilibrium mixture (106) is about 3, they show no difference in reactivity. Here the structures of the transition states are apparently related to those of the monomers, and conversion to the same radical, if it occurs, takes place subsequently.

More interesting results, however, are obtained on comparing the behavior of the dialkyl fumarates and maleates. Here the more stable fumarates turn out to be 6- to 40-fold more reactive. This surprising result has been ascribed to steric inhibition of resonance (106, 130). Thus, when a radical, $R\cdot$, adds to these monomers, the activated complex can be stabilized by resonance between forms I-III only if the oxygen of the carbonyl group lies in the same plane as the atoms attached to the doubly bound carbon atoms.



Consideration of models shows that the two ester groups in maleic esters cannot be coplanar simultaneously and that a coplanar configuration for either is not very probable. In the fumaric esters, there is no interference between the ester groups and either or both may be coplanar. Accordingly, more of the fumarate molecules should be in a form such that, on collision with a radical, the activated complex can be immediately formed, at one or either carbon atom of the double bond, at the lowest cost in activation energy. Since the difference between the maleic and fumaric esters increases with the donor ability of the reference radical, i.e., with the alternation tendency of the reference monomer, it may also be that contributions of resonance forms such as IV (see also Section III,E), in which the reference radical has donated an electron to the ester, may serve to increase the difference between the stereoisomeric forms. These explanations are supported by the fact that maleic anhydride is at least 7-8 times as reactive as diethyl fumarate toward the styrene radical (table 6): in the anhydride, both carbonyl groups must always be in the coplanar position favorable to maximum

reactivity. Price (157) has proposed that purely steric effects can account for the above differences, without considering resonance.

In contrast to the full esters, the half-esters show little difference in reactivity, although the differences in their energy contents are probably comparable. Here, however, there is less interference between substituents to be expected, and a planar configuration may possibly be favored by hydrogen bonding between carboxyl and ester groups within the same molecule.

The stilbenes are analogous to the dialkyl esters just discussed: Only one phenyl group at a time in the *cis* form can lie in the plane of the double bond, but both phenyl groups of the *trans* form may have the favorable coplanar configuration. It may be significant that the *trans* form is just about twice as reactive as the *cis*.

H. THE EFFECT OF TEMPERATURE ON MONOMER REACTIVITY RATIOS

Our discussion of the relation between structure and reactivity has so far assumed a direct relation between relative rates and differences in heats of activation, i.e., that the entropies of activation for the attack of a radical on a series of monomers are the same. Since monomer reactivity ratios represent ratios of rate constants for pairs of such reactions, the correctness of the assumption may be determined by the measurement of their temperature dependence through the relation:

$$r_1 = e^{(\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger)/R} e^{-(\Delta H_{11}^\ddagger - \Delta H_{12}^\ddagger)/RT} \quad (37)$$

where ΔS_{11}^\ddagger , ΔH_{11}^\ddagger , ΔS_{12}^\ddagger , and ΔH_{12}^\ddagger are, respectively, the entropies and heats of activation for the reaction of an $M_1\cdot$ radical with M_1 and M_2 .

Two series of such measurements have been carried out, one in this Laboratory (109) and another, more recently, by Goldfinger and Steidlitz (76). Data are summarized in table 13. Monomers are paired according to the combinations used in the experimental work and the monomer reactivity ratios given in each line are those for the radical corresponding to the indicated monomer in the indicated pair. As well as heat and entropy of activation differences, ratios of *PZ* factors are also included as an aid in visualizing the magnitude of any "steric" effect.

The first set of data shows that, in spite of the care used in making these measurements, the effects of temperature are small, and the experimental uncertainty is relatively large. In every case, the monomer reactivity ratio slowly approaches unity as the temperature rises, showing that a small difference in activation energy is the principal factor determining relative reactivities. The only clear case where the entropy difference is significant is in the reaction of the fumarate radical with fumarate and with styrene, the difference lying in the direction to be expected if the second ester group in the ester hindered reaction with the fumarate radical. A similar effect would be anticipated with the styrene radical in copolymerizations with both fumarate and maleate; although the observed effect is in the right direction, it is hardly significant.

The data of Goldfinger and Steidlitz (76) lead to different conclusions with three other pairs of monomers. They find rather large and unpredictable entropy

TABLE 13
Heat and entropy of activation differences in the copolymerization of some monomer pairs

RADICAL TYPE ^(a)	τ_1		$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger}$ cal./mole	$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger}$ E.U./mole	$P_{11}Z_{11}/P_{12}Z_{12}$
	60°C.	131°C.			
Styrene ^(b) Methyl methacrylate	0.520 ± 0.026	0.590 ± 0.026	480 ± 250	0.12 ± 0.68	1.06 ± 0.30
	0.460 ± 0.026	0.536 ± 0.026	580 ± 280	0.19 ± 0.76	1.10 ± 0.34
Styrene ^(b) Methyl acrylate	0.747 ± 0.028	0.825 ± 0.005	380 ± 140	0.54 ± 0.36	1.31 ± 0.16
	0.182 ± 0.016	0.238 ± 0.005	1020 ± 340	0.66 ± 0.86	1.39 ± 0.49
Styrene ^(b) Diethyl malceate	6.52 ± 0.05	5.48 ± 0.56	-660 ± 480	1.87 ± 1.36	2.55 ± 1.26
	<0.01				
Styrene ^(b) Diethyl fumarate	0.301 ± 0.024	0.400 ± 0.014	1070 ± 320	0.82 ± 0.82	1.50 ± 0.50
	0.0697 ± 0.0041	0.0905 ± 0.0008	990 ± 290	-2.35 ± 0.73	0.31 ± 0.14
Styrene ^(b) <i>p</i> -Chlorostyrene	0.742 ± 0.030	0.816 ± 0.015	360 ± 170	0.48 ± 0.43	1.27 ± 0.24
	1.032 ± 0.030	1.042 ± 0.015	35 ± 120	0.40 ± 0.32	1.22 ± 0.18
Styrene ^(c) Dichlorostyrene ^(d)	0.19 ± 0.03 ^(c)	0.32 ± 0.02 ^(c)	4100 ± 900(950) ^(c)	7 to 12.7	33 to 570
	0.22 ± 0.04	0.08 ± 0.02	-8300 ± 2200(2200)	-23.1 to -36.2	10 ⁻⁸ to 10 ⁻⁶
Styrene ^(c) Acrylonitrile	0.37 ± 0.015	0.46 ± 0.02	1400 ± 200(400)	1.4 to 3.8	20 to 66
	0.04 ± 0.01	0.03 ± 0.01	-2300 ± 500(<-1800)	<-12.3	<0.002
Dichlorostyrene ^(c, d) Acrylonitrile	0.09 ± 0.01	0.07 ± 0.02	-3200 ± 100(3300)	-5.0 to -21.6	2 × 10 ⁻⁶ to 0.06
	0.26 ± 0.01	0.21 ± 0.02	-1100 ± 300(1000)	-3.4 to -9.3	0.009 to 0.18

(a) Each monomer of the pair being considered as M₁ in turn.

(b) From reference 109.

(c) From reference 76.

(d) Presumably 2,5-dichlorostyrene.

effects, and, for four of the six monomer reactivity ratios studied, heats and free energies of activation are actually different in sign. Since the two investigations lead to such different conclusions it seems reasonable to compare them more closely. Apparently the experimental accuracy of the two studies (judged by the size of the intersections in the graphical solution of the copolymerization equation) is comparable,¹⁹ and while the first employed more experiments per system, the latter made measurements at three rather than two temperatures. However, quite different methods of estimating experimental error were employed in the two studies. Lewis *et al.* employ the standard deviation of duplicate experiments at each temperature and discuss the question of error at some length (109). Goldfinger and Steidlitz take the deviation of the "best" values of r_1 and r_2 at each temperature from the best straight line on a $\log r$ vs. $1/T$ plot (76). Since these values of r are in turn uncertain, and this uncertainty is not taken into account, this leads to a considerably smaller estimate of experimental error. In order to make the assigned uncertainties in the two sets of data comparable, errors in the Goldfinger and Steidlitz experiments have been recalculated, taking as the experimental error at each temperature the radius of the largest inscribed circle in the triangles obtained on an r_1 - r_2 plot (*cf.* Section II,C). The resulting range is indicated in parentheses in table 13. However, although this treatment suggests a considerably larger uncertainty in the magnitude of the heat and entropy of activation differences obtained from the experiments of Goldfinger and Steidlitz, the general conclusions remain the same.

The question of the importance of entropy effects is thus unsettled, and until more data on the variation of monomer reactivity ratios with temperature are available, any quantitative discussion of the relation between resonance and polar phenomena, on the one hand, and relative reactivities on the other, is built upon a dubious foundation. Resolution of this problem seems particularly difficult. First, measurements of temperature coefficients require extreme care. If the monomer reactivity ratios are close to unity, they can be measured accurately, but the change with temperature is usually small; if they differ greatly from one, they cannot be determined with precision. Second, in copolymerization, the ratio of the highest to the lowest known monomer reactivity is of the order of only 100 or 1000 to 1, and arises from a maximum difference of 3-5 kcal./mole in free energy of activation. Nevertheless, this difference is responsible for the widest possible differences in copolymer compositions. The result is that copolymerization work is fruitful in finding subtle differences in radical-monomer reactions; it may therefore be a field in which more reliable predictions than the semi-quantitative ones discussed earlier should be nearly impossible.

I. STERIC HINDRANCE; THE REACTIVITIES OF THE 1,2- AND 1,1-DISUBSTITUTED ETHYLENES

In general, both steric hindrance and changes in entropies of activation are associated with the introduction of bulky groups into a molecule near the point

¹⁹ On the other hand, the data of Goldfinger and Steidlitz on styrene-dichlorostyrene are in sharp disagreement with those of Alfrey, Merz, and Mark (18); one or the other group of investigators must be seriously in error.

at which it reacts. Thus, introduction of a 2-substituent into a 1-substituted monomer might be expected to decrease its reactivity in copolymerization, and an additional 1-substituent might decrease the reactivity of the corresponding radical. The effects of larger groups at a greater distance from the site of reaction are small and not certainly significant. Chapin, Ham, and Mills (43) found that the relative reactivities of vinyl formate, acetate, and 2-ethylhexanoate toward the acrylonitrile radical decreased as the chain length of the ester increased (although the benzoate was slightly more reactive than the acetate). On the other hand, Agron, Alfrey, Bohrer, Haas, and Wechsler (1) found no significant difference in the reactions of methyl, ethyl, and butyl methacrylates with vinylidene chloride.

The effect of 2-substituents is shown most clearly by comparing the reactivities of the chloroethylenes (10, 48). Figure 22 summarizes the relative reactivities of all the chloroethylenes toward the styrene, vinyl acetate, and acrylonitrile

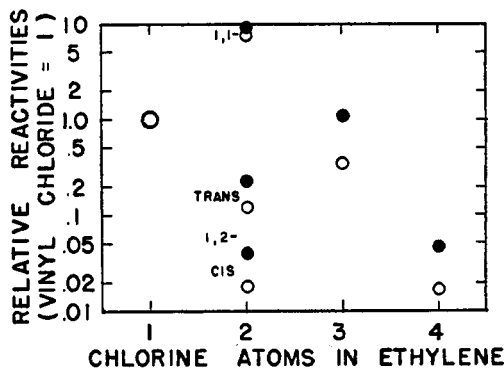


Fig. 22. Relative reactivities of chlorinated ethylenes toward the styrene radical (solid circles) and vinyl acetate radical (open circles).

radicals, the reactivity of vinyl chloride having been taken as unity in each series, and the reactivities of the perfectly symmetrical derivatives having been divided by two since they have two equally probable sites of reaction. An additional 1-substituent in vinyl chloride increases reactivity, because of the resonance effect on general activity mentioned previously, but 2-substitution materially decreases reactivity 5- to 50-fold. It is hard to see how this effect can be other than steric, since the additional substituent is located at the point of attack in the monomer, and since resonance explanations are inadequate (130). Comparison of trichloroethylene with vinyl chloride shows that the effects of the 1- and 2-substituents nearly offset each other. Similarly, in the ester series, table 6 shows that the double bond of diethyl fumarate is only 1/25 as reactive as that of methyl acrylate towards the vinylidene chloride radical. Comparison of *cis* and *trans* isomers and maleates and fumarates in particular (Section III,G) has already suggested another kind of steric effect of 2-substituents, also tending to decrease reactivity.

Results in both the halogen and the ester series are complicated by the fact that both these substituents, while introducing steric hindrance, also increase the acceptor properties of the double bond: the relative reactivities of the more chlorinated ethylenes are highest with the styrene and vinyl acetate radicals, the strongest donors, and lowest with the acrylonitrile radical, the poorest. Data on alternation tendencies point in the same direction. The r_1r_2 product for vinyl acetate and vinyl chloride is 0.38, while the products for vinyl acetate with the three dichloroethylenes are 0.11 or less. In the ester series, the polar effect is even larger. Here we are dealing with monomers having high alternation tendencies with electron-donating radicals, and the effect of the 2-substituent in increasing alternation tendency may equal its steric and retarding effect. Diethyl fumarate is twice as reactive as methyl acrylate toward the styrene radical and ten times as reactive toward the vinyl acetate radical; fumaronitrile is twice as

TABLE 14
Heats of polymerization and hydrogenation

MONOMER	-ΔH		REFERENCES
	Polymerization	Hydrogenation ^(a)	
	<i>kcal./mole</i>	<i>kcal./mole</i>	
Styrene.....	16.1, 16.7	28.6	(167, 199)
Methyl acrylate.....	18.7, 20.2		(56, 200)
Ethylene.....	22.3 ^(c)	32.8	(89)
Vinyl acetate.....	21.3	31.1	(200)
Acrylonitrile.....	17.3		(200)
Propylene.....	16.5 ^(b)	30.1	(62)
Methyl methacrylate.....	12.9, 13.0, 11.6	28.6	(52, 56, 198)
Vinylidene chloride.....	14.4		(200)
Isobutylene.....	12.8 ^(b)	28.4	(52)

^(a) Of ethylene bond at 82°C. (45).

^(b) For the low-temperature, acid-catalyzed polymerization.

^(c) Gaseous monomer to gaseous polymer.

reactive as acrylonitrile toward the styrene radical. When these ratios are divided by two, for two equivalent sites of reaction, the net effect of the second substituent is rather small.

That the possibility of steric hindrance to polymerization arises in the case of the 1,1-disubstituted ethylenes was suggested by Evans and Polanyi (52), and is supported by data on heats of polymerization, such as those of table 14, which indicate that heats of polymerization of monosubstituted ethylenes average about 18 kcal./mole, compared with 13 kcal. for those which are disubstituted. Since these differences are considerably greater than the differences in heats of hydrogenation of the corresponding monomers, they cannot be due only to conjugation in the monomers.

The possibility that such hindrance might be important in copolymerization was suggested to us in this Laboratory by a study of molecular models, and was

early proposed as a factor contributing to alternation (107). In this connection Tong and Kenyon have recently reported a study of heats of copolymerization (201). These investigators find that the heat of copolymerization of isopropenyl acetate-maleic anhydride (which form an alternating 1:1 copolymer) has the value of 17.8 kcal./mole. This result, while lower than the heat of copolymerization of vinyl acetate-maleic anhydride (20.2 kcal./mole), is still in the range of monosubstituted polymers, so that it is not clear whether separation of the isopropenyl acetate units by maleic anhydride residues (which, while disubstituted, are planar and compact) is effective in reducing steric hindrance.

Steric hindrance might serve to explain some of the inconsistencies in table 5, e.g., the fact that vinyl acetate alternates more than styrene with vinylidene chloride and diethyl fumarate, but less with vinyl chloride and acrylonitrile. If we assume that the phenyl group is a larger group, but a better electron donor than the acetoxy group, we might expect styrene to alternate better with small monosubstituted electron-accepting monomers, vinyl acetate with disubstituted ones. The same kind of reasoning may account for the very high alternation tendency between vinyl acetate, a small monomer, and trichloroethylene, a monomer too large to polymerize by itself; for the high alternation tendency of α -methylstyrene as compared to styrene; and also for the low alternation tendency between vinylidene chloride and diethyl fumarate, where the trisubstituted vinylidene chloride radical prefers not to react with the 1,2-substituted monomer.

Finally, it may be noted that, for the disubstituted monomer methyl methacrylate, not only is the heat of polymerization low, but it has a low entropy of activation for the chain-growth reaction. According to Matheson *et al.* (121), the *PZ* factor for chain growth has a value of 5.13×10^6 , compared with 1.93×10^9 for the chain growth of styrene. On the other hand, from table 12, entropy of activation differences for the reactions of either of these radicals with the two monomers are negligible. Thus, the frequency factors are here associated with the radicals alone, and seem little affected by the monomer being attacked.

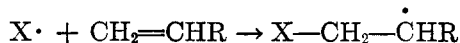
J. STRUCTURE AND REACTIVITY IN OTHER RADICAL REACTIONS

1. Addition of free radicals to double bonds

As we have seen in the preceding sections, the quantitative data provided by copolymerization studies on relative reactivities of olefins towards a number of radicals have led to several new conclusions on the relation between structure and reactivity in the addition of polymer radicals to double bonds. Of these, the most striking is the importance of the alternating or polar effect, the increased rate of reaction of electron donor radicals with acceptor molecules, and *vice versa*. Another is the importance of steric hindrance in determining reaction rates, and the purpose of this section is to consider the application of these ideas to some other radical reactions.

The radical reaction most resembling the chain propagation step in copolymerization is the step in the free-radical ("peroxide-catalyzed") addition of hy-

drogen bromide, halogens, mercaptans, carbon tetrachloride, etc. to olefins, in which a radical or atom adds to the double bond:



The possibility of a polar effect in this reaction was first suggested by Price (157) and has been considered recently by Evans, Gergely, and Seaman (55). Direct evidence was obtained by Walling, Seymour, and Wolfstirn (222), who compared the reactivity of a series of α -methylstyrenes towards the $\cdot\text{S}-\text{CH}_2-\text{COOH}$ radical derived from thioglycolic acid. Since the effect of substituents paralleled those observed on reactivity towards maleic anhydride rather than to-

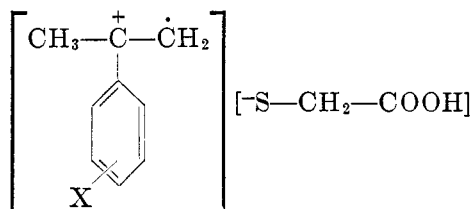
TABLE 15

Relative reactivities of α -methylstyrenes toward thioglycolic acid- and maleic anhydride-type radicals

SUBSTITUENT	REACTIVITIES TOWARD INDICATED RADICAL		
	Thioglycolic acid	Maleic anhydride	Styrene*
<i>p</i> -OCH ₃	215 ± 100	18.5	0.86
<i>p</i> -CH ₃	2.28 ± 0.54	1.72	
None.....	1.00	1.00	1.00
<i>p</i> -F.....	0.51 ± 0.13	0.72	
<i>p</i> -Br.....	0.90 ± 0.56	0.73	1.44
<i>m</i> -Br.....	0.96 ± 0.56	0.96	1.82

* Nuclear-substituted styrenes toward unsubstituted styrene radical, all without α -methyl groups.

wards styrene (table 15), it was concluded that the R-S· radical belonged to the extreme electron-acceptor class and that forms such as



must be important in the transition state.

Since most of the other radicals which undergo chain addition to double bonds, e.g., Cl·, Br·, HSO₃·, CCl₃·, should readily accept an electron to yield stable corresponding negative ions, it seems reasonable to expect that relative reactivities of olefins in all these radical reactions should be determined largely by their donor properties. Some data of Kharasch and Sage on relative reactivities toward the trichloromethyl radical (97) support this concept: 1-octene > 4,4,4-trichloro-1-butene; allylbenzene > allyl chloride > allyl cyanide;

β -methylstyrene > ethyl cinnamate, but most of the comparisons of two olefins by competitive addition (92, 97) have involved hydrocarbon substituents in which donor ability and resonance stabilization of the resulting radical run in the same direction.

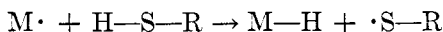
The importance of the steric effect in copolymerization now suggests that this factor should be considered in addition reactions. Identification of the products formed in the radical ("abnormal") addition of hydrogen bromide, mercaptans, bisulfite (132), and several polyhalomethanes (95, 96, 126) has shown that, in all known cases, attack on a 1-substituted ethylene occurs at the 2-position, and this choice, in turn, has been considered as decided by the relative resonance stabilization of the radicals formed (132, 227). However, it now appears likely that the resonance effect alone is inadequate to account for addition reactions to aliphatic olefins which yield 99 per cent or more of the primary derivative. Thus, although pyrolyses of alkyl iodides suggest that alkyl radicals are stabilized by at least 2-3 kcal. per substituent (39), comparison in table 6 of the reactivities of styrene, acrylonitrile, and methyl acrylate with α -methylstyrene, methacrylonitrile, and methyl methacrylate indicates that introduction of a methyl group increases reactivity by a factor of only about 2. On the other hand, comparison of the relative reactivities of the chloroethylenes (figure 22) shows that a chlorine atom (which is comparable in size to a methyl group) at the site of radical attack introduces enough steric hindrance to decrease reactivity 5- to 50-fold. The data of Kharasch and Sage (97) on relative reactivities toward trichloromethyl radicals also bring out the deactivating effect of a 2-substituent on a 1-substituted ethylene, β -methylstyrene being only one-hundredth as reactive as styrene and cyclohexene one-fifth as reactive as 1-octene. Apparently both the resonance and steric factors (which work together in all known cases) are required to produce a strongly directed addition. The same conclusion was recently reached by Flory and Leutner (61), who measured the amount of head-to-head addition in the polymerization of vinyl acetate. They found that the proportion of 1,2-glycol units (head-to-head) in polyvinyl alcohol varied from 1.23 per cent in alcohol derived from polyvinyl acetate made at 25°C. to 1.95 per cent in 110°C. polymer. They conclude that the strongly directed head-to-tail addition results from a combination of a frequency factor higher by a factor of 10 and an activation energy lower by 1250 cal./mole than for the corresponding head-to-head reaction. The course of reaction is governed mostly by the lower activation energy below 0°C. and by the higher frequency factor above that temperature.

For radical addition to some unsymmetrically substituted olefins, radical stabilization by substituents as judged from copolymerization data (phenyl > carbalkoxyl > halogen > alkyl > hydrogen; *cf.* table 6) accounts satisfactorily for the observed directions of addition. Thus, with hydrogen bromide, 1-chloro- and 1-bromo-propenes yield the 1,2-dihalopropenes (132); ethyl crotonate yields ethyl β -bromobutyrate (132); β -bromostyrene yields α,β -dibromostyrene (196); with mercaptans, styrene (132) and methyl acrylate (93) yield the β -thioethers

(although a steric effect must be active as well in the last two examples),²⁰ and with bromotrichloromethane (97) β -methylstyrene yields 1-phenyl-1-bromo-2-methyl-3,3,3-trichloropropane and ethyl cinnamate yields ethyl β -phenyl- β -bromo- α -trichloromethylpropionate.

2. Reactivities of radicals with butyl mercaptan

The radical-chain reactions discussed above, by which molecules are added to double bonds, differ from polymerizations in that they involve, besides the radical addition step which occurs in both reactions, a radical displacement (chain transfer) step as well; e.g., for chain transfer with mercaptans:



From a comparison of the rates of reaction of a number of radicals with *n*-butyl mercaptan, obtained from chain transfer constants and absolute rates of chain

TABLE 16

Relative rates of reaction of butyl mercaptan, acrylonitrile, and styrene with polymer radicals at 60°C.

(Rate of reaction with styrene radical = 1)

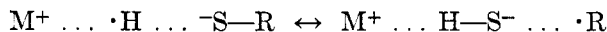
RADICAL	$k_p^{(a)}$	$C^{(b)}$	C ₄ H ₉ SH	CH ₂ =CHCN ^(c)	C ₆ H ₅ CH=CH ₂ ^(c)
Styrene.....	176	22	1.0	1.0	1.0
Methyl methacrylate..	367	0.67	0.08	0.64	4.6
Methyl acrylate.....	2100	1.53	1.0		61
Vinyl acetate.....	3700	48	57	160	1070

^(a) Rate constant for propagation step in polymerization, from Matheson *et al.* (121-124).

^(b) Transfer constant of mercaptan, from reference 211.

^(c) From table 6.

growth (somewhat expanded in table 16), one of us (211) has suggested that polar phenomena play a role in such displacement steps as well. The radicals are listed in order of increasing general reactivity and the notable feature of the table is the low rate of reaction of the carbonyl-conjugated radicals. For comparison, relative rates of addition of the radicals with acrylonitrile (an acceptor) and styrene (a donor-type monomer) have been included. Since the mercaptan resembles acrylonitrile in its relative reactivity, it seems probable that polar forms of the type,



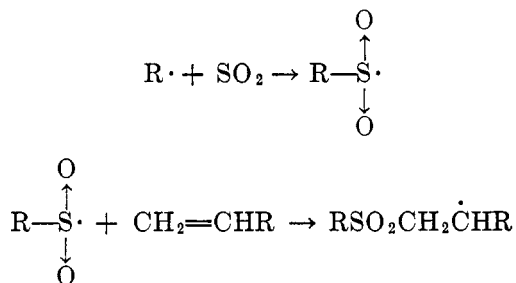
in which an electron has been transferred from the monomer radical to the mercaptan, contribute to the transition state, and that contributions from such

²⁰ Products obtained on addition of hydrogen bromide to cinnamic acid (β -bromocinnamic acid) and to bromomaleic and bromofumaric acids (α,β -dibromosuccinic acids) in the presence of peroxide are not in accord with this order, but there is reasonable doubt that these products resulted from a radical reaction (132).

polar structures reduce the activation energies of both of the two alternating steps in the free-radical addition of reagents to double bonds.²¹

3. "Copolymers" of oxygen or sulfur dioxide with olefins

Two reactions which bear a strong resemblance to olefin copolymerizations (157) are the formation of linear polymers of olefins with sulfur dioxide and with oxygen. The radical nature of the former appears well established by the catalytic effect of ultraviolet light, peroxides, and oxidizing agents and inhibition by phenolic materials (185), although the kinetics are complicated by a "ceiling temperature" effect (185, 186), perhaps arising from easy reversibility of one of the steps:



The observation that sulfur dioxide readily forms 1:1 copolymers with aliphatic olefins (171, 185, 187) and such materials as allyl ethers and allylacetic acid (171), but not with ethyl crotonate, crotonaldehyde, or methyl acrylate (171, 187, 190), suggests that both the $\text{RSO}_2\cdot$ radical and sulfur dioxide itself possess strong acceptor properties, the former to yield in the transition state the sulfinate ion, and the latter a number of resonance structures of the type $[\ddot{\text{O}}:\ddot{\text{S}}:\ddot{\text{O}}:]^-$. It is of interest that the two monomers yielding copolymers containing more than one mole of olefin unit per mole of sulfur dioxide are styrene (49), with a very reactive double bond, and vinyl chloride (114), with little tendency to donate an electron.

Similarly, linear copolymers with oxygen have been obtained with 1,1-diphenylethylene (188), styrene (189), diphenylketene (188), and conjugated dienes (57), while methyl methacrylate yields short chains with considerable hydroperoxide formed by chain transfer (23), a result which has been ascribed by Price (157) to the electron-accepting properties of the $\text{R}-\text{O}-\text{O}\cdot$ radical. The rate of absorption of oxygen by polymerizing styrene has been investigated by Medvedev and Zeitlin (136). From their data it is possible to calculate that at 70–90°C. oxygen is almost 1000 times as reactive as styrene towards the styrene radical.

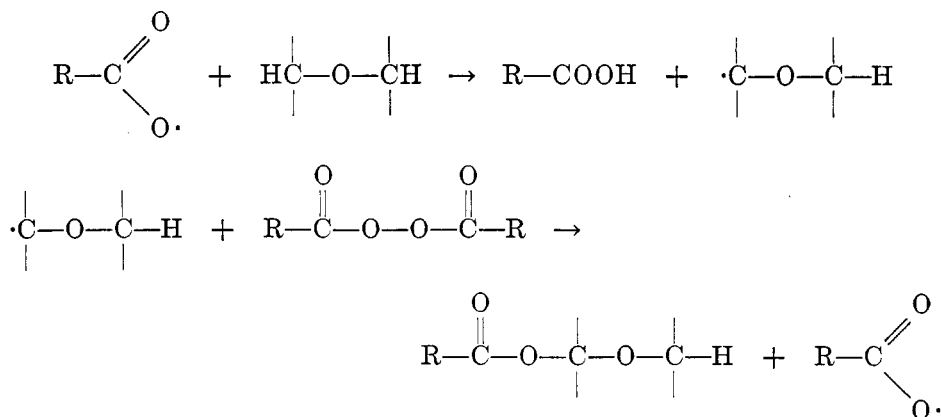
²¹ Qualitative data on the effect of substituents on the rate of radical addition of hydrogen bromide to olefins yielding the order phenyl > alkyl > hydrogen > halogen (132) are consistent with this picture. The displacement reaction is probably the rate-controlling step, since it is slightly endothermic.

4. Other reactions

If we extend further the idea of the importance of electron donor or acceptor properties in the reactants to radical reactions in general, explanations appear for a number of other phenomena. Thus, although the α -carbon-hydrogen bond in esters and acids is readily attacked by alkyl radicals from decomposing peroxides²² in preference to other positions (94), free-radical chlorination using chlorine and light (142) or sulfuryl chloride (91) gives preferential substitution at other points along the chain. Similarly, although attack on a carbon-hydrogen or carbon-chlorine bond by alkyl radicals is greatly increased by halogen substitution in the same carbon (95, 112), such substitution decreases reactivity in radical halogenation (21, 81). Since both carbalkoxy and halogen should stabilize the resulting radical, a polar effect seems to be involved. The results became entirely reasonable if the chlorine atom is considered an extreme acceptor radical, since carbalkoxy and halogen should both decrease the acceptor properties of the carbon-hydrogen bond being attacked. In the case of attack by alkyl radicals, the same substituents may even increase reactivity by electron acceptance in the transition state.

A similar effect may explain the low transfer constant of the $\text{CCl}_3\text{CH}_2\text{-}\dot{\text{C}}\text{H}$ (C_6H_5) radical with carbon tetrachloride in comparison with longer-chain styrene radicals (126). The electron-withdrawing properties of the $\text{CCl}_3\text{-}$ group apparently decrease the donor properties of the benzyl carbon atom, presumably important in the transfer reaction.

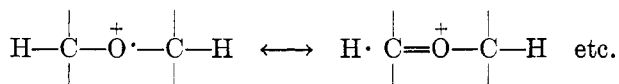
Another rather highly specific radical reaction is the rapid chain decomposition of benzoyl (and similar) peroxides by ethers, many alcohols, and amines. For ethers, the reaction appears to involve the chain (27, 41):



and similar chains seem to be involved in the other decompositions (27). Here we have a chain of two alternating radical displacement reactions, the first involving

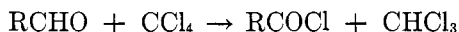
²² Or the alkyl portion of an acetoxy radical in the process of decarboxylation; *cf.* Mayo and Edwards (127).

an acceptor radical, with a stable negative ion, and a system easily able to lose an electron to give a variety of structures

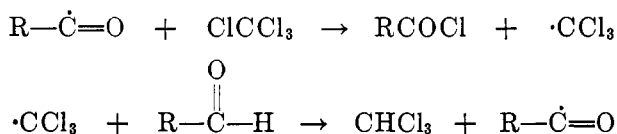


and the second involving a donor radical (*cf.* vinyl acetate and vinyl ether) and an acceptor system.

Another case of a chain of alternating displacement reactions is the reaction

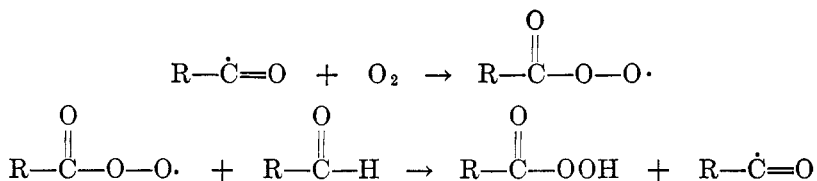


recently reported by Winstein and Seubold (231). Since it apparently involves the chain



in which $\text{R}-\overset{\cdot}{\text{C}}=\text{O}$ should be a donor radical (*cf.* the stability of $\text{R}-\overset{+}{\text{C}}=\text{O}$) and $\cdot\text{CCl}_3$ an acceptor, we again have a possible explanation for its easy course.

Similarly, the easy autoxidation of aldehydes with the chain



again involves one reactant with donor and the other with acceptor properties at each stage as does also the autoxidation of ethers and hydrocarbons. In the last case, incidentally, preferential attack at a benzyl or tertiary position gives both maximum donor properties and stabilization of the resulting radical.

Summarizing, the steps in known radical chain reactions appear quite regularly to involve interaction of electron-rich and electron-poor centers, and recognition of this fact should prove useful in the future in locating and interpreting further reactions of this type. Evidence for the participation of polar structures in the transition state of reactions involving radical coupling and bimolecular diradical formation is presented in the next section.

IV. OVERALL RATES OF COPOLYMERIZATION

A. DERIVATION OF EQUATIONS

In comparison with the study of copolymer compositions, copolymerization rates have received relatively little attention. The reason is chiefly the complexity of the problem; in addition to the four rate constants for chain growth, the overall rate involves, as well, at least three rate constants for chain termination

and a rate of chain initiation which may vary with the monomer ratio in the reaction mixture. As a result, with the exception of the measurements of Norrish and Brookman (149) discussions of copolymerization rates have, until very recently, been almost entirely qualitative (26, 129, 131) or have involved equations with many unknown rate terms (177). In the study of copolymer compositions, development of a feasible approach required the reduction of the four immeasurable rate constants for chain growth to two measurable ratios, the monomer reactivity ratios (*cf.* Section II,B). A similar simplification of the rate problem has been achieved by Melville, Noble, and Watson (138), employing essentially the same assumptions involved in the derivation of the copolymerization equation (equation 5).²³

Considering first the case of copolymerizations in which chain termination occurs by bimolecular interaction (coupling or disproportionation) of radicals, the overall rate is given by equations 3a, 3b, and 4, and the additional steady-state equation relating the rates of radical production and disappearance is

$$I = k_{t_1} [M_1 \cdot]^2 + 2k_{t_{12}} [M_1 \cdot] [M_2 \cdot] + k_{t_2} [M_2 \cdot]^2 \quad (38)$$

where I is the rate of production of kinetic chains, k_{t_1} the rate of termination of chains by interaction of two $M_1 \cdot$ radicals, etc. Solving equations 4 and 38 simultaneously for $[M_1 \cdot]$ and substituting into the sum of equations 3a and 3b yields

$$-\frac{d([M_1] + [M_2])}{dt} = \frac{(k_{21} k_{11} [M_1]^2 + 2k_{12} k_{21} [M_1][M_2] + k_{22} k_{12} [M_2]^2)(I)^{1/2}}{(k_{t_1} k_{21}^2 [M_1]^2 + 2k_{t_{12}} k_{21} k_{12} [M_1][M_2] + k_{t_2} k_{12}^2 [M_2]^2)^{1/2}} \quad (39)$$

similar to the overall rate expression of Simha and Branson (177, 178). Conversion of the rate constants to ratios employs the substitutions, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, $\delta_1^2 = k_{t_1}/k_{11}^2$, $\delta_2^2 = k_{t_2}/k_{22}^2$, $\phi = k_{t_{12}}/(k_{t_1} k_{t_2})^{1/2}$, and leads to the expression:

$$-\frac{d([M_1] + [M_2])}{dt} = \frac{(r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2)(I)^{1/2}}{(r_1^2 \delta_1^2 [M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [M_1][M_2] + r_2^2 \delta_2^2 [M_2]^2)^{1/2}} \quad (40)$$

Similarly, if chain termination is considered to occur by reaction with monomer, e.g., by chain transfer to produce an inactive radical, equation 38 may be replaced by

$$I = k_{tr_{11}} [M_1 \cdot][M_1] + k_{tr_{12}} [M_1 \cdot][M_2] + k_{tr_{21}} [M_2 \cdot][M_1] + k_{tr_{22}} [M_2 \cdot][M_2] \quad (41)$$

where $k_{tr_{12}}$ represents the rate constant for chain transfer of radical $M_1 \cdot$ with monomer M_2 , etc., and combination of equations 3a, 3b, 4, and 41 yields finally

$$-\frac{d([M_1] + [M_2])}{dt} = \frac{(r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2)(I)}{r_1 \lambda_1 [M_1]^2 + (\lambda_{12} + \lambda_{21}) [M_1][M_2] + r_2 [M_2]^2} \quad (42)$$

where $\lambda_{12} = k_{tr_{12}}/k_{12}$, etc. A similar expression for the rate of copolymerization for the case of "spontaneous" termination has also been obtained by Melville,

²³ The derivation given below is somewhat less general, but shorter, than that of Melville, Noble, and Watson (138); *cf.* Walling (212).

Noble, and Watson (138). However, although "spontaneous" termination may apply to copolymerization in the presence of an inhibitor, and termination by transfer occurs in systems containing allylic monomers which yield low-molecular-weight polymers (24, 25, 26), polymerizations in homogeneous media leading to *high-molecular-weight* polymers in general appear to involve bimolecular termination. Accordingly, discussion will be restricted to this case.

Here the seven rate constants for chain growth and termination have been reduced to five ratios and the relation is now susceptible to experimental test. r_1 and r_2 are determined from copolymer compositions, and δ_1 and δ_2 come from the rates of polymerization of the single monomers, leaving ϕ to be determined. ϕ is a measure of the cross-termination reaction, being the ratio of the rate constant for crossed termination to the geometrical mean of the rate constants for symmetrical termination.

B. MEASUREMENTS OF "CROSSED" TERMINATION

The first measurements of ϕ and tests of equation 40 were the recent ones of Walling (212), who used 2-azobisisobutyronitrile to obtain a constant rate of chain initiation from different monomer mixtures.²⁴ This approach avoided difficulties arising from changes in the rate of decomposition of benzoyl peroxide in different monomers (26, 129) and made relative, instead of absolute, rates of initiation sufficient for evaluation of ϕ .

Results for the systems styrene-methyl methacrylate and styrene-methyl acrylate are illustrated in figures 23 and 24, together with the calculated rate curves for $\phi = 1$ and for the choice of ϕ giving the best fit. The failure of the points to fit the curve with $\phi = 1$ is plain. For the other value, agreement is reasonable, all the points for the styrene-methyl methacrylate system, for example, being fitted by values of $6 < \phi < 19$. Since $\phi \gg 1$ in both systems, "cross" termination occurs several times as easily as the geometric mean of the symmetrical terminations.²⁵

Melville and coworkers have recently reported ϕ -values for styrene-methyl methacrylate at 30°C. as 14 or 30, depending on whether chain termination occurs by disproportionation or coupling (139a). For the system styrene-butyl acrylate ϕ is about 150 (20a); for styrene-*p*-methoxystyrene, $\phi = 1$ (137a); for methyl methacrylate-*p*-methoxystyrene, ϕ is about 20 (137a).

This ready coupling reaction between unlike radicals points to a polar effect like that responsible for the alternating tendency of the corresponding monomers. Polar interaction between radicals has been proposed by Lewis and Lipkin (111)

²⁴ 2-Azobisisobutyronitrile decomposes unimolecularly at the same rate in a number of solvents ($k = \sim 1.1 \times 10^{-5} \text{ sec.}^{-1}$ at 60°C.) (104). The efficiency of the fragments in starting chains appears close to 100 per cent in several monomers (121-124, 212).

²⁵ Two errors in this paper have kindly been pointed out to us by Dr. Leslie Valentine of the University of Birmingham (202). First, the correct value of δ_2 for methyl methacrylate is 11.7, not 1.76 (the correct value was actually used in the calculations). Second, the correct value of δ_2/δ_1 for styrene-methyl acrylate is 0.0385, not 0.0403. Recalculation of the data using this value yields an average value of $\phi = 50$ rather than $\phi = 40$, and figure 24 has been changed accordingly from that appearing in the original paper.

to account for the effect of substitution on the dissociation of tetraarylhya-zines, and mentioned also by Bartlett and Nozaki (27), who cited several ex-amples of the preferred union of unlike radicals. If the arguments of Section

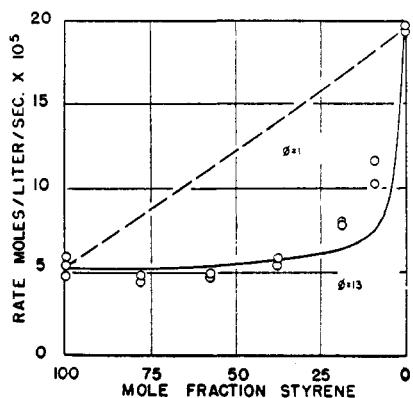


FIG. 23

FIG. 23. Rates of copolymerization of styrene-methyl methacrylate at 60°C. Catalyst, 1 g. of 2-azobisisobutyronitrile per liter.

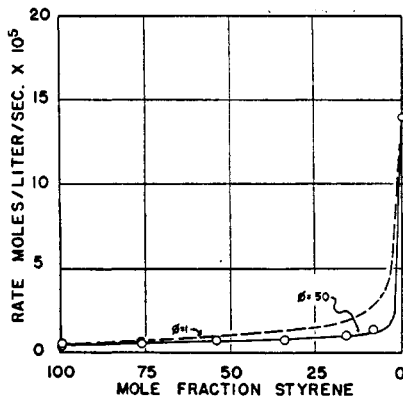
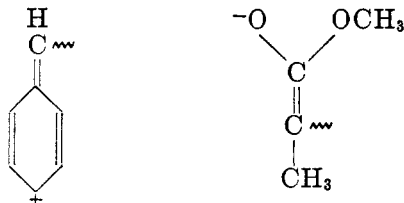


FIG. 24

FIG. 24. Rates of copolymerization of styrene-methyl acrylate at 60°C. (50 per cent total monomers in ethyl acetate plus 50 mg. of 2-azobisisobutyronitrile per liter).

III, E, 2 are correct, increased reactivity could arise from contributions to the transition state of forms such as



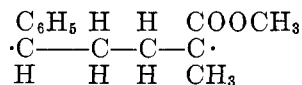
Since ϕ more or less parallels $1/r_1r_2$ as a measure of heightened reactivity (20a, 139a, 212), its larger value (e.g., 13 vs. 4 for styrene-methacrylate) indicates that, as might be expected, a radical is more easily polarized and more easily accepts or gives up an electron than a stable molecule.

C. "CROSSED" INITIATION

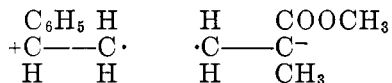
Determination of ϕ for the styrene-methyl methacrylate system permitted an estimate of the importance of a "crossed" initiation reaction in the *uncatalyzed* copolymerization. The rates of the bimolecular²⁶ uncatalyzed initiation reactions for these monomers are known (174, 214), and so the value of k_{i12} , the rate constant for cross initiation, may be obtained from a single experiment. Since

²⁶ The improbability on energetic grounds of unimolecular initiation was first pointed out by Flory (60) and is generally accepted.

three experiments at different feeds gave an average value 2.8 times that of the bimolecular initiation constant for styrene alone, 3000 times that for methyl methacrylate, and nearly 100 times the geometrical mean for the two monomers, a crossed initiation in this monomer pair is clearly favored over the symmetrical initiations. Paralleling our previous discussions, this tendency toward crossed initiation may also be ascribed (212) to the contribution of polar forms to the transition state, intermediate between the two monomers and the assumed biradical:



These additional resonance forms arise from transfer of an electron from the styrene monomer to the methyl methacrylate monomer and include many variations of



Such an interpretation suggests that the greater initiation constant of styrene compared with methyl methacrylate may arise from its "amphoteric" character. Since both benzyl carbanions and carbonium ions present possibilities for resonance, electron transfer between two styrene molecules may take place to yield a number of ionic resonance structures. It also suggests that thermal initiation of polymerization between strong donor and acceptor molecules, e.g., styrene-maleic anhydride, should be even easier. In practice, the difficulty of preventing copolymerization of such mixtures is well known, although the increased ease of reaction involves, too, the high rate of the chain-growth reaction. Since in copolymerization butadiene rather closely resembles styrene (*cf.* tables 5 and 6), rapid thermal initiation might be expected in mixtures of butadiene with carbonyl or nitrile-conjugated monomers. Actually, in the absence of a catalyst, a Diels-Alder reaction occurs, and the question might be raised whether here, too, a diradical is formed which readily forms a six-membered ring rather than adding further olefin units.²⁷ Such a biradical intermediate for the Diels-Alder reaction has been suggested by Coyner and Hillman (46) and is in keeping with its insensitivity to medium and to polar catalysts; the ineffectiveness of free-radical sources as catalysts presents no difficulty, since they produce single radicals. However, even in the case that the transition state actually involves the simultaneous formation of two new bonds, the close parallel between the resonance forms advanced by Woodward (232) for the Diels-Alder reaction and structures such as that just given suggest a very close mechanistic parallel between the two.

²⁷ Cyclic dimer formation also occurs with a number of (catalytically) polymerizable monoolefins and may account for their failure to undergo thermal polymerization, e.g., acrylonitrile (46) and methyl vinyl ketone (2).

D. QUALITATIVE GENERALIZATIONS

Although results on styrene-methyl methacrylate and styrene-methyl acrylate represent the bulk of the usable data on copolymerization rates,²⁸ it is possible to draw a few useful generalizations concerning relative rates of copolymerization at the same rate of chain initiation.²⁹ Considering first the relation between overall rates of polymerization of single monomers and their reactivity in copolymerization, when chain termination occurs by bimolecular reaction between radicals, the overall rate of polymerization is given by $-dM_1/dt = k_{11}I^{1/2}/k_{t1}^{1/2} [M_1]$. The general effect of increasing the conjugation of the double bond of a monomer is to decrease k_{11} (cf. table 10, Section III,F). Since k_{t1} does not appear to vary greatly with structure (121-124), the expected result would be decreased polymerization rate with increased conjugation. Conversely, increased conjugation, in general, increases the reactivity of the monomer (but not of the resulting radical) in copolymerization. Unfortunately, this picture which would predict a simple inverse relation between reactivity in copolymerization and polymerization rate of a monomer alone is confused by the fact, first pointed out by Bartlett and Altschul (24, 25), that many monomers possess allylic hydrogen atoms which readily undergo chain transfer. Since the resulting allylic radical is too unreactive to react readily with any but extremely reactive or strongly accepting double bonds, the result is an alternative method of chain termination. Accordingly, many monomers which should otherwise be expected to polymerize rapidly, polymerize either not at all or at a very low rate (e.g., allyl derivatives, propylene, etc.). On the other hand, in combination with another monomer capable of reacting with such allylic radicals, copolymerization proceeds readily enough (26), and chains are terminated only bimolecularly. De Haes and Smets (76a) have found both kinds of termination mechanism in copolymerizations of α -methylstyrene.

Accordingly, it seems reasonable to discuss copolymerizations (at least those yielding high polymers) in general on the basis of equation 40. For monomers of similar reactivity and little tendency to alternate (e.g., styrene-*p*-chlorostyrene) both monomers and their mixtures will copolymerize at roughly the same rate. As one goes to systems in which M_1 is markedly the more reactive (r_2 approaching zero) equation 40 may be replaced by

$$-\frac{d([M_1] + [M_2])}{dt} = \left([M_1] + \frac{2}{r_1} [M_2] \right) \frac{I^{1/2}}{\delta_1} \quad (43)$$

²⁸ The overall rates of copolymerization of butadiene-acrylonitrile systems have recently been measured by Gindin, Abkin, and Medvedev (71). However, their kinetic treatment assumes the same rate constant for termination of all types of chains, and so is of doubtful validity. Further, their experimental results involving many hours heating at 60°C. are probably complicated by the competing Diels-Alder reaction.

²⁹ It is possible that a given amount of benzoyl peroxide starts chains at closely similar rates in different monomers (26): plots of rates of benzoyl peroxide-catalyzed copolymerizations of styrene-methyl methacrylate (129, 149) closely approximate figure 24. However, most data on copolymerization rates, gathered incident to determining copolymer compositions, appear erratic and unreliable, partly because of induction periods due to the presence of air. Further, comparable polymerization rates of the pure monomers have not, in general, been determined.

a form which is a good approximation, at least for systems high in M_1 , but fails as pure M_2 is approached.³⁰ Styrene-vinyl chloride and styrene-vinyl acetate represent such cases. Data for the latter ($r_1 = 55$, $r_2 = 0.02$) are shown in figure 25. The striking inhibition of vinyl acetate polymerization by a trace of styrene (131) is plainly evident. It arises since (1) the unreactive vinyl acetate is a fairly inert diluent for the styrene polymerization and (2) such vinyl acetate radicals as are formed are rapidly converted back to unreactive benzyl (styrene) radicals. When the copolymerization is complicated by allylic transfer with the monomer yielding the more reactive radical, the situation will be similar to figure 25, except that there will be no final marked increase in rate in going to the right side of the figure, e.g., styrene-allyl acetate.

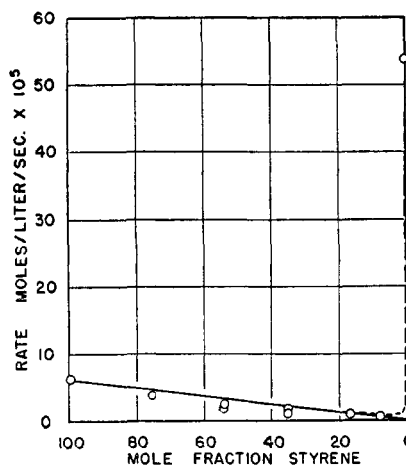


FIG. 25

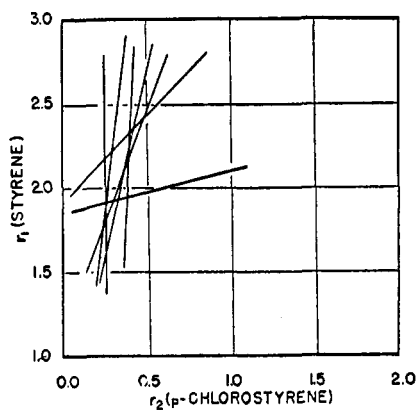


FIG. 26

FIG. 25. Copolymerization of styrene-vinyl acetate at 60°C. (1 g. of 2-azobisisobutyronitrile per liter).

FIG. 26. Graphical solution of copolymerization equation for styrene-*p*-chlorostyrene; stannic chloride catalyst.

When the monomers tend to alternate in copolymerization, increased rate of chain growth and of chain termination (large values of ϕ) work against each other, and rate curves similar to figures 23 and 24 result. If the monomers differ appreciably in reactivity, systems rich in the more reactive monomer will still follow equation 43, but, for $r_1 < 2.0$, rates will rise rather than decrease as the less reactive monomer is added, e.g., styrene-acrylonitrile, and, where one or

³⁰ The applicability of equation 43 to systems containing moderate proportions of M_2 depends chiefly upon r_1 . Equation 43 also assumes $\delta_2/\delta_1 \gg r_2$. The opposite relation apparently arises in cases of polymerization inhibition by materials such as benzoquinone. The analogy of inhibition by such materials to copolymerization has been noted by Bartlett and Nozaki (26), and recently evidence has appeared that they actually form copolymers with styrene (32, 33, 128). However, since they have very low rate constants for chain growth, presumably because of the very high stability of their radicals, their overall rates of copolymerization lie far below that given by equation 43.

both monomers polymerize poorly alone, may go through pronounced maxima, e.g., styrene-maleic anhydride, allyl acetate-maleic anhydride (26). A number of calculated curves for various assumed parameters are given by Melville, Noble, and Watson (138).

In passing from instantaneous rates to variation of rate with conversion, integration of equation 40 has been achieved for the special case of $\phi = 1$ by Melville, Noble, and Watson, and for the general case by deButts (40). However, the resulting expression is very complex. No experimental study of copolymerization rates over appreciable extents of conversion appears to have been carried out, and the field appears to be a difficult one because of the marked accelerations observed in the polymerization of some monomers alone, apparently due to decreased rates of bimolecular termination in viscous media.

Although the compositions of copolymers formed in emulsion are predicted by the same equations as those for homogeneous reaction, except insofar as monomer concentrations are changed by solution in the aqueous phase (*cf.* Section II,E), overall rates of copolymerization should no longer obey equation 40. Instead, if the mechanism of emulsion polymerization of Smith and Ewart (183, 184) is correct, the rate should be equal to rate per unit radical concentration (i.e., the quantity V defined by Wall (207)), multiplied by one-half the particle concentration, N .

$$-\frac{d([M_1] + [M_2])}{dt} = \frac{N}{2} \frac{k_{11} k_{22} (r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2)}{k_{22} r_1 [M_1] + k_{11} r_2 [M_2]} = \frac{NV}{2} \quad (44)$$

Since N itself is a function of the rate of polymerization, the final rate expression in the terms used here should be

$$\frac{d([M_1] + [M_2])}{dt} = kI^{2/5}[S]^{3/5}V^{3/5} \quad (45)$$

where k is a numerical constant dependent on several variables, and $[S]$ is the concentration of emulsifying agent (184).

V. COPOLYMERIZATION BY IONIC MECHANISMS

A. CARBONIUM-ION POLYMERIZATIONS

Equation 5, which relates the composition of a copolymer and the composition of the monomer mixture of from which it is being formed, makes no assumption as to the nature of the active center involved. All previous data and discussion in this review have referred to polymerization where the active center was a free radical, and have stressed the conclusion that the composition of the copolymer formed was essentially independent of the reaction medium or the particular radical source employed. On the other hand, it was pointed out in the first paper on copolymerization from this Laboratory (129) that catalysts leading to polymerization through a carbonium ion, i.e., boron trifluoride, aluminum chloride or stannic chloride,³¹ could give very different results, styrene-methyl methac-

³¹ A trace of promoter such as water or halogen acid is also apparently required (53, 62, 151). For recent reviews of such polymerizations, see references 82 and 156.

rylate being cited as an example. Data on this and several other systems have recently been published by several workers, and differences due to mechanism are summarized in table 17. Although the data of table 17 illustrate the changes in copolymer composition brought about by change in polymerization mechanism (only in the styrene-vinyl acetate and styrene- α -methylstyrene systems is a change not clearly apparent), most pairs differ too much in reactivity for any quantitative verification of the applicability of the copolymerization equation to

TABLE 17

Comparison of initial products formed from 1:1 feeds using peroxide and carbonium-ion catalysts

MONOMERS	MOLE PER CENT FIRST MONOMER IN PRODUCT		REFERENCES
	Radical	Carbonium ion	
Styrene-butadiene ^(a)			(115)
Styrene-methyl methacrylate	51	>99	(215)
Styrene- α -methylstyrene	ca. 50	<50	(20)
Styrene- <i>p</i> -chlorostyrene	46	73	(20, 109)
Styrene-2,5-dichlorostyrene	40	93	(18, 59)
Styrene- <i>p</i> -methoxystyrene	54	<1	(215)
Styrene-acrylonitrile	58	>99	(215)
Styrene-vinylidene chloride	72	>99	(59, 215)
Styrene-vinyl acetate	98.3	>90	(215)
Styrene-diethyl fumarate	55	>96	(215)
Styrene-vinyl ethyl ether	>99	<9 ^(b)	(215)
<i>o</i> -Chlorostyrene-anethole	>99	5	(4)
<i>p</i> -Chlorostyrene- α -methylstyrene	67	5	(76a)
Isobutylene-isoprene	5-10 ^(c)	>70 ^(c)	(197)
Isobutylene-butadiene	5-10 ^(c)	>95 ^(c)	(197)
Vinylidene chloride-vinyl butyl ether	>98 ^(d)	<10	(59, 110)
Vinyl acetate-vinyl ethyl ether	80	<4	(215)

^(a) From a feed containing 15 mole per cent styrene, the initial copolymer obtained with aluminum chloride catalyst and ethyl bromide solvent at -75°C . contained 41 mole per cent styrene, as compared with ca. 10 per cent expected with a free-radical catalyst.

^(b) Similar result with vinyl butyl ether (59).

^(c) Radical results estimated from table 6; carbonium ion results estimated for $0-30^{\circ}\text{C}$.

^(d) Vinyl ethyl ether.

carbonium-ion copolymerization. The first such verification was obtained by Alfrey and Wechsler (20) for the system styrene-*p*-chlorostyrene copolymerized by stannic chloride at 30°C . in carbon tetrachloride solution. The graphical solution of the copolymerization equation, plotted from the data of their experiments for which yields are reported, is shown in figure 26. The intersection is good, but from their curve-fitting method, Alfrey and Wechsler have chosen somewhat different values of r_1 and r_2 (cf. Section II,C,2). These results, together with recent data by Florin (59), by Alfrey, Arond, and Overberger (4), and by De Haes and Smets (76a), and our calculations from the patents of Thomas and Sparks (197) and of Denoon (47a), are summarized in table 18.

From the data in tables 17 and 18, together with some indications of tempera-

ture coefficients (197), the relative reactivities of some monomers toward carbonium ions have been estimated in table 19. This order is very different from

TABLE 18
Monomer reactivity ratios in carbonium-ion copolymerizations

M ₁	r ₁	M ₂	r ₂	CONDITIONS	REFERENCES
Styrene.....	2.7 ± 0.3 2.2 ± 0.3	<i>p</i> -Chloro- styrene	0.35 ± 0.05 0.35 ± 0.1	SnCl ₄ at 30°C. in CCl ₄	(20) Figure 26
Styrene.....	14.8 ± 2	2,5-Dichloro- styrene	0.25 ± 0.15	AlCl ₃ at 0°C. in C ₂ H ₅ Cl	(59)
α -Methyl- styrene	28 ± 2	<i>p</i> -Chloro- styrene	0.12 ± 0.03	SnCl ₄ at -78°C.	(76a)
<i>o</i> -Chlorostyrene	0.03 ± 0.005	Anethole	18 ± 3	SnCl ₄ at 0°C. in CCl ₄	(4)
Isobutylene....	115 ± 15 ^(a)	1,3-Butadiene	0.01 ± 0.01	AlCl ₃ + CH ₃ Cl	(197)
Isobutylene....	2.5 ± 0.5 ^(a)	Isoprene	0.4 ± 0.1	in C ₂ H ₄ at -103°C.	(197)
Isobutylene....	8 ^(b)	Vinylacety- lene	0.13 ^(b)	BF ₃ at -100°C.	(47a)

^(a) Butadiene (or isoprene) contents of polymers taken as 40 per cent (or 55 per cent) of values given in patent, as suggested by Rehner and Gray (163); r_1r_2 assumed to be unity.

^(b) Estimated from single run.

TABLE 19
*Approximate relative reactivities of monomers toward carbonium ions at 0-30°C.**

MONOMER	RELATIVE REACTIVITY
<i>p</i> -Methoxystyrene } Vinyl ethers }	> 50
Isobutylene.....	8-12
α -Methylstyrene.....	10
Anethole.....	2-5
Isoprene.....	2
Vinylacetylene.....	1-1.5
Styrene.....	1.0
<i>p</i> -Chlorostyrene.....	0.3
Butadiene.....	0.2-0.3
<i>o</i> -Chlorostyrene.....	0.1-0.3
2,5-Dichlorostyrene.....	0.07
Vinyl acetate } Vinylidene chloride } Methyl methacrylate } Acrylonitrile } Diethyl fumarate }	< 0.01 Not differentiated

* Assuming that the *relative* reactivities are the same toward all carbonium ions.

that found in radical polymerization in table 6, and distinguished by the high reactivities of the vinyl ethers and isobutylene. Reactivities correspond to the expected effects of substituents upon the reactivity of double bonds towards

electrophilic reagents, arising from differences in electron availability in the double bond, and resonance stabilization of the resulting carbonium ion.³² However, this order is not necessarily that of the relative rates of polymerization of these monomers alone; overall rates also depend on the attacking carbonium ion and of the chain termination mechanism, about which little is known.

Compared with radical-induced copolymerizations, these carbonium-ion reactions show a much wider range of reactivity among the common monomers, and no signs (so far) of any tendency to yield alternating copolymers. These characteristics mean that relatively few monomer pairs easily yield copolymers containing large proportions of both monomers, and it is noteworthy that butyl rubber (isobutylene-isoprene) (224) is the only carbonium-ion copolymer at present of real technical importance.

B. CARBANION COPOLYMERIZATIONS

The mechanism of alkali metal-catalyzed polymerizations has been suggested as both radical (31) and as involving a carbanion intermediate (159). Recently arguments in favor of the latter have been presented by Beaman (30), who has shown that Grignard reagents, triphenylmethylsodium, and sodium in liquid ammonia all polymerize monomers such as methacrylonitrile. That carbon dioxide inhibits the sodium- or benzylsodium-catalyzed polymerization of butadiene and isoprene also points strongly to a carbanion mechanism (168). Further evidence that the sodium- and radical-catalyzed polymerizations of butadiene and butadiene-styrene do involve different mechanisms comes from the work of Marvel, Bailey, and Inskeep (113) and of Kolthoff, Lee, and Mairs (100). From perbenzoic acid titration, the latter group concluded that polybutadienes made at 50°C. with a free radical or a sodium catalyst contained about 22 per cent and 58 per cent, respectively, of butadiene units polymerizing by 1,2-addition to the conjugated system (yielding vinyl side chains). The effect of temperature on these ratios is insignificant in the radical reaction (79a) and rather large in the carbanion reaction (233). Ross (169) has recently shown that this difference is due to a difference in polymerization mechanism, not to the action of sodium on the polymer. The most conclusive evidence for the nonradical nature of sodium-catalyzed polymerizations comes from copolymer compositions. This work is summarized in table 20. Although the effect of mechanism change in the styrene-butadiene system is small, in other systems the effects are as marked as between free radical and carbonium ion catalysts. Differences in reactivity in carbanion polymerizations seem to be as large as in carbonium-ion reactions.

Foster (68) has determined the composition of the copolymer formed in the carbanion copolymerization of the methyl methacrylate-methacrylonitrile system at several feeds, and monomer reactivity ratios at -55°C. in liquid ammonia

³² Alfrey, Arond, and Overberger (4), from their results on *o*-chlorostyrene-anethole, concluded that the retarding effect of 2-substituents on ionic polymerizations of 1-substituted monomers is not nearly as great as in free-radical polymerizations. In view of the very large activating effects of alkoxy groups in carbonium-ion polymerizations, their experiments do not seem conclusive.

solution were found to be 0.67 ± 0.2 (methacrylate), 5.2 ± 1.0 (methacrylonitrile). With this result, the applicability of the copolymerization equation has been established for examples of all known types of vinyl polymerization. The data of table 20 yield an order of reactivity in carbanion polymerizations: acrylonitrile > methacrylonitrile > methyl methacrylate > styrene > butadiene. This order is entirely different from that found in both radical and carbonium-ion polymerizations and therefore provides additional evidence for the carbanion nature of the active center in sodium-catalyzed and related polymerizations. The order also indicates that reactivity in carbanion polymerizations is determined by the ability of the substituents to withdraw electrons from a double bond and to stabilize the carbanion formed upon reaction.

TABLE 20
Comparison of initial products formed with peroxide and carbanion catalysts

MONOMERS	MOLE PER CENT FIRST MONOMER IN			REFERENCES
	Feed	Product		
		Radical	Carbanion	
Styrene-butadiene.....	15	11	15-18 ^(a)	(113, 176)
Styrene-methyl methacrylate.....	50	51	< 1 ^(a)	(215)
Methyl methacrylate-acrylonitrile.....	50	69	< 10 ^(a)	(215)
Methyl methacrylate-methacrylonitrile.....	50	5	22 ^(b)	(68)

^(a) Using sodium metal at 10-50°C.

^(b) Using sodium in liquid ammonia.

C. COMPARISON OF MECHANISMS

The contrast between the three mechanisms of vinyl polymerization has been brought out most clearly by Walling, Briggs, Cummings, and Mayo (215): the initial polymer formed from a 1:1 feed of styrene and methyl methacrylate may be nearly pure styrene, nearly pure methacrylate, or a 1:1 copolymer, depending on whether the catalyst is a metal halide, an alkali metal, or a peroxide. The existence of three very different mechanisms is thus established, and a means of determining the mechanism of a polymerization is also suggested. Thus copolymer compositions have established the mechanism of the uncatalyzed copolymerization of styrene and methyl methacrylate (129), of the polymerization in thymol solution (215), and of the benzoyl peroxide-, light-, and magnesium perchlorate-catalyzed reactions (215) as due to free radicals. General understanding of differences between mechanisms and catalysts should assist in resolving much of the confusion in the technical literature relating to vinyl polymerization.

The inception of work on copolymerization at the General Laboratories in 1942 was largely due to the decision of Dr. R. T. Armstrong that such a study would be one of the best approaches to an understanding of polymerization as a whole. Since that time, our numerous associates, many of whom are named in the

list of references, have contributed substantially to that portion of the experimental work carried out in these Laboratories and to the development of many of the ideas presented here. Of these collaborators we wish to mention particularly Drs. F. M. Lewis and K. W. Doak. We also wish to acknowledge the cooperation of Professors Turner Alfrey, Jr., of the Polytechnic Institute of Brooklyn; R. E. Florin, of the University of Nebraska; C. S. Marvel, of the University of Illinois; H. W. Melville, of the University of Birmingham; R. V. V. Nicholls, of McGill University; C. C. Price, of the University of Notre Dame; G. Smets, of the University of Louvain; Drs. E. G. Ham, of the Central Research Department, Monsanto Chemical Company; F. C. Foster of the Firestone Tire and Rubber Company, and E. H. deButts of Harvard University, who have made manuscripts available to us in advance of publication.

VI. REFERENCES

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