

in 50% alcohol. Using the curve developed by Bell and Roblin<sup>10</sup> for correcting these values to those in aqueous solution gave figures close to the 5.38 given for N<sup>1</sup>-acetyl-sulfanilamide itself.

**Preparation and Diazotization of 2-(*o*-Aminophenyl)-ethene-1-sulfonic Acid.**—Hydrolysis and reduction of II was carried out by the method described for the preparation of orthanilic acid.<sup>20</sup> Isolation of the product was made difficult by the surprisingly great water solubility of this aminosulfonic acid. A small amount of the aminosulfonic acid crystallized on slow evaporation of an acid solution in the cold room. It was identified by qualitative tests and analysis.

*Anal.* Calcd. for C<sub>8</sub>H<sub>9</sub>O<sub>3</sub>NS·H<sub>2</sub>O: neut. equiv., 217. Found: neut. equiv., 219, 216.

A 0.35-g. sample of this aminosulfonic acid dissolved in acid solution reacted with the theoretical quantity of sodium nitrite solution (end-point determined with starch-iodide paper). Heating the diazonium solution caused a

vigorous evolution of nitrogen. The mixture of salts obtained on evaporation of this solution was insoluble in organic solvents and completely soluble in water. The aqueous solution gave a deep blue coloration with ferric chloride solution showing the presence of a phenol.

### Summary

1. Two simple vinylogs of sulfanilamide and two of sulfacetamide have been prepared and were found to have no bacteriostatic activity *in vitro*.

2. Evidence has been presented to show that the *ortho* vinylogs have a *trans* configuration.

3. The hypothesis of Kumler and Daniels,<sup>11</sup> concerning the relationship between the structure and activity of sulfonamides, has been criticized on several counts.

(20) Wertheim, "Organic Syntheses," Coll. Vol. II, p. 472.

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[CONTRIBUTION FROM CELANESE CORPORATION OF AMERICA, PLASTICS DIVISION]

## Copolymerization: the Composition Distribution Curve

BY IRVING SKEIST

When two or more monomers are copolymerized, the product is a mixture of polymer molecules which vary in composition as well as in chain length. If, *e.g.*, the polymer first formed is richer in one component than the monomer mixture, then some of the polymers formed subsequently must be poorer in that component than the original monomer mixture. Some mixtures of monomers yield a polymer aggregate of fairly uniform composition, while others give a product whose molecules vary so widely in composition that technical usefulness is impaired. Thus it becomes important to know the distribution of compositions in the polymer.

At any instant, the composition of the polymer in a binary mixture is related to the composition of the monomer according to the expression<sup>1,2,3</sup>

$$\frac{\Delta A}{\Delta A + \Delta B} = A_p = \frac{\alpha A^2 + AB}{\alpha A^2 + 2AB + \beta B^2}$$

where  $A$  and  $B$  are the mole fractions of the two components in the monomer,  $\Delta A$  and  $\Delta B$  are the amounts (*e.g.*, moles per unit weight) of the corresponding components which enter the polymer in a differential time interval,  $A_p$  is the mole fraction of the first component in the polymer formed during the differential time interval, and  $\alpha$  and  $\beta$  are the monomer reactivity ratios<sup>2,3</sup>;  $\alpha$  is  $k_{A^*A}/k_{A^*B}$  and  $\beta$  is  $k_{B^*B}/k_{B^*A}$ , where  $k_{A^*B}$ , for example, is the rate constant for the propagation reaction involving the addition of B monomer to A radical.

For a three-component system, the relation be-

tween  $A_p$  and  $A$  is found similarly from the following set of equations<sup>4,5</sup>

$$\frac{\Delta A}{\Delta B} = \frac{A(A/\beta^a\gamma^a + B/\beta^a\gamma^b + C/\beta^c\gamma^a)(A + B/\alpha^b + C/\alpha^c)}{B(A/\alpha^b\gamma^a + B/\alpha^b\gamma^b + C/\alpha^c\gamma^b)(A/\beta^a + B + C/\beta^c)} \quad (2a)$$

$$\frac{\Delta A}{\Delta C} = \frac{A(A/\beta^a\gamma^a + B/\beta^a\gamma^b + C/\beta^c\gamma^a)(A + B/\alpha^b + C/\alpha^c)}{C(A/\alpha^c\beta^a + B/\alpha^b\beta^c + C/\alpha^c\beta^c)(A/\gamma^a + B/\gamma^b + C)} \quad (2b)$$

where  $\beta^a$ , for example, is  $\beta$  for the binary system A-B. The information needed to solve these equations, as well as the equations for systems involving a greater number of monomers, can be obtained entirely from experiments on the binary systems involved.

Integration of equations (1) and (2) should give a relationship between the conversion, or amount of polymer formed, and its composition. These integrations have been performed by Mayo and Lewis<sup>2</sup> and Walling and Briggs.<sup>5</sup> Even in a binary system, the integral is complex; in a ternary system it becomes nearly unmanageable. An attempt to simplify the integral relationship for a ternary system results in an approximate expression which is precise only when the polymer composition is close to that of the feed.

It is the purpose of this paper to present a more convenient method for determining the relationship between conversion and composition, and from this the distribution of compositions, in a polymer of any number of components. The method is applicable to any system for which one knows the relation between composition of monomer and composition of polymer, regardless of whether the system can be described in terms of the monomer reactivity ratios of equations 1 and 2.

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

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

(3) Wall, *ibid.*, **66**, 2050 (1944).

(4) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 322 (1944).

(5) Walling and Briggs, *THIS JOURNAL*, **67**, 1774 (1945).

**Analogy between Copolymerization and Distillation.**—It is interesting to compare copolymerization with fractional distillation. Figure 1 gives the relationship between monomer composition and composition of polymer immediately formed, for some binary systems (see Table I, below). The similarity to a liquid-vapor composition diagram is obvious; the term "azeotrope" has been suggested<sup>3</sup> for the case in which both monomer and polymer have the same composition, which in our diagram would occur where the curve crosses the 45° diagonal.

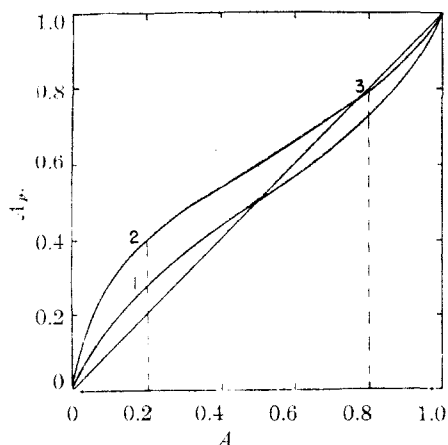


Fig. 1.—Instantaneous relationship between mole fraction of first component in the monomer,  $A$ , and its mole fraction in the polymer,  $A_p$ .

In distillation, composition and yield are known to be related by the Raleigh equation<sup>6</sup>

$$\ln \frac{L}{L_0} = \int_{x_0}^x \frac{dx}{y-x} \quad (3)$$

where  $L$  is the quantity of liquid,  $x$  is the mole fraction of the higher boiling component in the liquid, and  $y$  is the mole fraction of that component in the vapor.

It will be shown in the following that the same equation, with analogous quantities, can be derived for copolymerization.

**The Conversion-Composition Equation.**—Consider a mixture of two monomers, of mole fractions  $A$  and  $B$ , respectively, such that the polymer first formed is richer in component  $A$  than the monomer (for example, System 1 in Fig. 1). If the total amount of both monomers is  $M$  moles, then there are  $AM$  moles of the first component in the original monomer. If  $dM$  moles of monomer polymerize, the number of moles of component  $A$  in the polymer is  $A_p dM$ . At the same time, the number of moles of component  $A$  in the monomer has been reduced to  $(M - dM)(A - dA)$ . Consequently, the material balance of  $A$

$$AM - (M - dM)(A - dA) = A_p dM$$

(6) Raleigh, *Phil. Mag.*, **8**, 534 (1902).

Neglecting the product of two differentials

$$AdM + MdA = A_p dM$$

$$dM/M = dA/A_p - A) \quad (4)$$

$$\ln \frac{M}{M_0} = \int_{A_0}^A \frac{dA}{A_p - A} \quad (5)$$

This is the conversion-composition equation. In combination with equations (1) and (2), it makes possible the computation of the proportion of original monomer which is still unreacted.

**Binary Systems.**—In Fig. 1 are plotted the instantaneous monomer-polymer composition relationships for styrene-methyl methacrylate<sup>2</sup> and styrene-methyl acrylate.<sup>7</sup>

TABLE I  
INITIAL MONOMER COMPOSITIONS

Sys-tem	Component A	Component B	Mole fraction $A_0$	$\alpha$	$\beta$
1	Styrene	Methyl methacrylate	0.20	0.50	0.30
2	Styrene	Methyl acrylate	.20	.75	.20
3	Styrene	Methyl acrylate	.80	.75	.20

For the three original compositions indicated, the integral has been determined graphically and the percentage conversion computed from equation (5). In Fig. 2, conversion is plotted against instantaneous *polymer* composition ( $A_p$ ) to give integral distribution curves. The dotted lines indicate the original monomer mixture. The horizontal lines indicate the portions of the curves lying between 25 and 75% conversion. The corresponding differences in polymer composition, appearing as the projections to the horizontal, may be termed the "interquartile ranges," and are a measure of the dispersion of compositions in the polymer aggregate.

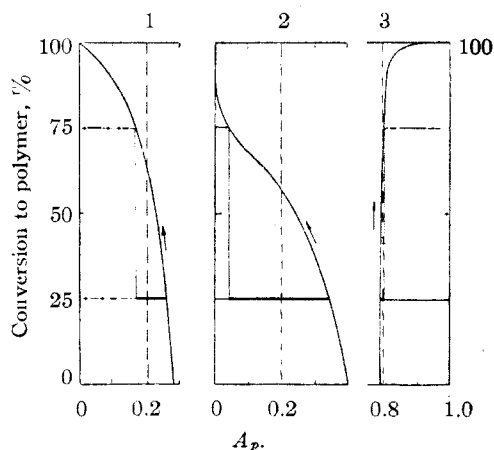


Fig. 2.—Integral distribution of compositions in polymer; conversion vs. instantaneous polymer composition.

Not only do the three curves have very different interquartile ranges, but they approach 100% conversion in markedly different manners. Curve 1 (9% interquartile range) has a slope of unity at the finish (proceeding from the bottom toward

(7) Alfrey, Merz and Mark, *J. Polymer Research*, **1**, 37 (1940).

the top of the figure); curve 2 (30% range) has an infinite slope; the slope of curve 3 (1% range) is zero. These differences are shown more strikingly when the slopes of the curves of Fig. 2 are plotted against the same instantaneous polymer compositions to give the frequency curves (differential distribution curves) of Fig. 3. The curves of systems 1 and 3 are L-shaped with only a single peak. On the other hand, the curve of System 2 is U-shaped, indicating a decided cleavage of compositions into two very different groups. The interquartile range tells us that the molecules of one-fourth of the polymer aggregate differ from the molecules of another fourth by at least 30% in composition.

The three systems were polymerized to completion at 60° in the presence of 0.1 mole per cent. benzoyl peroxide. Systems 1 and 3 remained clear and transparent throughout the polymerization, but system 2 developed an opalescence and was very brittle compared to the other specimens. This is not surprising; it is known that polymers of differing chemical compositions are generally "incompatible"—that is, they cannot be blended mechanically to give a product of good physical properties.

One approximation is involved in Figs. 2- and 3—it is assumed that all the polymer formed at any instant is of the same composition. Simha and Branson<sup>8</sup> and Stockmayer<sup>9</sup> have pointed out that there is a dispersion in composition just as there is a dispersion in molecular weight. Thus, the polymer formed at any instant, while predominantly of one composition, also contains some polymer molecules of other compositions over the entire range of 0-100% *A*. Fortunately, the distribution becomes sharper with increasing chain length. The chief effect of this correction would be to soften the sharp edge corresponding to zero conversion.

**Monomer Reactivity Ratios and the Distribution Curve.**—The shape of the distribution curve near 100% conversion depends on the values of the monomer reactivity ratios.

From equation 1, we find that as *A* approaches zero,  $\lim A_p = A/\beta$ . (Similarly, as *A* approaches 1,  $\lim B_p = B/\alpha$ )

At the *B* terminal, therefore, substitution in eq. (4) gives

$$\frac{dM}{M} = \frac{dA}{A/\beta - A}$$

$$\ln \frac{M_2}{M_1} = \frac{\beta}{1-\beta} \ln \frac{A_2}{A_1} \quad (6)$$

or, since  $A_{p2}/A_{p1} = A_2/A_1$  near the *B* terminal

$$\frac{M_2}{M_1} = \left( \frac{A_{p2}}{A_{p1}} \right)^{\beta/1-\beta} \quad (7)$$

Equation 7 may be applied to the special cases as follows

**System 1.**—Here  $\beta = 0.5$  and consequently  $M_2/M_1 = A_{p2}/A_{p1}$ . Near 100% conversion, the

(8) Simha and Branson, *J. Chem. Phys.*, **12**, 253 (1944).

(9) Stockmayer, *ibid.*, **13**, 199 (1945).

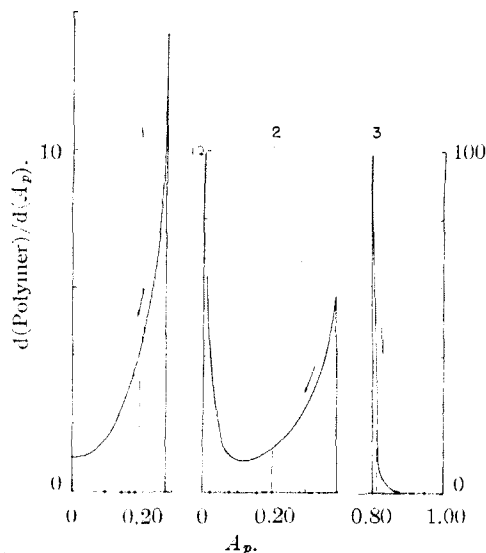


Fig. 3.—Frequency distribution of compositions in polymer.

decrease in amount of unreacted monomer is proportional to the change in instantaneous polymer composition; the integral distribution curve has a slope of 1, and the frequency distribution curve has finite intercept.

**System 2.**— $\beta = 0.2$ ;  $M_2/M_1 = (A_{p2}/A_{p1})^{0.25}$ . The distribution curves have infinite slope at 100% conversion, consequently an appreciable amount of polymer is almost pure *B*. The polymer is necessarily quite mixed in composition.

**System 3.**— $\alpha = 0.75$ ;  $M_2/M_1 = (B_{p2}/B_{p1})^3$ . The distribution curves have zero slope at 100% conversion, indicating that practically none of the polymer is almost pure *A*.

It is apparent that the value of 0.5 for the monomer reactivity ratio is critical. Lower values give a polymer aggregate of widely heterogeneous composition.

In each of these systems, both  $\alpha$  and  $\beta$  are less than 1. If  $\alpha$  is less and  $\beta$  is greater than or equal to 1, the last bit of unreacted monomer is pure *A*, and the value of  $\alpha$  is critical. If both  $\alpha$  and  $\beta$  are greater than 1, the last trace of monomer is neither pure *A* nor pure *B*, but has the composition of an azeotrope. It can be shown that, in such cases, if  $\alpha = \beta$ , a value of 2 is critical. However, no system has yet been found for which both monomer reactivity ratios are greater than 1.

The case in which  $\alpha = 1/\beta$ , which was thought at one time to have special significance, was investigated by Wall,<sup>10</sup> who showed that the monomer reactivity ratios have critical values of 0.5 and 2, respectively. It is now believed that this case has no special meaning; the value of 0.5 for a monomer reactivity ratio is always critical, regardless of the value of the other monomer reactivity ratio.

**Ternary Systems.**—When there are three or more components, equation (5) becomes an especially useful tool for relating the conversion

(10) Wall, *This Journal*, **63**, 1862 (1941).

to the distribution of polymer compositions. For a ternary system, the method is as follows:

The computation makes use, alternately, of equations (2) and (5), evaluating the total in consecutive steps. The polymer compositions corresponding to the initial monomer compositions are calculated from equation (2). This gives a value of  $(A_p - A)_0$  (Fig. 4) which is assumed to be constant for limited variations in  $A$ . Equation (5) gives the per cent. conversion for such a variation  $dA$ . From  $A_1 (= A + dA)$ , and the corresponding  $B_1$  and  $C_1$ , the new polymer compositions are calculated from equation (2), thus giving  $(A_p - A)_1$ , which is used for the next conversion calculation according to equation (5).

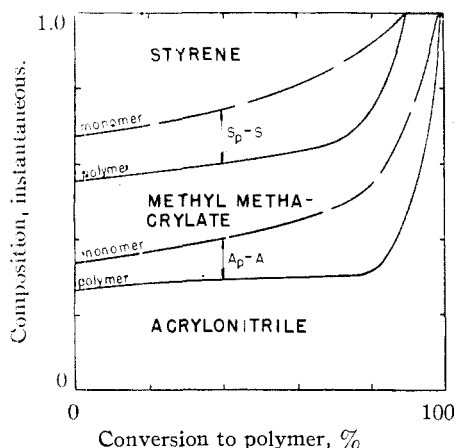


Fig. 4.—Compositions of monomer and polymer vs. conversion, for an equimolar mixture of acrylonitrile, methyl methacrylate and styrene.

If  $(A_p - A)$  is found to vary over the interval  $dA$ , a more suitable value for  $(A_p - A)$  can be chosen (for example, the average of  $(A_p - A)_0$  and  $(A_p - A)_1$ ), and the conversion recalculated. To reduce the number of calculations this preferable value for  $(A_p - A)$  is anticipated from the

trend of the curves. In regions where  $(A_p - A)$  is changing rapidly, precision is maintained by calculation over smaller intervals.

Figure 4 shows the conversion–composition relationship obtained by this method for an equimolar mixture of acrylonitrile, methyl methacrylate and styrene.<sup>11,5</sup>

The first polymer is richer in styrene and poorer in acrylonitrile than the monomer; consequently the monomer is depleted of styrene and enriched in acrylonitrile. As polymerization proceeds, compositions of both unreacted monomer and instantaneous polymer change; but the change in the latter is less. Thus, up to 70% conversion, the polymer aggregate is fairly uniform in composition. At that point, however, the changes become more marked. At 90% conversion, the styrene is virtually gone; and the last 1% of polymer is almost pure acrylonitrile.

In a technical process, if uniformity of polymer composition were desired, the polymerization could be stopped at approximately 70% conversion.

For systems of more than three components, computation of instantaneous monomer–polymer relationships becomes more tedious, but with this accomplished, the calculation of the conversion from equation (5) is just as easy as for a ternary or binary system.

**Acknowledgment.**—The author wishes to thank Dr. Ernest P. Irany for helpful discussion and criticisms.

### Summary

A new method of computation of the composition distribution of copolymers is proposed which permits evaluation of systems containing any number of components.

NEWARK, N. J.

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(11) Lewis, Mayo and Hulse, *THIS JOURNAL*, **67**, 1701 (1945).

(12) Presented before the High Polymer Forum at the Atlantic City meeting of the American Chemical Society, April, 1946.

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

## Multilayer Adsorption Equations

BY P. H. EMMETT

Brunauer, Emmett and Teller<sup>1</sup> have suggested that, if low temperature adsorption data are plotted according to the equation

$$\frac{p}{v(p_0 - p)} = \frac{1}{V_m C} + \frac{(C - 1)p}{V_m C p_0} \quad (1)$$

a straight line is obtained over a relative pressure range extending from about 0.05 to 0.35.  $V_m$ , in this equation, represents the volume of adsorbate required to form a monolayer over the solid ad-

sorbent.  $v$  is the volume of gas adsorbed at relative pressure  $p/p_0$ ; and  $C$  is a constant. A simple multiplication of the number of adsorbed molecules corresponding to  $V_m$ , by their average cross-sectional area, would then yield an absolute value for the surface area of the solid being measured. This equation has been applied successfully to a large number of finely divided and porous solids.

Recently, Harkins and Jura<sup>2,3</sup> have published a

(2) Harkins and Jura, *ibid.*, **66**, 919 (1944).

(3) Harkins and Jura, *ibid.*, **66**, 1366 (1944).

(1) Brunauer, Emmett and Teller, *THIS JOURNAL*, **60**, 310 (1938).