benzene which enters into reaction appears as phenyltrichlorosilane and diphenyldichlorosilane in the approximate molar proportion of one to three.

Copper also is a catalyst for the reaction of chlorobenzene with silicon, but is not as effective as silver in the lower concentrations. In the form of a 50% copper–silicon alloy disintegrated by intergranular oxidation, the copper brings about an acceptable conversion of chlorobenzene to phenylchlorosilanes at 430°, yielding diphenyldichlorosilane as the principal product. Variations in yield have been noticed with different batches of the contact mass, possibly because of variations in the degree of oxidation and hence in the extent of disintegration. More investigation of the metallurgical changes which take place upon oxidation is necessary before an assured reactivity toward chlorobenzene can be brought about by a fixed sequence of operations.

The effect of hydrogen chloride in expediting the reaction of elementary silicon and chlorobenzene could not be called catalytic, because the chlorine appears in the product. The hydrogen chloride undergoes a simultaneous reaction which attaches the chlorine to silicon atoms and in some way facilitates the reaction of the chlorobenzene. Since its use in effective proportions leads to the formation of considerable silicon tetrachloride and phenyltrichlorosilane, hydrogen chloride could more logically be used in a direct synthesis of substituted trichlorosilanes, where extra chlorine is necessary.

The separation of diphenyldichlorosilane prepared by direct synthesis is complicated by the necessity of removing aluminum chloride, which presumably would not be present in preparations by other methods. While the use of aluminum-free silicon would obviate the necessity of such removal, it seems easier and more economical to use the commercial grades of silicon and to carry out the filtration procedure as described. Once this has been done the phenylchlorosilanes may be distilled at atmospheric pressure without decomposition. In this investigation no evidence has been found to support the inference that the phenylchlorosilanes must be distilled at reduced pressure to maintain their purity.[6]

Heretofore only the reduced-pressure boiling points have been given for diphenyldichlorosilane and triphenylchlorosilane. The normal boiling points for all the phenylchlorosilanes, as determined on the products from these experiments, are: $C_6H_5SiCl_3$, 201.5° cor.; $(C_6H_5)_2SiCl_2$, 305.2 cor.; $(C_6H_5)_3SiCl$, 378.0 cor.

Summary

The general reaction of hydrocarbon halides with elementary silicon is applied to the direct synthesis of diphenyldichlorosilane from chlorobenzene and commercial silicon. The effects of various catalysts are described, and conditions for carrying out the reaction and for separating the phenylchlorosilanes by distillation at atmospheric pressure are given.

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(6) Krause and von Grosse, "Die Chemie der Metallorganischen Verbindungen," Borntraeger Geb., Berlin, 1937, pp. 274, 276.

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[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Copolymerization. III. Systems Containing More than Two Monomers

BY CHEVES WALLING AND EMORENE R. BRIGGS

The theory of copolymerization recently developed by Alfrey and Goldfinger,[1] Mayo and Lewis,[2] and Wall[3] may be extended to the case of n monomers and the composition of product expressed in terms of the initial composition of the reaction mixture and the $n(n - 1)$ monomer reactivity ratios[2] involved. This fact has been pointed out by Alfrey and Goldfinger, who have developed the expression for the initial polymer composition in a system of three monomers.[4] This paper contains a discussion of the more general case of n monomers, and experimental work on combinations of styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride, for which the necessary monomer reactivity ratios are now available.[5]

Differential Equation for Copolymerization of n Monomers.—If n monomers, A, B, C, . . ., N, are allowed to copolymerize, their rates of disappearance (making the same assumptions as in the copolymerization of two monomers[2]) are given by the system of equations

$$\frac{-d[A]}{dt} = k_{aa}[A][A\cdot] + k_{ab}[A][B\cdot] + \ldots + k_{an}[A][N\cdot] \tag{1a}$$

$$\frac{-d[B]}{dt} = k_{ba}[B][A\cdot] + k_{bb}[B][B\cdot] + \ldots + k_{bn}[B][N\cdot] \tag{1b}$$

. . . .

$$\frac{-d[N]}{dt} = k_{na}[N][A\cdot] + k_{nb}[N][B\cdot] + \ldots + k_{nn}[N][N\cdot] \tag{1n}$$

where $[A\cdot]$, $[B\cdot]$, . . ., $[N\cdot]$ are concentrations of growing polymer chains ending in A, B, . . ., N type radicals, respectively, and k_{ij}, in general, is the rate constant for reaction of monomer I with

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

a J-type radical. Applying the conventional steady state assumption to each radical yields the auxiliary equations

$$k_{\mathrm{aa}}[\mathrm{A}][\mathrm{A}\cdot] + k_{\mathrm{ab}}[\mathrm{A}][\mathrm{B}\cdot] + \ldots + k_{\mathrm{an}}[\mathrm{A}][\mathrm{N}\cdot] = k_{\mathrm{aa}}[\mathrm{A}][\mathrm{A}\cdot] + k_{\mathrm{ba}}[\mathrm{B}][\mathrm{A}\cdot] + \ldots + k_{\mathrm{na}}[\mathrm{N}][\mathrm{A}\cdot] \quad (2a)$$

$$k_{\mathrm{ba}}[\mathrm{B}][\mathrm{A}\cdot] + k_{\mathrm{bb}}[\mathrm{B}][\mathrm{B}\cdot] + \ldots k_{\mathrm{bn}}[\mathrm{B}][\mathrm{N}\cdot] = k_{\mathrm{ab}}[\mathrm{A}][\mathrm{B}\cdot] + k_{\mathrm{bb}}[\mathrm{B}][\mathrm{B}\cdot] + \ldots + \ldots k_{\mathrm{nb}}[\mathrm{N}][\mathrm{B}\cdot] \quad (2b)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$k_{\mathrm{na}}[\mathrm{N}][\mathrm{A}\cdot] + k_{\mathrm{nb}}[\mathrm{N}][\mathrm{B}\cdot] + \ldots + k_{\mathrm{nn}}[\mathrm{N}][\mathrm{N}\cdot] = k_{\mathrm{an}}[\mathrm{A}][\mathrm{N}\cdot] + k_{\mathrm{bn}}[\mathrm{B}][\mathrm{N}\cdot] + \ldots + k_{\mathrm{nn}}[\mathrm{N}][\mathrm{N}\cdot] \quad (2n)$$

As the left side of each of equations (2) is identical with the right side of the corresponding equation (1), substituting (2a) into (1a), factoring out [A·], etc., solving each equation for $-\mathrm{d}t$, and equating yields

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}\cdot](k_{\mathrm{aa}}[\mathrm{A}] + k_{\mathrm{ba}}[\mathrm{B}] + \ldots + k_{\mathrm{na}}[\mathrm{N}])} = \frac{\mathrm{d}[\mathrm{B}]}{[\mathrm{B}\cdot](k_{\mathrm{ab}}[\mathrm{A}] + k_{\mathrm{bb}}[\mathrm{B}] + \ldots + k_{\mathrm{nb}}[\mathrm{N}])} = \ldots = \frac{\mathrm{d}[\mathrm{N}]}{[\mathrm{N}\cdot](k_{\mathrm{an}}[\mathrm{A}] + k_{\mathrm{bn}}[\mathrm{B}] + \ldots + k_{\mathrm{nn}}[\mathrm{N}]} \quad (3)$$

Equations (2) may be regarded as a series of n homogeneous equations in n unknowns, [A·], [B·], . . ., [N·], so that simultaneous solution of all but one will give the ratios of each unknown to the others.[6] This may be accomplished most conveniently by the method of determinants,[7] and the resulting determinants may then be substituted into equation (3) without evaluation. In order to use equation (3), it is then necessary to replace the (at present immeasurable) rate constants by measurable monomer reactivity ratios.[2] Let these quantities be defined as follows

$$\begin{array}{llll} & k_{\mathrm{aa}}/k_{\mathrm{ba}} = \alpha_{\mathrm{b}} & k_{\mathrm{aa}}/k_{\mathrm{ca}} = \alpha_{\mathrm{c}} \ldots & k_{\mathrm{aa}}/k_{\mathrm{na}} = \alpha_{\mathrm{n}} \\ k_{\mathrm{bb}}/k_{\mathrm{ab}} = \beta_{\mathrm{a}} & & k_{\mathrm{bb}}/k_{\mathrm{cb}} = \beta_{\mathrm{c}} \ldots & k_{\mathrm{bb}}/k_{\mathrm{nb}} = \beta_{\mathrm{n}} \\ \cdots & \cdots & \cdots & \cdots \\ k_{\mathrm{nn}}/k_{\mathrm{an}} = \nu_{\mathrm{a}} & k_{\mathrm{nn}}/k_{\mathrm{bn}} = \nu_{\mathrm{b}} & k_{\mathrm{nn}}/k_{\mathrm{cn}} = \nu_{\mathrm{c}} \ldots & \end{array}$$

Dividing the denominator of each fraction of equation (3) by $k_{\mathrm{aa}}k_{\mathrm{bb}}k_{\mathrm{cc}} \ldots k_{\mathrm{nn}}$ (by dividing each column of the determinant by the appropriate k and the polynomial by the remaining k), and factoring [A], [B], . . ., [N] from the successive determinants, gives the desired equation

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]D_{\mathrm{a}}\,([\mathrm{A}] + [\mathrm{B}]/\alpha_{\mathrm{b}} + \ldots [\mathrm{N}]/\alpha_{\mathrm{n}})} = \frac{\mathrm{d}[\mathrm{B}]}{[\mathrm{B}]D_{\mathrm{b}}\,([\mathrm{A}]/\beta_{\mathrm{a}} + [\mathrm{B}] + \ldots [\mathrm{N}]/\beta_{\mathrm{n}})} = \ldots = \frac{\mathrm{d}[\mathrm{N}]}{[\mathrm{N}]D_{\mathrm{n}}\,([\mathrm{A}]/\nu_{\mathrm{a}} + [\mathrm{B}]/\nu_{\mathrm{b}} + \ldots [\mathrm{N}])} \quad (4)$$

where

$$D_{\mathrm{a}} \equiv \begin{vmatrix} -1/\nu_{\mathrm{a}} & 1/\beta_{\mathrm{a}} & 1/\gamma_{\mathrm{a}} & \ldots & 1/\mu_{\mathrm{a}} \\ -[\mathrm{B}]/\nu_{\mathrm{b}} & -([\mathrm{A}]/\beta_{\mathrm{a}} + [\mathrm{C}]/\beta_{\mathrm{c}} + \ldots [\mathrm{N}]/\beta_{\mathrm{a}}) & [\mathrm{B}]/\gamma_{\mathrm{b}} & \ldots & [\mathrm{B}]/\mu_{\mathrm{b}} \\ -[\mathrm{C}]/\nu_{\mathrm{c}} & [\mathrm{C}]/\beta_{\mathrm{c}} & -([\mathrm{A}]/\gamma_{\mathrm{a}} + [\mathrm{B}]/\gamma_{\mathrm{b}} + \ldots [\mathrm{N}]/\gamma_{\mathrm{a}}) & \ldots & \\ \ldots & \ldots & \ldots & \ldots & \\ \ldots & \ldots & \ldots & & \\ -[\mathrm{M}]/\nu_{\mathrm{m}} & \cdots\cdots & \cdots\cdots & & -([\mathrm{A}]/\mu_{\mathrm{a}} + [\mathrm{B}]/\mu_{\mathrm{b}} + \ldots + [\mathrm{N}]\mu_{\mathrm{n}}) \end{vmatrix}$$

etc.[8] Equation (4) describes the relative rates of polymerization of each monomer (and, hence, the composition of polymer formed at any instant) in terms of monomer concentrations and the $n(n - 1)$ monomer reactivity ratios.

For the case of three monomers, expansion of the determinants yields

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]([\mathrm{A}]/\beta_{\mathrm{a}}\gamma_{\mathrm{a}} + [\mathrm{B}]/\beta_{\mathrm{a}}\gamma_{\mathrm{b}} + [\mathrm{C}]/\beta_{\mathrm{c}}\gamma_{\mathrm{a}})([\mathrm{A}] + [\mathrm{B}]/\alpha_{\mathrm{b}} + [\mathrm{C}]/\alpha_{\mathrm{c}})} = \frac{\mathrm{d}[\mathrm{B}]}{[\mathrm{B}]([\mathrm{A}]/\alpha_{\mathrm{b}}\gamma_{\mathrm{a}} + [\mathrm{B}]/\alpha_{\mathrm{b}}\gamma_{\mathrm{b}} + [\mathrm{C}]/\alpha_{\mathrm{c}}\gamma_{\mathrm{b}})([\mathrm{A}]/\beta_{\mathrm{a}} + [\mathrm{B}] + [\mathrm{C}]/\beta_{\mathrm{c}})} = \frac{\mathrm{d}[\mathrm{C}]}{[\mathrm{C}]([\mathrm{A}]\alpha_{\mathrm{c}}\beta_{\mathrm{a}} + [\mathrm{B}]/\alpha_{\mathrm{b}}\beta_{\mathrm{c}} + [\mathrm{C}]/\alpha_{\mathrm{c}}\beta_{\mathrm{c}})([\mathrm{A}]/\gamma_{\mathrm{a}} + [\mathrm{B}]/\gamma_{\mathrm{b}} + [\mathrm{C}])} \quad (5)$$

Equation (5) is identical with that of Alfrey and Goldfinger,[4] except that the monomer reactivity ratios in keeping with the usage of Mayo, *et al.*,[2,5] are the reciprocals of the constants which Alfrey and Goldfinger employ. In the case of four or more monomers, use of equation (4) is simplified if numerical values are substituted before the determinants are expanded.

Comparison with Experiment.—In Table I are tabulated results on the copolymerization of seven three component and one four component systems of the monomers styrene (S), methyl methacrylate (M), acrylonitrile (A), and vinylidene chloride (V). For calculation of the polymer compositions by equations (4) or (5) the monomer reactivity ratios of Mayo, Lewis and Hulse[5] listed below were employed.

Probably the greatest source of error in calculating polymer compositions is in the values of the monomer reactivity ratios involved, particularly (as they enter the equations as their reciprocals) when these are very small. Thus, if we substitute 0.06 for 0.04 and 0.10 for 0.15 for the monomer reactivity ratios for the acrylonitrile-type radical with styrene and methyl methacrylate respectively (results which are well within the possible error of the original determinations[5]) it amounts to saying that an acrylonitrile-type radical, instead of preferring styrene to methyl methacrylate by a factor of 3.5 to 1, prefers it by a factor of only 1.67 to 1. Recalculation of the data of expt. 6 with these new values for the reactivity of the acrylonitrile radical changes the predicted composition of the polymer from 41.4 to 37.2% styrene, from 22.7 to 27.7% methyl methacrylate and from 35.9 to 35.1% acrylonitrile. These changes, which are within experimental error, are as large as the discrepancies between calculated and observed values found in Table I. In short, agreement between theory and experi-

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[6] This statement requires that the n equations are consistent. As the determinant of their coefficients can be shown to be equal to zero, this is so.

[7] For a discussion of determinants see, for example, Ch. III, Sokolnikoff and Sokolnikoff, "Higher Mathematics for Engineers and Physicists," McGraw-Hill Book Company, Inc., New York, N. Y., 1941.

[8] In order to factor [N] from D_{n} it is convenient to add all the rows together giving a sum of the form $-[\mathrm{N}]/\alpha_{\mathrm{n}} - [\mathrm{N}]/\beta_{\mathrm{n}} - [\mathrm{N}]/\alpha_{\mathrm{n}} - \ldots - [\mathrm{N}]/\mu_{\mathrm{n}}$. This sum may be used to replace any row without altering the value of the determinant.

TABLE I

THREE AND FOUR COMPONENT POLYMERIZATIONS OF STYRENE (S), METHYL METHACRYLATE (M), ACRYLONITRILE (A) AND VINYLIDENE CHLORIDE (V) AT 60°

Expt.	Feed Mole %	Monomers	Time, hr.	Yield, wt. %	Polymer analyses, %		Polymer (mole %) Found	Polymer (mole %) Calcd.
1	31.24	S	16	18.2			43.4	44.3
	31.12	M			C, 68.53	68.79	39.4	41.2
	37.64	V			Cl, 12.01	12.13	17.2	14.5
2	35.10	M	12	18.1			50.8	54.3
	28.24	A			N, 4.60		28.3	29.7
	36.66	V			Cl, 17.24	17.17	20.9	16.0
3	34.03	S	8	16.5			52.8	52.4
	34.49	A			N, 6.02	6.12	36.7	40.5
	31.48	V			Cl, 8.78	8.83	10.5	7.1
4	35.92	S	3.5	13.6			44.7	43.6
	36.03	M			C, 78.35	78.86	26.1	29.2
	28.05	A			N, 4.67	4.69	29.2	26.2
5	53.23	S	5.75	15.4	C, 80.99	81.90	52.6	52.9
	26.51	M			N, 4.22	4.32	20.2	23.2
	20.26	A					27.2	23.9
6	28.32	S	4.5	18.4			38.4	41.4
	28.24	M			C, 77.38	77.46	23.0	22.7
	43.44	A			N, 6.47	6.48	38.6	35.9
7	27.76	S	5.75	17.2			36.4	36.8
	52.06	M			C, 74.51	74.45	40.6	43.8
	20.18	A			N, 3.52	3.62	23.0	19.4
8	25.21	S	8.5	18.9	C, 73.18	73.27	40.7	41.0
	25.48	M			N, 4.02	4.01	25.5	27.3
	25.40	A			Cl, 6.39	6.39	25.8	24.8
	23.91	V					8.0	6.9

Monomer radical	S	M	A	V
S	..	0.50	0.41	2.00
M	0.50	..	1.20	2.53
A	0.04	0.15	..	0.91
V	0.14	0.24	0.37	..

ment is as good as can be hoped for at this time, and indicates that the theory of copolymerization can be satisfactorily extended to systems of more than two monomers.

The "Azeotropic Copolymer" of *n* Components.—An "azeotropic copolymer" has been defined by Wall[3] as one in which the polymer being formed contains the same ratio of monomers as the feed, and both he and Alfrey and Goldfinger have determined the conditions in two monomer systems under which such a copolymer may be formed. It is of interest to determine whether such a copolymer can occur in multicomponent systems. If Equation (2a) is substituted into (1a), (2b) into (1b), etc., the resulting set may be solved for [A·], [B·] . . ., etc., as ratios of determinants. Since the condition for the formation of an azeotropic copolymer is that $\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{B}]}{[\mathrm{B}]\mathrm{d}t} = \ldots = \frac{\mathrm{d}[\mathrm{N}]}{[\mathrm{N}]\mathrm{d}t}$, the results may be finally expressed (after dividing the *i*th column of each determinant by k_{ii}) in the form $k_{\mathrm{aa}}\,[\mathrm{A}\cdot] = \frac{-\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]\mathrm{d}t}\,\frac{\overline{D}_{\mathrm{a}}}{\overline{D}}$, $k_{\mathrm{bb}}\,[\mathrm{B}\cdot] = \frac{-\mathrm{d}[\mathrm{B}]}{[\mathrm{B}]\mathrm{d}t}\,\frac{\overline{D}_{\mathrm{b}}}{\overline{D}}$, . . ., etc., where

$$\frac{\overline{D}_{\mathrm{a}}}{\overline{D}} = \frac{\begin{vmatrix} 1 & 1/\beta_{\mathrm{a}} & 1/\gamma_{\mathrm{a}} & \ldots \\ 1 & 1 & 1/\gamma_{\mathrm{b}} & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{vmatrix}}{\begin{vmatrix} 1 & 1/\beta_{\mathrm{a}} & 1/\gamma_{\mathrm{a}} & \ldots \\ 1/\alpha_{\mathrm{b}} & 1 & 1/\gamma_{\mathrm{b}} & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{vmatrix}} \text{ etc.}$$

Substituting these values into equations (1) and (2) yields as the condition for the formation of an azeotropic copolymer, the system of equations

$$\left(1 - \frac{\overline{D}_{\mathrm{a}}}{\overline{D}}\right)[\mathrm{A}] + [\mathrm{B}]/\alpha_{\mathrm{b}} + [\mathrm{C}]/\alpha_{\mathrm{c}} + \ldots + [\mathrm{N}]/\alpha_{\mathrm{n}} = 0 \quad (6\mathrm{a})$$

$$[\mathrm{A}]/\beta_{\mathrm{a}} + \left(1 - \frac{\overline{D}_{\mathrm{b}}}{\overline{D}}\right)[\mathrm{B}] + [\mathrm{C}]/\beta_{\mathrm{c}} + \ldots + [\mathrm{N}]/\beta_{\mathrm{n}} = 0 \quad (6\mathrm{b})$$

. . . .

As equations (6) are linear, for any set of monomers only one composition is capable of yielding an azeotropic copolymer, regardless of the number of monomers present.[9] Furthermore, as no concentrations or monomer reactivity ratios may be negative if the result is to have physical significance, all determinants must have the same sign. In the case of a two component system, this reduces to the condition, found by Wall, that for an azeotropic polymer to be possible the two monomer reactivity ratios must both be larger or both be smaller than unity.[10] Substitution of the monomer reactivity ratios of Lewis, Mayo and Hulse[5] into the determinants shows that azeotropic copolymers are not possible with any of the possible three or four component systems of styrene, methyl methacrylate, acrylonitrile or vinylidene chloride as in none of them do all the determinants have the same sign.

Integration of the Copolymerization Equation.—If polymer compositions in multicomponent systems are desired at high extents of reaction, integration of equation (4) is necessary. Although this integration has not been accomplished in closed form, a simple approximation which appears to give quite accurate results is possible, and any higher degree of precision is possible by means of series expansion. Let there be a series of quantities *u*, *v*, *w*, . . . such that $u = \ln[\mathrm{A}]/[\mathrm{A}_0]$, $v = \ln\,[\mathrm{B}]/[\mathrm{B}_0]$, . . ., where subscript zeros refer to initial concentrations. It follows that $[\mathrm{A}] = [\mathrm{A}_0]e^{-u}$, $[\mathrm{B}] = [\mathrm{B}_0]e^{-v}$, . . . and $\mathrm{d}u = \mathrm{d}[\mathrm{A}]/[\mathrm{A}]$, $\mathrm{d}v = \mathrm{d}[\mathrm{B}]/\mathrm{B}$, ... Substituting these quantities into equation (4) and multiplying each denominator by $e^{u+v+w+}\,. . .$ yields

$$\frac{\mathrm{d}u}{D_{\mathrm{a}}^{*}\left([\mathrm{A}_0] + \frac{[\mathrm{B}_0]}{\alpha_{\mathrm{b}}}e^{u-v} + \frac{[\mathrm{C}_0]}{\beta_{\mathrm{b}}}e^{u-w\cdot\cdot}\right)} = \frac{\mathrm{d}v}{D_{\mathrm{b}}^{*}\left(\frac{[\mathrm{A}_0]}{\beta_{\mathrm{a}}}e^{v-u} + [\mathrm{B}_0] + \frac{[\mathrm{C}_0]}{\beta_{\mathrm{c}}}e^{v-w} + \ldots\right)} = \ldots \quad (7)$$

where

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(9) Excepting the trivial case of two or more monomers having identical reactivities.

(10) Although no simpler statement of the general condition for the formation of the *n* component "azeotropic" copolymer has been found than the above condition on the sign of the determinants, a sufficient (but not necessary) condition appears to be that all monomer reactivity ratios are simultaneously greater or less than unity.

$$D_a^* = \begin{vmatrix} -1/\nu_a & 1/\beta_a & \ldots \\ -[B_0]/\nu_b & -\left(\frac{[A_0]}{\beta_a} e^{v-u} + \frac{[C_0]}{\beta_c} e^{v-w} + \ldots\right) & \ldots \\ -[C_0]/\nu_c & \ldots\ldots\ldots\ldots & \ldots \\ \ldots\ldots & \ldots\ldots\ldots\ldots & \ldots \\ \ldots\ldots & \ldots\ldots\ldots\ldots & \ldots \end{vmatrix} \text{ etc.}$$

If it is assumed that $u - v$, etc., are small, so that e^{u-v}, etc., $\cong 1$, (5) may be integrated to give

$$\frac{\log [A]/[A_0]}{D_{a_0}([A_0] + [B_0]/\alpha_b + [C_0]\alpha_c + \ldots)} = \frac{\log [B]/[B_0]}{D_{a_0}([A_0]/\beta_a + [B^0] + [C_0]/\beta_c + \ldots)} = \ldots \quad (8)$$

where $D_{a_0} = D_a$, etc., with all concentrations receiving a zero subscript. Equation (8) necessarily gives the correct polymer composition at the beginning and end of a copolymerization. How nearly it is correct at intermediate points depends upon how small is the numerical difference between log $[A]/[A_0]$ and log $[B]/[B_0]$, etc. In the case of a system of two monomers, for which the exact integral is known, a determination of the accuracy of equation (8) is possible. In this case, equation (8) may be written (using the nomenclature of Mayo and Lewis[2])

$$[S]/[S_0] = ([M]/[M_0])^{\frac{\sigma [S_0]/[M_0] + 1}{\mu + [S_0]/[M_0]}} \quad (9)$$

where σ and μ are the monomer reactivity ratios for the radicals derived from the monomers S and M, respectively, and the form chosen is one convenient for calculation. The exact expression may be written as

$$[S]/[S_0] = k^{1/1-\mu} \{([M_0]/[S_0] - p)/([M_0]/[S_0] - pk)\}^{\frac{p\mu+1}{1-\sigma}} \quad (10)$$

where $p = (1 - \sigma)/(1 - \mu)$ and $k = [M_0][S]/[S_0][M]$.[11] For calculation, initial monomer compositions of 20 mole per cent. styrene–80 mole per cent. methyl methacrylate and 20 mole per cent. styrene–80 mole per cent. acrylonitrile were chosen and the monomer reactivity ratios listed earlier used to calculate integral polymer compositions during the course of the reaction. The first system is one showing moderate and the second a rather extreme difference between the feed and the composition of the resulting polymer. Results are plotted in Fig. 1. In the styrene–methyl methacrylate system, the discrepancy never exceeds 0.4%. In the extreme styrene-acrylonitrile case, where the polymer initially contains over twice as much styrene as the feed, it is as large as 6%. If higher precision is required, any degree is possible by setting *u*, *v*, *w*, *etc.*, equal to power series in *t* (it will be recalled that in equation (3) all the fractions are equal to $-dt$). Using only the first term in such expansions gives equation (8). Higher terms result in terms of increased complexity.

As the experiments in Table I were all carried out to less than 20% reaction and polymer compositions agree with those calculated by the differential equation to within experimental error, application of equation (8) would be expected to improve the agreement with experiment very little. For example, the polymer composition in mole per cent. for experiment (2), calculated by equation (8) becomes 51.3% methacrylate, 30.4% acrylonitrile and 18.3% vinylidene chloride.

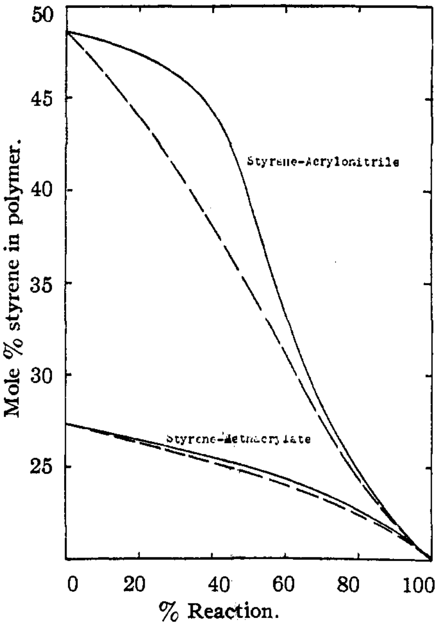

Fig. 1.—Polymer composition *vs.* % reaction for initial compositions of 20 mole % styrene + methyl methacrylate and + acrylonitrile: solid lines, exact equation; dashed lines, approximate equation.

Acknowledgment.—The authors wish to thank Dr. Frank R. Mayo for much helpful discussion and Dr. Melvin Mooney for aid in the mathematical section of this paper, in particular for suggestion of the power series method of solution of equation (4).

Summary

1. A general differential equation has been developed, predicting the composition of the polymer formed in the copolymerization of *n* monomers in terms of monomer concentrations and the $n(n - 1)$ monomer reactivity ratios for all the two-component systems.

2. The predicted and observed polymer compositions agree within experimental error for three and four component systems of styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride.

3. It is shown that for any number of monomers, only one monomer ratio is able to yield an "azeotropic copolymer" in the sense of Wall.

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[11] Equation (10) is equivalent to Mayo and Lewis' equation (12), but has been transformed into a more convenient form for the calculation of polymer compositions when σ and μ are known. For use, values of *k* are chosen and the corresponding $[S]/[S_0]$, calculated.

The conditions under which such a copolymer is possible are described.

4. A method of approximating the integral of the differential copolymerization equation is described.

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The Mechanism of the Alkylation of Paraffins

BY LOUIS SCHMERLING

The catalytic alkylation of isoparaffins with olefins has been studied extensively ever since the reaction was discovered by Ipatieff and Pines[1] more than a decade ago. A number of mechanisms,[2] none of which is completely satisfactory, were proposed during the succeeding years in order to explain how the reaction occurs. A mechanism which appears to have none of the objectionable features of the previous ones and which seems to give a truer picture of what occurs during alkylation was described[3] in a recent "Communication to the Editor" of this Journal. The present paper presents a more complete discussion of the reaction scheme there outlined.

Previous Mechanisms

The principal difficulty encountered in developing a paraffin alkylation mechanism is the formulation of a rational explanation for the structure of the products obtained. As may be seen from Table I, the products of the alkylation of isobutane with ethylene and propene, for example, are not those which may be obtained by simple addition of an alkyl group and a hydrogen atom across the olefinic double bond. A brief discussion of how each of the earlier mechanisms accounted for the products obtained is given below.

TABLE I

COMPOSITION OF THE PRODUCTS OF THE ALKYLATION OF ISOBUTANE WITH ETHYLENE AND PROPENE IN THE PRESENCE OF ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

Olefin	Major products	Principal minor products[a]
Ethylene[b]	2,3-Dimethylbutane	2-Methylpentane Octanes Ethane Isopentane
Propene[c]	2,3-Dimethylpentane 2,4-Dimethylpentane	Trimethylpentanes Propane Isopentane 2,3-Dimethylbutane

[a] References given below and unpublished results from the Research Laboratories of the Universal Oil Products Company. [b] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, **8**, 438 (1943). [c] H. Pines, A. V. Grosse and V. N. Ipatieff, THIS JOURNAL **64**, 33 (1942).

Ipatieff and Grosse[2a] postulated that the alkylation of an isoparaffin proceeds via the addition of the corresponding *t*-alkyl group and hydrogen to the olefin to yield a paraffin containing a quaternary carbon atom; this compound is not isolated but undergoes isomerization to yield the isomeric products which are actually obtained. Thus, the alkylation of isobutane with ethylene would yield 2,2-dimethylbutane as the unstable intermediate and 2,3-dimethylbutane as the final product. The chief objection to this mechanism is that neohexane is the predominant hexane in equilibrium mixtures of hexanes at temperatures up to 200° and even higher.[4] Therefore, it would be expected that a substantial amount of 2,2-dimethylbutane would be present in the alkylation product. Another objection to this mechanism is that in many cases, especially with sulfuric acid as catalyst, isomerization of the "expected" product does not take place under the conditions of the alkylation.[2c,d]

The mechanism offered by Birch and Dunstan[2b] differs from that of Ipatieff and Grosse in that it proposes that the alkylation involves a primary rather than the tertiary carbon atom. Alkylation of isobutane with propene, for example, would occur by way of addition of isobutyl and hydrogen to the double bond to yield 2,4-dimethylpentane. Isomerization of part of this heptane would then produce 2,3-dimethylpentane which is also a major product of the reaction. Birch and Dunstan suggest that the isoparaffin is activated (*via* the formation of a complex with the catalyst) and dissociates into a negative alkyl ion (in this example, isobutyl) and a proton, the proton coming from a methyl group. The olefin is activated by addition of a proton to form a positive alkyl ion (in this example, isopropyl). Combination of the carbanion (isobutyl) and the carbonium ion (isopropyl) yields the paraffinic product (2,4-dimethylpentane). The objections to the mechanism of Birch and Dunstan are similar to those raised against the mechanism of Ipatieff and Grosse, *i. e.*, the postulated isomerization of the primary product is improbable.[2c]

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[1] V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, N. Y., 1936, p. 673.

[2] (a) V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **57**, 1616 (1935); *J. Org. Chem.*, **8**, 438 (1943); Presented at Rochester Meeting of the American Chemical Society, September, 1937; (b) S. F. Birch and A. E. Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939); (c) P. D. Caesar and A. W. Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941); (d) S. H. McAllister, J. Anderson, S. A. Ballard and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941).

[3] L. Schmerling, THIS JOURNAL, **66**, 1422 (1944).

[4] F. D. Rossini, E. J. R. Prosen and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **27**, 529 (1941).