dimethylnaphthalene. The principal reactions of cyclohexene under the conditions studied were (1) isomerization, (2) polymerization and (3) hydrogen transfer. The hydrogen transfer was primarily from the polymer resulting in the formation of dimethylnaphthalenes and the hydrogenation of the methylcyclopentenes to methylcyclopentane.

Naphthalene was the product formed most abundantly from tetralin. Scission of the hydroaromatic ring gave benzene, toluene, xylenes, possibly ethylbenzene, and higher boiling alkylated benzenes. No alkenylbenzenes were isolated. They may have been formed and then converted into the corresponding alkyl derivatives by hydrogen made available by the conversion of tetralin to naphthalene. Some of the tetralin was converted to bicycloparaffins, presumably decalin or its isomers. The products can be explained by reactions of (1) scission of the hydroaromatic ring and (2) hydrogen transfer. Apparently, isomerization also occurred, for the xylene fraction contained xylenes other than *o*-xylene.

The chief products formed from decalin were "isodecalins," C_3 and C_4 olefinic and paraffinic gases in which isobutane predominated, methylcyclopentane, and probably cyclohexane and the corresponding olefins. In addition, tetralin or its isomers was found and the aromatic reaction products of tetralin conversion indicated above. The products can be explained by the following reactions of decalin and the intermediate tetralin: (1) isomerization, (2) ring scission and (3) hydrogen transfer.

CHICAGO, ILL. RECEIVED APRIL 7, 1944

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

Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate

BY FRANK R. MAYO AND FREDERICK M. LEWIS

Although considerable progress has been made in interpreting the polymerization of single monomers, a systematic study of copolymerization has been hampered by the absence of a theoretical basis for comparing the behavior of monomers in copolymerization. This paper describes the development of such a basis for addition (vinyl) polymerizations, the application of the general concept to the copolymerization of styrene and methyl methacrylate by a free radical mechanism, and the scope of the present development.

The Problem of Copolymerization.—When two monomers such as styrene (S) and methyl methacrylate (M) copolymerize, there are two kinds of free radicals which form the growing ends of the polymer molecules. These two kinds of radicals will be designated as S· and M·, respectively, depending on whether the active center at the instant chosen ends in a styrene or in a methyl methacrylate unit. The reactions of these radicals are assumed (and will be shown) to be independent of the number and kind of attached units. Each kind of radical may react with either kind of monomer molecule

$$\mathrm{S\cdot} + \mathrm{S} \xrightarrow{k_1} \mathrm{S\cdot} \qquad (1)$$

$$\mathrm{S\cdot} + \mathrm{M} \xrightarrow{k_2} \mathrm{M\cdot} \qquad (2)$$

$$\mathrm{M\cdot} + \mathrm{M} \xrightarrow{k_3} \mathrm{M\cdot} \qquad (3)$$

$$\mathrm{M\cdot} + \mathrm{S} \xrightarrow{k_4} \mathrm{S\cdot} \qquad (4)$$

The problem is to develop from these equations an expression which will permit correlation of data on products of copolymerizations in the simplest possible terms.

Previous Work.—Norrish and Brookman[1] studied the rates of copolymerization of styrene–methyl methacrylate mixtures. They considered the problem on the basis of the four chain growth steps given above, but they also made an assumption about the concentration of active centers, the validity of which will be discussed later.

Wall[2] has presented a relatively simple basis for studying copolymerizations. In terms of the nomenclature in this paper, he defines the relative reactivity (α) of two monomers in copolymerization as the quotient of the rate constants for the individual polymerizations (k_s and k_m, respectively): *i. e.*,

$$\frac{d[\mathrm{S}]}{d[\mathrm{M}]} = \frac{k_s[\mathrm{S}]}{k_m[\mathrm{M}]} = \alpha\frac{[\mathrm{S}]}{[\mathrm{M}]}$$

where [S] and [M] refer to concentrations of unreacted monomers. Actually, Wall's equation applies only to the limiting case of ideal copolymerizations, where both radical types, S· and M·, have the same relative preferences for reacting with the monomers S and M, *i. e.*, where $k_1/k_2 = k_4/k_3$. If this relation does not hold, then α will vary with the ratio of S·/M·, and since S·/M· will depend on [S]/[M], α will vary with the composition of the monomer mixture. Although Wall's equation seemed at first to be an attractive approach to the problem of copolymerization, our initial experiments with styrene and methyl methacrylate showed that α varied considerably with [S]/[M]. The α-concept also cannot apply to ethylene derivatives which do not polymerize

---

[1] Norrish and Brookman, *Proc. Roy. Soc.* (London), **171A**, 147 (1939).

[2] Wall, THIS JOURNAL, **63**, 1862 (1941).

easily alone but form 1:1 copolymers with maleic anhydride or maleic imides.[3] A general copolymerization equation must therefore allow for the individual preferences of certain radicals for certain monomers.

In their studies of copolymerization, Marvel and co-workers[4] have employed Wall's equation, but they did not vary the composition of their reaction mixtures sufficiently to give the equation a rigorous test. Jenckel[5] has used the chain growth steps (1) to (4) to account for some copolymerizations; he considered some special cases without attaining a general solution to the problem.

The Copolymerization Equation.—In the copolymerization of two monomers, S and M, according to Equations (1)–(4), the rates of disappearance of S alone and of M alone are given by the expressions

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k_1[\mathrm{S}][\mathrm{S}\cdot] + k_4[\mathrm{S}][\mathrm{M}\cdot] \qquad (5)$$

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_2[\mathrm{M}][\mathrm{S}\cdot] + k_3[\mathrm{M}][\mathrm{M}\cdot] \qquad (6)$$

where the monomer consumed in chain initiation and termination is neglected. Dividing (5) by (6) gives

$$\frac{-\mathrm{d}[\mathrm{S}]}{-\mathrm{d}[\mathrm{M}]} = \frac{k_1[\mathrm{S}][\mathrm{S}\cdot] + k_4[\mathrm{S}][\mathrm{M}\cdot]}{k_2[\mathrm{M}][\mathrm{S}\cdot] + k_3[\mathrm{M}][\mathrm{M}\cdot]} \qquad (7)$$

It is now assumed[1] that a steady state is soon reached and maintained where the rate at which S· type radicals are converted to M· type radicals is equal to the rate at which M· type radicals are converted to S· type radicals, so that

$$k_2[\mathrm{M}][\mathrm{S}\cdot] = k_4[\mathrm{S}][\mathrm{M}\cdot] \qquad (8)$$

Substituting [S·] in (7) by its equivalent from (8), and multiplying numerator and denominator of the right-hand member of (7) by $[\mathrm{M}]/k_4[\mathrm{M}\cdot]$, we obtain

$$\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}[\mathrm{M}]} = \frac{[\mathrm{S}]}{[\mathrm{M}]} \cdot \frac{\frac{k_1}{k_2}[\mathrm{S}] + [\mathrm{M}]}{[\mathrm{S}] + \frac{k_3}{k_4}[\mathrm{M}]} \qquad (9)$$

We shall now define σ as k_1/k_2 and μ as k_3/k_4; (9) then becomes:

$$\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}[\mathrm{M}]} = \frac{[\mathrm{S}]}{[\mathrm{M}]} \cdot \frac{\sigma[\mathrm{S}] + [\mathrm{M}]}{\mu[\mathrm{M}] + [\mathrm{S}]} \qquad (10)$$

Equation (10)[5a] describes the relative rate at which S and M react and enter a copolymer in terms of two constants, σ and μ, which we shall designate as *monomer reactivity ratios* of the two types of radicals involved. Each constant is the ratio of the rate constants for the reactions of one type of radical with the corresponding monomer and with the other monomer, respectively. In the case under discussion, σ is the rate constant for the reaction of a styrene-type radical with styrene divided by the rate constant for the reaction of a styrene-type radical with methyl methacrylate. Similarly, μ is the monomer reactivity ratio for the radical derived from methyl methacrylate. Since there are two constants needed to describe the copolymerization of two monomers, experiments with at least two monomer ratios must be carried out before σ and μ can be evaluated and the behavior of all combinations of the monomers predicted.

The differential equation (10) can be applied directly in experiments where the relative concentrations of the unreacted monomers remain essentially constant. In most monomer systems, unless the conversions are very low, use of the integrated form, described below, is necessary for accuracy.

Utilization of the Copolymerization Equation.—Equation (10) has been integrated to yield

$$\log\frac{[\mathrm{M}]}{[\mathrm{M}_0]} = \frac{\mu}{1-\mu}\log\frac{[\mathrm{M}_0][\mathrm{S}]}{[\mathrm{S}_0][\mathrm{M}]} - \frac{1-\mu\sigma}{(1-\mu)(1-\sigma)}\log\frac{(\sigma-1)\frac{[\mathrm{S}]}{[\mathrm{M}]} - \mu + 1}{(\sigma-1)\frac{[\mathrm{S}_0]}{[\mathrm{M}_0]} - \mu + 1} \qquad (11)$$

where $[\mathrm{S}_0]$ and $[\mathrm{M}_0]$ represent the initial concentrations of S and M. Direct application of (11) is very difficult, but it has been transformed into

$$\mu = \frac{\log\frac{[\mathrm{M}_0]}{[\mathrm{M}]} - \frac{1}{p}\log\frac{1-p\frac{[\mathrm{S}]}{[\mathrm{M}]}}{1-p\frac{[\mathrm{S}_0]}{[\mathrm{M}_0]}}}{\log\frac{[\mathrm{S}_0]}{[\mathrm{S}]} + \log\frac{1-p\frac{[\mathrm{S}]}{[\mathrm{M}]}}{1-p\frac{[\mathrm{S}_0]}{[\mathrm{M}_0]}}} \qquad (12)$$

where

$$p = \frac{1-\sigma}{1-\mu} \qquad (13)$$

The constants, μ and σ, corresponding to the monomers designated as M and S, respectively, are evaluated graphically as follows. In a single polymerization of styrene and methyl methacrylate, the concentrations of monomers at the start of the reaction ($[\mathrm{S}_0]$, $[\mathrm{M}_0]$) and at the point where polymerization is stopped ([S], [M]) are determined experimentally and substituted in equation (12). Since the equation deals only with ratios of concentrations, the concentrations may be expressed in moles per chosen weight or volume. Arbitrary (positive or negative) values of the parameter, p, chosen (at first by trial and error) to give points in a significant region, are substituted in equation (12), yielding corresponding values of μ; σ is then calculated from equation (13) for each value of p. These values of p are now of no further use. In this paper, values of μ and σ are plotted with μ as abscissa and σ as ordinate. The plot corresponding to a single experiment is a practically straight line. Another experiment (line) is necessary to give a unique solution for σ and μ, repre-

---

[3] Wagner-Jauregg, *Ber.*, **63**, 3213 (1930); Arnold, Brubaker and Dorough, U. S. Patent 2,301,356, issued Nov. 10, 1942.

[4] Marvel, Jones, Mastin and Schertz, THIS JOURNAL, **64**, 2356 (1942); Marvel and Schertz, *ibid.*, **65**, 2054 (1943).

[5] Jenckel, *Z. physik. Chem.*, **190A**, 24 (1942).

[5a] Since this manuscript was submitted, a similar equation has been published by Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

sented by the intersection of the two lines. The slopes of these lines are positive and increase as [M]/[S] increases. If the experimental technique and theoretical development were entirely satisfactory, then presumably lines corresponding to all experiments with two given monomers at one temperature would have a common intersection.

While the plot corresponding to each equation is nearly straight in the positive quadrant (the only quadrant with experimental significance) the function has a discontinuity (certain values of p give an imaginary solution) in the negative quadrant between the points

$$\mu = -[S_0]/[M_0],\ \sigma = -[M_0]/[S_0],\ \text{and}$$
$$\mu = -[S]/[M],\ \sigma = -[M]/[S]$$

and a curve on approaching this discontinuity. In general, the lower the conversion, the less is the curvature and the shorter is the discontinuity; at very low conversions, the curve approaches the straight line corresponding to the differential equation (10).

Experimental

Reagents.—For most of the experiments reported, a pure grade of styrene supplied by the Dow Chemical Company was distilled at reduced pressure in an atmosphere of nitrogen; b. p. 20 mm. 46.0°, m. p. −31.0°, $n^{20}\text{D}$ 1.5462; commercial methyl methacrylate, supplied by the Peters Chemical Company, was treated similarly: b. p. 61 mm. 33.3°, m. p. −48.7°, $n^{20}\text{D}$ 1.4138. Samples were stored in a refrigerator. For a few experiments, the above monomers were recrystallized until further recrystallization changed the melting point by less than 0.02°. A large sample was frozen slowly, with stirring, to the extent of about 90% and the unfrozen portion was poured off; this process was repeated fifteen times. The best styrene melted at −30.7°[6]; methyl methacrylate at −48.2°.

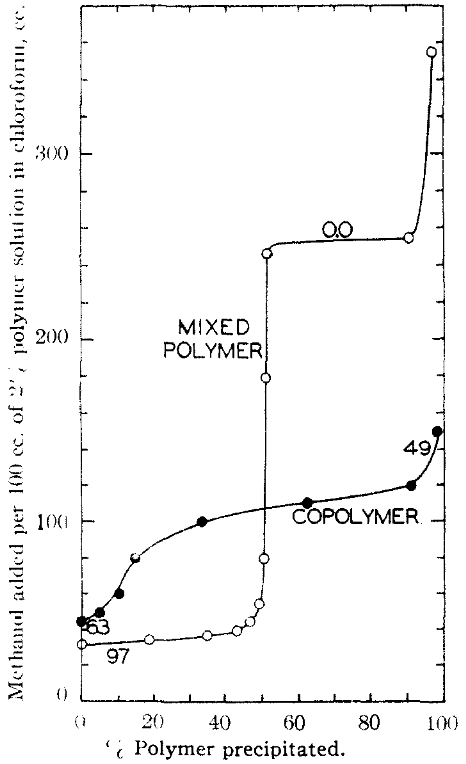

Fig. 1.—Proof of copolymerization. The numbers indicate the per cent. of styrene in some fractions.

Experimental Procedure.—Mixtures containing 0.08 mole of monomer and 0.00008 mole of benzoyl peroxide (0.1 mole %) were measured out in Pyrex tubes of 20–30 cc. capacity, and by the use of a conventional all-glass vacuum system, each reaction mixture was degassed at least twice, and the vessel (cooled in liquid nitrogen) evacuated to 10^{-4} mm. pressure or better before sealing off. Polymerization was then carried out in a water-bath held at 60.0 ± 0.1°.

Beyond this stage, several procedures were employed with gradual improvement in the results obtained. (1) In the earliest experiments (not included in Table I), the partially polymerized reaction mixtures were simply heated for fifteen to twenty-five hours at 100° and 1 mm. to remove the monomers, leaving hard, frothy products. Although fairly consistent results were obtained with this procedure (as long as comparable quantities of copolymer were obtained), it was abandoned when it was found that the copolymer always contained more styrene (the less volatile monomer) than products which had been precipitated to remove the monomer. (2) In experiments 6–13, the partially polymerized reaction mixtures were dissolved in 10–30 cc. of benzene and the polymers were precipitated by addition of 200–300 cc. of methanol. That precipitation was complete, even with polymers of high ester content, was established by evaporation of the liquors in one instance. The precipitates were then treated as in (1). (3) In Expts. 1, 2, and 3, the freshly precipitated polymer was dissolved in about ten parts of benzene and the solution was frozen in dry-ice. The frozen solution was then kept in a 0°-bath at 1 mm. pressure for at least ten hours while the benzene sublimed off, leaving a white, very porous product; the remaining solvent and monomers were then removed by heating to 60° for seventy-two hours at 1 mm. pressure. This procedure[7] gave better results and a more easily handled product. Procedure (4) was used for Expts. 4 and 5. It was like (3) except that the polymer was precipitated three times before being frozen in benzene and except that this solution stood at 1 mm. pressure for seventeen hours at 0°, four hours at room temperature, and twenty hours at 70° to remove benzene and monomers. The period at room temperature was found to eliminate some sintering of the spongy polymer which otherwise often occurred.

After all procedures, the polymer was weighed, and analyzed for carbon by combustion. The final proportion of unreacted monomers in the reaction mixture ([S] and [M]) was calculated from the initial proportion ([S₀] and [M₀]) and the amounts which appeared in the polymers. This method of determining [S] and [M] becomes inaccurate at high conversions; hence conversions were seldom allowed to exceed 40%. Polymers made from styrene or methyl methacrylate alone gave carbon analyses as much as 1% low unless freshly-distilled monomers were used and oxygen was excluded during polymerization. Distillation of the monomers *in vacuo* into the reaction vessel was found unnecessary.

Proof of Copolymerization.—The following evidence shows that a mixture of styrene and methyl methacrylate yields a true copolymer. Chloroform solutions of a copolymer containing 58.5% styrene and of equal weights of polystyrene and polymethyl methacrylate were treated with methanol at room temperature as shown in Fig. 1,

---

[6] The melting point of styrene is reported to be −30.60° by Smoker and Burchfield, *Ind. Eng. Chem., Anal. Ed.*, **15**, 128 (1943). The difference between their result and ours is probably due to the calibration of the five-junction copper–constantan thermocouple which we used, but the differences between our monomer samples are considered significant.

[7] Experiments which establish the reliability of this frozen benzene technique are described by Lewis and Mayo, paper to be submitted to *Analytical Edition of Industrial and Engineering Chemistry*.

precipitates being collected at the points indicated. Some of the fractions were analyzed for carbon; their styrene contents are given in Fig. 1. The results show that the mixture of polymers is easily resolved while the copolymer is essentially homogeneous. The copolymer had been isolated by Procedure (1); the fractionation suggests that some residual styrene polymerized during the heating period.

Results and Discussion

Data on the copolymerization of styrene and methyl methacrylate are collected in Table I. The reactions were carried out at 60° and (except in Expt. 5) in the presence of 0.1 mole % of benzoyl peroxide. Each line in Figs. 2–5 corresponds to one run in Table I and is a portion of the curve corresponding to all values of σ and μ which satisfy Equation (12) for that run. Experiments were nearly always carried out as three simultaneous runs with three different proportions of monomers. Although there is no evidence that different lots of freshly distilled monomers showed any significant variations, each set of runs has been treated separately in the table. The lines with least, intermediate, and greatest slope correspond, respectively, to runs which initially contained 80, 50 and 20 mole % of styrene. Within experimental error (to be discussed in the next section),

TABLE I

COPOLYMERIZATION OF STYRENE (S) AND METHYL METHACRYLATE (M) AT 60°[a]

Expt. no.	Concentrations of unreacted monomers[b] $[S_0]$	$[M_0]$	$[S]$	$[M]$	Reaction time, hrs.	Polymer Yield, wt. %	Carbon,[c] %	α[d]	σ	μ
1a	0.8043	0.1957	0.532	0.110	24	35.70	84.76 84.78	0.72	0.49-0.58	0.46-0.56
b	.498	.502	.3295	.3345	18	33.65	76.56 76.53	1.02		
c	.203	.797	.1017	.518	10.6	38.10	68.90 68.77	1.61		
c*	.203	.797	.1036	.516	10.6	38.10	68.35	1.56		
2a	.804	.196	.530	.1133	24	35.60	85.08 84.93	0.76	0.44-0.65	0.41-0.64
b	.4975	.5025	.344	.348	18	30.80	76.18 76.65	1.01		
c	.200	.800	.1023	.534	10.6	36.40	68.93 68.98	1.66		
d	.796	.204	.535	.114	24	34.92	84.35 84.28 84.16	0.69		
e	.502	.498	.3375	.345	18	31.75	76.96 77.22 77.07	1.08		
f	.1898	.8102	.0987	.542	10.6	36.10	68.63 68.31 68.31 68.28	1.62		
3a	.806	.194	.1395	.00291	35	85.6	85.35 85.37 85.29	0.417	0.67	0.35
b	.503	.497	.0619	.0263	35	91.1	76.02 74.94 76.12	.714		
4a	1.0000	.0000			5	7.98	92.22 92.12		0.48-0.50	0.48-0.50
b	0.7980	.2020	.7435	.1813	5	7.57	83.66 83.77 83.94	0.654		
c	.5010	.4990	.4571	.4556	5	8.74	76.52 76.61	1.005		
d	.2021	.7979	.1828	.7468	2.68	7.05	69.13 69.11	1.52		
e	.0000	1.0000			1.37	10.73	59.68 59.72 59.72[k]			
5a[a]	.8004	0.1996	.7450	.1796	89	7.53	83.98 84.00	0.678	0.48-0.52	0.48-0.52
b[a]	.5020	.4980	.4552	.4520	89	9.28	76.70 76.53	1.01		
c[a]	.1980	.8020	.1623	.7058	68.5	13.23	68.90 69.07	1.55		
6a	.800	.200	.610	.134	24.5	25.6	84.12 84.29	0.68	0.51-0.52	0.48-0.50
b	.502	.498	.3785	.377	16.5	24.45	76.60	1.01		
c	.201	.799	.1455	.649	10	20.55	69.04	1.56		
7a	.7982	.2018	.537	.118	26.5	34.5	84.73 84.59	0.73	0.59-0.70	0.45-0.55
b	.501	.499	.3375	.3495	19.25	31.3	76.80 77.60	1.01		
c	.2003	.7997	.1268	.585	11	28.85	68.70 68.49 68.26	1.47		
8a	.800	.200	.608	.1353	20.5	25.6	84.41 84.33	0.694	0.54-0.62	0.44-0.54
b	.498	.502	.3375	.348	20.5	31.5	76.72 76.93	1.07		
c	.1717	.8283	.069	.472	12.25	46.5	67.67 67.20	1.62		
9a[e]	.799	.201	.573	.125	23.75	30.18	84.40 84.36 84.57	0.71	0.52-0.59	0.43-0.50
b[e]	.501	.499	.350	.356	18.75	29.65	76.85 76.97 76.79 76.93	1.05		
c[e]	.201	.799	.1288	.598	11	27.45	68.80 68.76 68.96	1.54		

TABLE I (*Concluded*)

Expt. no.	Concentrations of unreacted monomers[a] $[S_0]$	[M]	$[S]$	$[M]$	Reaction time, hrs.	Polymer Yield, wt. %	Polymer Carbon[c] %		Polymer α[d]	σ	μ
10a[f]	0.798	0.202	0.539	0.1136	25	34.65	84.30	84.08	0.685	0.51–0.53	0.50–0.52
							84.57	84.18			
b[f]	.502	.498	.346	.345	18	30.90	76.60	76.60	1.01		
							76.70	76.44			
c[f]	.199	.801	.117	.567	11	31.65	68.69	68.64	1.54		
							68.74				
11a[g]	.797	.203	.667	.1572	40.75	17.50	84.24	84.03	0.697	0.46–0.62	0.35–0.49
b[g]	.501	.499	.402	.4075	22	18.42	76.49	76.68	1.005		
c[g]	.201	.799	.1323	.613	16.25	25.50	69.10		1.59		
12a[h]	.799	.201	.537	.1203	42.3	34.2	84.86	84.90	0.775	0.41–0.63	0.32–0.53
b[h]	.501	.499	.3935	.398	21	20.9	76.88		1.06		
c[h]	.201	.799	.1234	.626	15.75	25.1	69.76		2.00		
13a[i]	.7986	.2014	.502	.1084	21	38.9	84.91	84.71	0.745	0.42–0.62	0.35–0.53
b[i]	.4998	.5002	.3745	.380	21.5	24.5	76.51	77.09	1.03		
							76.86				
c[i]	.2007	.7993	.117	.598	16	28.55	69.74	69.82	1.87		

[a] In presence of 0.1 mole % of benzoyl peroxide except that Expt. 5 contained no catalyst. [b] Concentrations are expressed in mole fractions of the total monomers initially present. [c] Carbon analyses given were averaged in making calculations. [d] Relative reactivity of styrene as compared with methyl methacrylate as defined by the equation $\log([S]/[S_0]) = \alpha \log([M]/[M_0])$. [e] Runs in Expt. 9 contained 5 mole % ethylbenzene. [f] Runs in Expt. 10 contained 1% by weight of water. [g] Runs in Expt. 11 contained 0.1 mole % of dodecyl mercaptan. [h] Runs in Expt. 12 contained 5 cc. ethyl acetate per 0.08 mole of monomers. [i] Runs in Expt. 13 contained 5 cc. benzene per 0.08 mole of monomers. [j] Calculated for C_8H_8: C, 92.26. [k] Calculated for $C_5H_8O_2$: C, 59.98.

all the lines intersect at a point close to $\sigma = 0.50$, $\mu = 0.50$, justifying development and use of Equations (10)–(12).

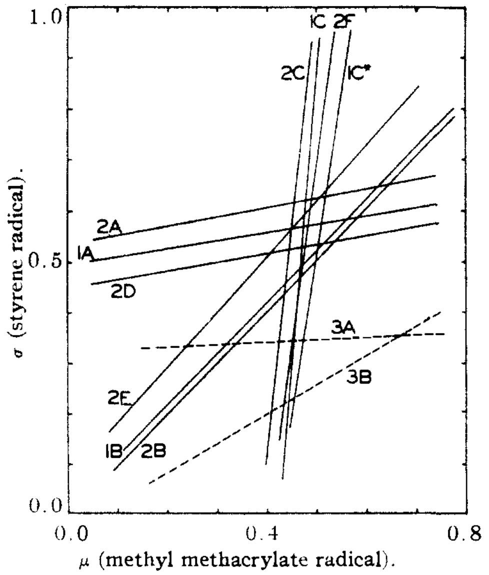

Fig. 2.—Copolymerization results with isolation procedure (3).

This value of σ means that the rate constant for the reaction of a styrene-type radical with styrene divided by the rate constant for reaction of a styrene-type radical with methyl methacrylate is 0.50; the μ value means that the rate constant for the reaction of a methyl methacrylate-type radical with ester divided by the rate constant for its reaction with styrene is also 0.50. Since in an equimolecular mixture of the two monomers, two-thirds of the styrene-type radicals react with ester molecules and two-thirds of the ester radicals react with styrene molecules, there is a distinct tendency for styrene and ester units to alternate in entering the polymer chain. Wall's equation does not account for this tendency: Table I shows that α varies regularly with the initial proportion of styrene and ester.

Precision.—The reproducibility of the results and the size of the triangular intersection obtained in an experiment depend on both the procedure for isolating the polymer and the precision of the carbon analyses. Experiments 1a, b, c in Table I were carried out with the most carefully purified monomers; they show how much the results depend on carbon analyses. Three carbon analyses were obtained in run 1c, only two of which checked closely. Only these two analyses were considered in calculating results of Expt. 1c in Table I and Fig. 2. In Expt. 1c*, all three carbon analyses were averaged, with the result that 1a, b, and c* in Fig. 2 bound a much smaller area than 1a, b and c. The experimental error, measured by the size of the area bounded by the three lines, is halved by a change of only 0.16% in the carbon analysis (0.5% in the styrene content) of the copolymer. Use of only the lowest carbon analysis would place line 1c well to the right of the a, b intersection. While a small change in the observed composition of a copolymer leads to a relatively large change in the calculated values of σ and μ, it must follow that a considerable change in the assumed values of σ and μ results in a relatively small change in the calculated composition of a copolymer.

Experiments 2a–f were carried out simultaneously with distilled (instead of recrystallized) monomers. The plot in Fig. 2 shows that the agreement between duplicate experiments is about as good as can be expected from the carbon analyses, considering the difference between 1c and 1c*, also that all the lines may be considered to intersect at a point, within experimental error. There is no significant difference between distilled and specially purified monomers.

Figures 2, 3 and 4 show how the precision of the results (size of triangular intersections) improved with the technique for isolating the polymer. Figure 3 shows our best results ($\sigma = 0.50 \pm 0.02$, $\mu = 0.50 \pm 0.02$). The polymer was precipitated three times and isolated with the frozen benzene technique (Procedure 4), and the carbon analyses show the best agreement. The experiments in Fig. 2 were the first to use this technique, but they involved only one precipitation of the polymer (Procedure 3). Experiments 6, 7 and 8 in Fig. 4 show the largest variation in results. They were carried out with different lots of monomers over a period of several months. The polymers were isolated by procedure (2) with only one precipitation. The precision of these experiments determines the significance of the experiments in Fig. 5. It should be noted here that a change of 50% in the value of σ, from 0.40 to 0.60, represents a change from only 28.6% to 37.5% in the fraction of styrene radicals which react with styrene, a change without great import.

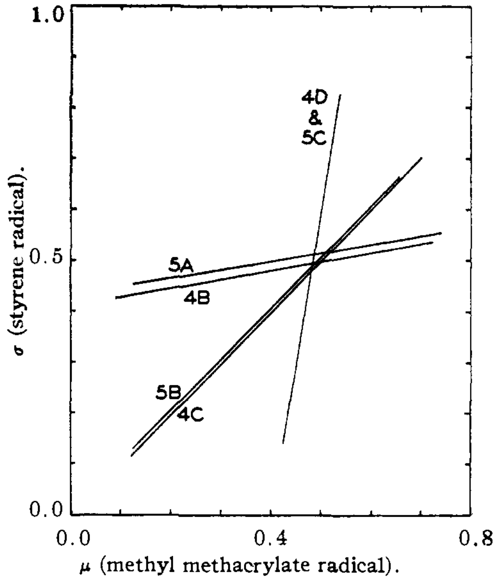

Fig. 3.—Copolymerization results using isolation procedure (4).

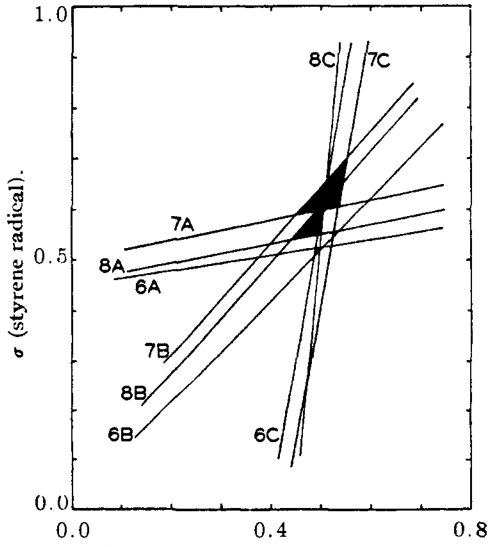

Fig. 4.—Copolymerization results using isolation procedure (2).

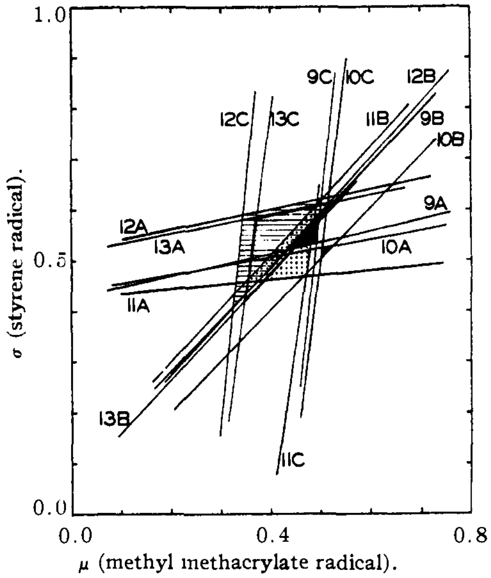

Fig. 5.—Copolymerization results using isolation procedure (2).

Experiments 3 (Fig. 2) and 4 (Fig. 3) show the application of Equation (10) and its integrated form to high and low conversion experiments.[8] The differential form can be used for calculations in low-conversion runs; the form of Equation (12) sometimes makes the use of (10) necessary. Experiments 3a and 3b show results obtained at about 90% conversions. The small final value of [M] in 3a is the difference between the large quantities, $[M_0]$ and the ester found by analysis in the polymer, and cannot be known accurately

[8] Sample calculation for run 4b using equation (12)

$$\mu = \frac{0.0469 - \frac{1}{p}\log\frac{1 - 4.100p}{1 - 3.951p}}{0.0309 + \log\frac{1 - 4.100p}{1 - 3.951p}}$$

For p equal to 0.5, 0.7 and 1, respectively, $\mu = -0.272$, 0.209, and 0.499. Inserting these respective values of p and μ in (13) gives $\sigma = 0.364$, 0.446, and 0.499. In this low-conversion experiment, the line passing through these points is barely distinguishable from the line corresponding to use of the differential equation (10).

enough to permit conclusion that the monomer reactivity ratios obtained in Expt. 3 are different. Similar considerations apply in various degrees to all experiments where most of one monomer has reacted.

Effects of Added Materials.—Early difficulties in reproducing results led us to test the purest obtainable monomers and the effects of some probable impurities in the styrene. The preceding section showed no effect of extensive purification on the monomer reactivity ratios of the radicals. The conclusions drawn in this section are based on comparison of Figs. 4 and 5 (polymers isolated by Procedure 1). Experiments 9 and 10 show no significant effect from adding small proportions of ethylbenzene (a probable impurity in styrene) and water. Experiment 11 shows no effect on σ and μ from the addition of small proportions of dodecyl mercaptan, a common regulator of certain polymerizations. Experiments 12 and 13 show that ethyl acetate and benzene as solvents also have no clearly significant effect. Experiment 3 shows that the same results are obtained in an uncatalyzed as in a catalyzed reaction. Consequently the monomer reactivity ratios of the radicals are independent of the proportion of catalyst and rate of polymerization.

Before adoption of the precipitation technique, the dry polymer finally obtained was high in styrene, but the σ and μ values obtained (about 0.7 and 0.2, respectively) were fairly consistent. In such experiments, the same results were obtained in a nitrogen-filled as in an evacuated tube. No effect of oxygen was observed beyond that which might be due to oxygen absorption by the monomer; the odor of formaldehyde was noted. In experiments in the absence of air, addition of hydroquinone did not alter the monomer reactivity ratios.

Uses and Limitations of the Copolymerization Equation.—Equation (10) and its integrated forms permit us to evaluate the monomer reactivity ratios for any monomer pair from two or more experiments; once the ratios are evaluated, we may predict the composition of the polymer formed at any conversion from any mixture of that monomer pair.[9] Since the development of the equation considers only the chain growth process, the equation will not apply to very low molecular weight polymers if one monomer predominates unduly among the terminal groups. The ratios, σ and μ, determine the directions in which the polymer chains grow; although they are in general dependent on temperature; thus far there is no evidence that they are affected by the addition of small quantities of added materials or moderate quantities of solvents. In the copolymerization of styrene and methyl methacrylate, an uncatalyzed as well as a peroxide-catalyzed reaction is possible. Since no difference in σ and μ was noted, the growth processes in the two reactions presumably have the same (free radical) mechanism. On the other hand, polymerization of styrene–methyl methacrylate mixtures with stannic chloride (a catalyst for the carbonium ion mechanism of polymerization) yields almost exclusively polystyrene,[10] suggesting that constancy of σ and μ is a criterion for a single mechanism of chain growth.

The present development supplies a quantitative method for comparing the rates of reaction of any radical (which occurs in a growing polymer) with a series of monomers. For example, the copolymerization of styrene with a series of monomers will give a series of σ values, all of which are quotients with a common dividend, the rate constant for the reaction of a styrene-type radical with styrene. If the σ values are independent of the reaction medium, then the rate constants for the reaction of a styrene-type radical with a series of double bonds are easily related, although their absolute values are not determined.

We have tested the applicability of the copolymerization equation with many pairs of monomers; we expect to publish some of our data in the near future. The results are as consistent as those presented here, and there is no reason as yet to doubt that Equation (10) is generally applicable. While our work shows conclusively that small changes in the structure of ethylene derivatives produce large effects in their reactivities with a given radical, the reactivity of any given type of free radical is not affected (beyond possible experimental error) by the monomer units attached to the terminal group.[11] In about half the monomer pairs thus far investigated, the monomer reactivity ratios of both radicals are less than one; the monomers in these pairs therefore tend to alternate in copolymerization. In all the other cases, one ratio is less than unity, the other greater than unity, but only a few of these cases approximate that where $\sigma = 1/\mu$, the only one where Wall's α equation is strictly applicable. No copolymerization has yet been found where both ratios are greater than unity (where each radical prefers to react with the monomer type from which it was derived).

The copolymerization equation neither requires nor yields any information about rates of polymerization. The rate of a polymerization depends on the concentration of free radicals, and until this concentration can be evaluated on an absolute (or at least relative) basis, rates of polymerization and copolymerization cannot be definitely correlated; neither can any information be obtained as to the relative rates of reaction of a series of radicals with a single monomer.

This problem of free radical concentrations is not peculiar to copolymerizations; it is impossible

---

(9) Practically, if σ, μ, $[S_0]$, $[M_0]$ and $[S]$ (or $[M]$) are known, then $[M]$ (or $[S]$) may be calculated.

(10) Unpublished experiments at 30–40° by Dr. Cheves Walling.

(11) Strictly speaking, the attached units do not affect the ratios $k_1/k_2 (= \sigma)$ or $k_3/k_4 (= \mu)$; the individual rate constants have not been evaluated.

to determine the effect of structure on the polymerization of monomers by themselves without such knowledge: the rate at which a styrene-type radical reacts with styrene (Equation 1) cannot be compared with the rate at which a methyl methacrylate-type radical reacts with methyl methacrylate (Equation 3) unless the radical concentrations can be related. Comparison of the overall rates of polymerization is of no assistance unless both the rates of chain initiation and chain termination can be compared. It should not be assumed that two different monomers containing the same concentration of peroxide will contain the same concentration of active centers. As shown in the next section, such an error was apparently made by Norrish and Brookman in one of the earliest and ablest papers on the theory of copolymerization.

The Rates and Products of Copolymerization.—Norrish and Brookman[1] measured the initial rates of polymerization of styrene, methyl methacrylate, and their mixtures at 90° in the presence of 0.0114 mole % of benzoyl peroxide. On the basis of equations like (1), (2), (3), (4) and (8) in this paper and the additional assumption that the total concentration of active centers was the same in all experiments, they expressed the initial overall rate of polymerization (in mole % per hour) as

$$\frac{dp}{dt} = \frac{17.2 + 0.25S + 6.7 \times 10^{-5}S^2}{1 + 0.079S}$$

where S is the mole % of styrene present.[12] All the constants (except 1) in this expression are functions only of k_1, k_2, k_3 and k_4, and we could calculate that $\sigma = 1.443$, $\mu = 0.579$. Unfortunately, Norrish and Brookman made no mention of polymer analyses and these values at 90° (much different from ours at 60°) could not be checked by our equations.

Experiment 4 in Table I was therefore carried out at 60°. According to the methods of Norrish and Brookman, the rate of polymerization is represented by

$$\frac{dp}{dt} = \frac{7.83 + 0.0496S + 0.00084S^2}{1 + 0.1226S}$$

From these rate data alone, it was calculated that $\sigma = 2.06$, $\mu = 0.76$. From analyses of runs 4b–d, it was found (Fig. 3) that $\sigma = 0.49$, $\mu = 0.49$. If the σ and μ values based on rate data are used to calculate the compositions of the copolymers, polymers 4b, c and d should contain 88.7, 80.8 and 69.0% carbon, respectively, as compared with 83.8, 76.6 and 69.1% found by analyses. The first two differences are far beyond experimental error. Apparently, Norrish and Brookman erred in assuming that the concentration of free radicals was independent of the monomer mixture. In support of this conclusion, it has been found that at 60° benzoyl peroxide decomposes faster in a benzene solution of methyl methacrylate than in a similar solution of styrene.

Acknowledgment.—The authors are indebted to many of their associates at the General Laboratories for assistance and advice. Dr. Melvin Mooney transformed Equation (11) into Equation (12) for us in August, 1942; without this transformation, utilization of the integrated copolymerization equation would have been impractical. Numerous members of the Analytical Department have expended much time and effort in carrying out all the carbon determinations.

Summary

On the basis that the copolymerization of any two monomers involves the reactions of the two kinds of monomer molecules with the two kinds of active centers derived therefrom, it has been found that the composition of a copolymer can be expressed as a function of the initial monomer concentrations, of the conversion, and of two constants which are characteristic of each monomer pair. In free-radical type polymerizations, each constant (called a monomer reactivity ratio) refers to one of the two radical types; it is the ratio of the rate constants for the reaction of the chosen radical with the monomer from which it was derived and with the other monomer, respectively.

A study of the copolymerization of styrene and methyl methacrylate by a free radical mechanism at 60° indicates that the monomer reactivity ratios are independent (within experimental error) of the composition of the monomer mixture, the extent and rate of conversion, small quantities of certain added materials, moderate proportions of benzene and ethyl acetate as solvents, and the presence or absence of benzoyl peroxide as catalyst. In this system, the styrene-type radical has a marked preference for reacting with ester; the ester-type radical prefers to react with styrene.

The equation developed permits calculation of the products of copolymerization and accurate comparison of the rates of reaction of a series of monomer molecules with a chosen radical. It does not require or yield any information about rates of polymerization or the relative rates of reaction of a series of radicals with a chosen monomer. For a full interpretation of copolymerization, it is necessary to relate the concentrations of active centers in polymerization reactions.

PASSAIC, N. J. RECEIVED MAY 26, 1944

---

(12) That Norrish and Brookman could describe a simple rate-composition curve with four arbitrary constants proves nothing about the validity of their development.