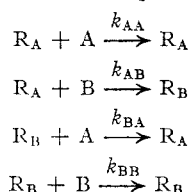


[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## The Polymerization of Allyl Compounds. III. The Peroxide-induced Copolymerization of Allyl Acetate with Maleic Anhydride<sup>1</sup>

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**Introduction.**—The theory of copolymerization has been the subject of a number of recent papers.<sup>3-10</sup> The authors of all of these have recognized four chain-propagating rate constants, governing the addition of monomer molecules A and B to growing chains ending in A and B units. In terms of the free radical mechanism of chain growth, if  $R_A$  and  $R_B$  are free radicals ending in monomer units A and B, respectively



Wall<sup>8</sup> has explored the theoretical possibilities attendant upon many kinds of variation in the relative values of the constants  $k_{AA}$ ,  $k_{AB}$ ,  $k_{BA}$ , and  $k_{BB}$ , and has provided graphical representations of a number of such cases, showing the dependence of the rate of polymerization and of polymer composition upon the composition of the mixture of monomers. Jenckel<sup>3</sup> made an experimental study of the products of polymerization of four monomer mixtures by fractionation and recognized that three of them represented true copolymers, while the fourth—the product of reaction of styrene and vinyl acetate—more closely resembled a mixture of separate polymers. Mayo and Lewis<sup>7</sup> derived an elegant general method for the evaluation of the ratios  $k_{AA}/k_{AB}$  and  $k_{BB}/k_{BA}$  from quantitative determinations of the composition of the copolymers relative to that of the initial monomer mixtures, and found that for the copolymerization of styrene and methyl methacrylate at 60° under a variety of conditions both these ratios were near 0.50. These authors opened the way by which such ratios can be evaluated for many copolymerizing monomer pairs.

From the present literature, the actual existence of a number of the cases envisaged by the theory can only be surmised. This paper concerns the existence and characteristics of a rather extreme

case of entry of the two monomers into the polymer in a 1:1 ratio, *i.e.*,  $k_{AB} \gg k_{AA}$  and  $k_{BA} \gg k_{BB}$ . This case acquires heightened interest in view of evidence<sup>11</sup> that such selectivity in many copolymerizations is absent or slight.

Wagner-Jauregg<sup>12</sup> discovered that maleic anhydride has the property of forming copolymers with stilbene, benzalfluorene, and anisalfluorene, and remarked upon the tendency toward a 1:1 ratio of the components in the copolymer. Observations have also been reported on the somewhat selective copolymerization of styrene and dimethyl maleate or dimethyl fumarate<sup>11</sup> and there is increasing reference in the patent literature to copolymerizations involving maleic anhydride.<sup>13</sup> The copolymerization of allyl acetate and maleic anhydride was found especially suitable for the present investigation for three reasons. First, a convenient method was devised for the quantitative determination of these two monomers present in a mixture; second, we had for comparison a background of information about the polymerization of allyl acetate<sup>1</sup>; and, third, the two monomers polymerize separately with low chain lengths of similar magnitudes which can be accurately determined for comparison.

### Experimental

**Method of Following Copolymerizations.**—Allyl acetate reacts quantitatively with bromine from a standard bromate-bromide mixture.<sup>1</sup> Maleic anhydride and maleic acid are unaffected by this treatment, but maleic acid is titrated quantitatively in the presence of mercuric sulfate.<sup>14</sup> This was made the basis of a method by which either allyl acetate alone or the two monomers together could be titrated. The course of a copolymerization and the relative rates of consumption of the monomers could thus be followed without purification and analysis of the polymeric product. Table I summarizes the experiments carried out in developing the analytical method. Surprisingly, the mercuric sulfate, which promotes the bromination of maleic acid, inhibits that of allyl acetate (run 2). Run 3 shows that mercuric sulfate does not adversely affect the results with allyl acetate if added after its bromination is complete. Run 12 illustrates the complete procedure for the mixed monomers. In the procedure adopted, the reaction titration vessel was first evacuated on the aspirator and an acetic anhydride solution of the mixture to be analyzed was added, followed by 5 cc. of 6 *N* sulfuric acid and 10 cc. of water. The mixture was heated to 50° for five to ten minutes, after which the bromide—

(1) Parts I and II: Bartlett and Altschul, *THIS JOURNAL*, **67**, 812, 816 (1945).

(2) Pittsburgh Plate Glass Fellow.

(3) Jenckel, *Z. physik. Chem.*, **190A**, 24 (1941).

(4) Wall, *THIS JOURNAL*, **63**, 1862 (1941).

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

(6) Alfrey and Goldfinger, *ibid.*, **12**, 205 (1944).

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

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

(9) Stockmayer, *J. Chem. Physics*, **13**, 199 (1945).

(10) Norrish and Brookman, *Proc. Roy. Soc. (London)*, **A171**, 147 (1939).

(11) Marvel and Schertz, *THIS JOURNAL*, **65**, 2054 (1943), and previous papers of the series.

(12) Wagner-Jauregg, *Ber.*, **63**, 3213 (1930).

(13) Arnold, Brubaker and Dorrough, U. S. Patent 2,301,356 (1942); E. I. du Pont, British Patent 549,682 (1942); Gerhart U. S. Patent 2,297,351 (1943); Van Melsen, U. S. Patent 2,297,039 (1943); Swan, U. S. Patent 2,299,189 (1943); Stoops and Denison, U. S. Patent 2,324,740 (1944); D'Alelio, U. S. Patent 2,340,110 (1944); Halbig, Matthias and Treibs, U. S. Patent 2,344,085 (1944).

(14) Lucas and Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

bromate solution was added. The addition of the mercuric sulfate solution was made three to five minutes later and the mixture was allowed to stand for thirty minutes. The excess bromine was then titrated iodometrically. The difference between the titers with and without mercuric sulfate added gives the concentration of maleic anhydride.

TABLE I  
ANALYSIS OF ALLYL ACETATE-MALEIC ANHYDRIDE MIXTURES

Run	Unsaturated compound	Ml. of 0.2 M HgSO <sub>4</sub> added	Minutes for hydrolysis	Minutes for bromination	Equivalents Added $\times 10^3$	Found
1	Allyl acetate	0	0	10	1.855	1.84
2	Allyl acetate	25	0	30	1.855	1.08
3 <sup>a</sup>	Allyl acetate	25	0	30	1.855	1.85
4	Maleic anhydride	0	0	10	2.04	0.00
5	Maleic anhydride	7.5	0	30	2.04	0.25
6	Maleic anhydride	20	0	60	2.04	1.76
7	Maleic anhydride	25	0	30	2.04	1.34
8 <sup>b</sup>	Maleic acid	20	0	30	1.73	1.25
9 <sup>b</sup>	Maleic acid	25	0	30	1.73	1.69
10	Maleic anhydride	25	5	45	2.04	2.09
11	Maleic anhydride	25	2	30	2.04	2.07
12 <sup>a</sup>	Allyl acetate + maleic anhydride	25	2	30	2.02	2.03

<sup>a</sup> Sulfuric acid added after bromine and allyl acetate had been allowed to react for two minutes. <sup>b</sup> Crude maleic acid.

**Titration of Benzoyl Peroxide.**—The weighed sample containing the peroxide was dissolved in 5 cc. of acetic anhydride and 0.5 cc. of 50% potassium iodide was added. The mixture was allowed to stand in a 125-cc. glass-stoppered flask for ten minutes with occasional swirling. About 50 cc. of water was then added and the iodine was titrated with 0.01 *N* thiosulfate, using starch indicator.

**Materials.**—The exploratory work was carried out with a batch of allyl acetate which had been standing for several months and which was found to contain an impurity with active hydrogen to the extent of five mole per cent. Two new preparations of allyl acetate were made, one from allyl alcohol, acetyl chloride, and pyridine, and the other from allyl alcohol, acetic anhydride, acetic acid, and sulfuric acid. In the first case pyridine was removed by washing with ice-cold 2 *N* sulfuric acid and water; in the second case acids were removed by careful washing with sodium carbonate solution and water, and drying over potassium carbonate. In each case the product was distilled through an 8-inch Widmer column. Practically all the material distilled from 102.9 to 103.4° under 754 mm. pressure. It showed no detectable active hydrogen, and yielded a colorless copolymer with maleic anhydride.

The maleic anhydride was obtained from the Eastman Kodak Company and was purified by crystallization from a mixture of equal volumes of chloroform and carbon

tetrachloride, a few cc. of petroleum ether being added to decrease the solubility of the maleic anhydride. The crystals collected by filtration, washed with carbon tetrachloride, and dried in the air, melted at 53°.

The benzoyl peroxide was purified by dissolving in chloroform and precipitating by the addition of methanol. The product was dried in a vacuum desiccator over calcium chloride.

**Procedure for Polymerization.**—Test-tubes, 10  $\times$  70 mm., were carefully washed, dried and drawn out. Known amounts of benzoyl peroxide and the monomer or monomers were added and the tubes were cooled in a Dry Ice-methanol bath. The tubes were evacuated on a Cenco Hyvac oil pump and then flushed with nitrogen which had been passed through Fieser solution.<sup>15</sup> This was repeated six times, after which the tube was sealed off under vacuum. A check of the evacuation procedure on pure allyl acetate indicated that no observable loss of monomer resulted. The tubes were suspended in the thermostat in a rocking wire basket. At measured intervals tubes were removed, chilled in an ice-bath, opened, and the contents dissolved in acetic anhydride, the total volume being made up to 10 or 25 cc., in a volumetric flask. Known volumes were pipetted out and the peroxide concentration, allyl acetate concentration, and total unsaturation were determined.

Exploratory polymerizations were carried out in air. After conditions were chosen for the more careful experiments, all samples were sealed in evacuated glass tubes after repeated evacuation and flushing with nitrogen.

**The Conditions of Copolymerization of Allyl Acetate and Maleic Anhydride.**—In the presence of 5% of benzoyl peroxide (in air) at 80° the copolymerization of equimolar quantities of these monomers proceeded violently, with self-heating and with consumption of 97% of the peroxide and 56% of the monomer in three minutes. The temperature was therefore progressively lowered in subsequent experiments. In a similar experiment, started at 70° with one gram of each monomer, the temperature of the mixture rose in six minutes to over 105°. These experiments were performed with the impure allyl acetate referred to above. All experiments described hereafter were performed with the purest materials. At 60° in the presence of air the temperature of a mixture during copolymerization remained nearly constant, but when this experiment was repeated in a stream of nitrogen the temperature rose to 71° in eighteen minutes. The inhibition by oxygen thus revealed proved to be very serious, and was never eliminated nor made entirely reproducible, even by the most careful application of the procedure for degassing. Exploratory polymerizations at 55° in sealed tubes showed that maleic anhydride is polymerized by benzoyl peroxide under much the same conditions as allyl acetate, but the inhibitory effect of oxygen is more conspicuous in the case of maleic anhydride. The copolymerization at this temperature proceeded as far in eleven minutes as the separate polymerization of either monomer in over a thousand minutes. The decomposition of the peroxide was also much more rapid in the copolymerization (see Fig. 1), and the results were so variable as to suggest strong inhibition by traces of oxygen. Because of the rapidity of the copolymerization at 55° the lower temperature of 30° was chosen for the most careful study of the reaction. This temperature carried with it the disadvantage that maleic anhydride, being solid, could not be polymerized separately for comparison.

**The Polymerization of Allyl Acetate at Different Temperatures.**—At 30° the polymerization of allyl acetate is very slow. The benzoyl peroxide is only about 10% decomposed in a month. Nevertheless three points were obtained which made possible a determination of  $k_1$ , the unimolecular rate constant for decomposition of the peroxide, and of the quantity  $dM/dP$ , which is constant throughout the polymerization in the case of allyl acetate.<sup>1</sup> (Here, as in Parts I and II,  $M$  denotes monomer concentration,  $P$  is peroxide concentration, and all concentrations

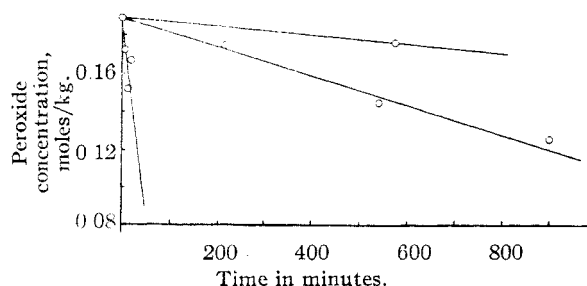


Fig. 1.—Rate of decomposition of benzoyl peroxide at 55° in allyl acetate (upper), maleic anhydride (middle), and an equimolar mixture of allyl acetate and maleic anhydride (lower).

(15) Fieser, THIS JOURNAL, 46, 2689 (1924).

are expressed in moles per kilogram of solution.) Table II compares these values as determined at 80°, 55° and 30°. Representative polymerizations of allyl acetate have been described in Part II of this series.<sup>1</sup>

TABLE II  
POLYMERIZATION OF ALLYL ACETATE AT THREE TEMPERATURES WITH 4.58% BY WEIGHT OF BENZOYL PEROXIDE

Temp., °C.	IDE $k_1$ for peroxide decomposition		$dM/dP$
	Minutes	Hours	
80	$3.5 \times 10^{-3}$	$2.1 \times 10^{-1}$	19.3
55	$1.28 \times 10^{-4}$	$7.7 \times 10^{-3}$	30.7
30	$2.17 \times 10^{-6}$	$1.3 \times 10^{-4}$	36.4

**The Polymerization of Maleic Anhydride at Different Temperatures.**—Because maleic anhydride is solid at 30°, its polymerization could not be followed at that temperature, but polymerizations were carried out at 79.5° and at 55° with precautions against contamination with air. Before the final flushing, evacuation, and sealing of each tube the contents were heated to 55° to melt the maleic anhydride and insure equilibrium between phases. Tables III and IV show the data for these runs. Zero time was taken as the time of immersion in the thermostat, although some reaction had of course already occurred at that time.

The values of  $k_1$  were determined by plotting  $\log P$  against time and drawing the best straight line through the points. The value of  $dM/dP$  was determined in each case from the slope of the plot of  $M$  vs.  $P$ , ignoring the 6770-minute point of Table III, which was off the line that passed through all the other points.

TABLE III  
POLYMERIZATION OF MALEIC ANHYDRIDE AT TWO TEMPERATURES WITH 4.58% BY WEIGHT OF BENZOYL PEROXIDE

Minutes	Peroxide, moles/kg.	Monomer, moles/kg.
Temperature 79.5°		
0	0.1780	9.48
10	.1650	9.15
30	.1418	8.57
80	.1000	7.59
150	.0633	6.65
Temperature 55°		
0	0.1890	9.75
555	.1450	
630	.1433	8.44
1440	.1137	7.50
1590	.1080	
2880	.0794	6.58
6770	.0320	5.90
1440 <sup>a</sup>	.1323	8.15
2880 <sup>a</sup>	.0889	7.18

<sup>a</sup> Sealed in air.

TABLE IV  
POLYMERIZATION OF MALEIC ANHYDRIDE AT DIFFERENT TEMPERATURES WITH 4.58% BY WEIGHT OF BENZOYL PEROXIDE

Temp., °C.	Decomposition of peroxide $k_1$ (min. <sup>-1</sup> )	$dM/dP$
79.5	$7.0 \times 10^{-3}$	24.6
55	$2.5 \times 10^{-4}$	28.9
30	$5.6 \times 10^{-6}$ (extrapolated)	

Since the decomposition of benzoyl peroxide in maleic anhydride does not approximate the first order as closely as

in allyl acetate, the extrapolation to 30° is not trustworthy. No attempt is made to extrapolate  $dM/dP$ , since this quantity for allyl acetate does not fit the Arrhenius equation.

TABLE V  
EFFECT OF OXYGEN ON COPOLYMERIZATION AT 29-31°

Tube no.	Conditions	Time to first precipitate	% Peroxide decomposition in three days	% Polymerization in three days
1	Air	2 days	4.9	3.1
2	Vac. (25°)	3 hours		
3	Vac. (-80°)	2 hours	22.4	82.5

**Kinetics of Copolymerization at 30°.**—A preliminary experiment carried out at 29-31° showed that oxygen strongly inhibits both the copolymerization and the decomposition of benzoyl peroxide in the mixture of allyl acetate and maleic anhydride. Three tubes were prepared containing equimolar quantities of allyl acetate and maleic anhydride and 4.58% by weight of benzoyl peroxide. Tube 1 was sealed in air, tube 2 was sealed after evacuation and nitrogen flushing at room temperature, and tube 3 was sealed at -80° after maximum evacuation on a Cenco Hyvac oil pump. The results are summarized in Table V. The differing efficiencies of the two deaeration procedures offer no assurance that inhibitors have been eliminated even in the vacuum-sealing method, but the results indicate that the utmost precautions must be taken to eliminate oxygen from the tubes. In Table V the time to the first precipitate is recorded, for precipitation of the sparingly soluble copolymer offers a qualitative indication that polymerization has proceeded to the extent of 2-3%. The possibility that iodometric titration is measuring new peroxide formed from the oxygen, and not merely inhibition of peroxide decomposition, is not excluded. However, the reality of such inhibition has been repeatedly demonstrated, both with oxygen and with other inhibitors under oxygen-free conditions.<sup>16</sup>

The absence of self-heating effects in the oxygen-free copolymerization at 30° was shown by observation of a tube prepared in the usual manner except that it had a thermometer sealed in with heavy-walled rubber tubing and vinylite prior to the evacuation, flushing, and sealing of the tube. The temperature of the contents of this tube remained equal to that of the thermostat bath throughout the period of heating.

Tables VI and VII record the results of quantitative runs carried out at 30° in which the tubes were all sealed off in a vacuum. The results are plotted in Fig. 2. Several points of contrast to the peroxide-induced polymerization of allyl acetate alone are immediately apparent. In the first place, the decomposition of benzoyl peroxide in this mixture of monomers shows an initial rate corresponding to an apparent unimolecular rate constant of  $k_1 = 4.26 \times 10^{-4}$  min.<sup>-1</sup>, which is 196 times greater than the value at this temperature in pure allyl acetate and 76 times greater than the calculated value in liquid maleic anhydride at 30°. In the second place, the peroxide decomposition is not unimolecular, becoming markedly slower as the copolymerization proceeds.<sup>16</sup> In the third place, the concentration of monomer is not a linear function of that of peroxide; the value of  $dM/dP$  is least at the beginning of the reaction and increases as polymerization proceeds. The great sensitivity of the copolymerization to inhibition by oxygen constitutes a fourth point of contrast to the polymerization of pure allyl acetate, although this is probably a corollary of the greater chain length of the copolymerization (Point 1). The fifth, and experimentally most troublesome, point of contrast is the insolubility of the copolymer in the mixture of monomers, a fact which prevents exact reasoning from any of the kinetic measurements because the con-

(16) This deviation of the decomposition of benzoyl peroxide from first order kinetics is an extreme example of a quite general characteristic of this reaction, which is the subject of a forthcoming paper from this Laboratory.

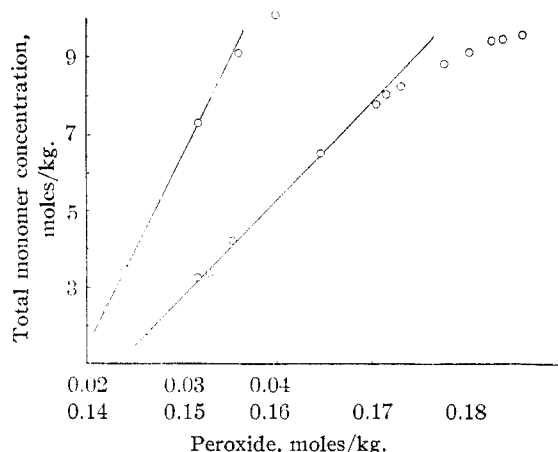


Fig. 2.—Copolymerization of allyl acetate and maleic anhydride at 30°; upper curve, peroxide 0.949%; lower curve, peroxide 4.58%.

centrations of the molecular species in the two phases are not known.

TABLE VI

Time, min.	Peroxide, moles/kg.	Maleic anhydride, moles/kg.	Allyl acetate, moles/kg.	Total unreacted monomer concentration, moles/kg.
0	0.1850	4.87	4.78	9.65
20	.1828	4.76	4.67	9.38
100	.1778	4.46	4.32	8.79
230	.1717	4.05	3.97	8.01
532	.1530	2.05	1.80	3.85
3 days <sup>a</sup>	.1800	4.76	4.58	9.34

<sup>a</sup> Tube sealed in air.

TABLE VII

COPOLYMERIZATION OF ALLYL ACETATE AND MALEIC ANHYDRIDE AT 30° WITH 0.949% BY WEIGHT OF BENZOYL PEROXIDE

Time, min.	Benzoyl peroxide, moles/kg.	Maleic anhydride, moles/kg.	Allyl acetate, moles/kg.	Sum of monomers, moles/kg.
0	0.0400	5.15	4.95	10.10
1220	.0361	4.62	4.47	9.09
2518	.0318	3.80	3.50	7.30
4964	.0240	1.76	1.68	3.44
8708	.0220	1.35	1.07	2.42

TABLE VIII

COPOLYMERIZATION OF ALLYL ACETATE AND MALEIC ANHYDRIDE AT 30° WITH FIVEFOLD EXCESS OF ALLYL ACETATE

Time, hours	Peroxide, moles/kg.	Maleic anhydride, moles/kg.	Allyl acetate, moles/kg.	Monomer reacted in time interval	Maleic anhydride	Allyl acetate
0	0.0642	1.66	8.08			
7.0	.0592	1.19	7.60	0.47		0.48
20.0	.0539	0.535	6.99	.655		.61
41.2	.0508	.243	6.70	.292		.29
114.8	.0490	.112	6.56	.131		.14

**Selectivity of the Monomers in the Copolymerization.**—In an attempt to determine how persistent the tendency is toward entrance of the monomers in a 1:1 ratio into the copolymer, the experiments of Tables VIII and IX were

TABLE IX

COPOLYMERIZATION OF ALLYL ACETATE AND MALEIC ANHYDRIDE AT 38.5° WITH FIVEFOLD EXCESS OF MALEIC ANHYDRIDE

Time, hours	Peroxide, moles/kg.	Maleic anhydride, moles/kg.	Allyl acetate, moles/kg.	Monomer reacted in time interval	Maleic anhydride	Allyl acetate
0	0.0679	8.35	1.64			
22.33	.0456	6.58	0.171	1.77		1.47
71.75	.0433	6.33	0.024	0.25		0.15

carried out, with allyl acetate and maleic anhydride, respectively, in fivefold excess. In the former case the results show that the selectivity is very high, for even in the late time interval in which the allyl acetate and maleic anhydride are initially present in the ratio of 58:1, these monomers enter the copolymer mole for mole within the experimental error of about 10%. In the run using excess maleic anhydride initial homogeneity was attained only at 38.5°. As the run progressed and the excess of maleic anhydride increased, precipitation was rapid and the contents of the tubes solidified. The ever-present difficulty caused by the two phases was therefore aggravated in this case. It is clear from the results, however, that with excess of maleic anhydride this monomer enters the copolymer in a definite excess over the 1:1 proportion. Figure 3 shows the selectivity of the copolymerization in the manner proposed by Wall.<sup>3</sup>

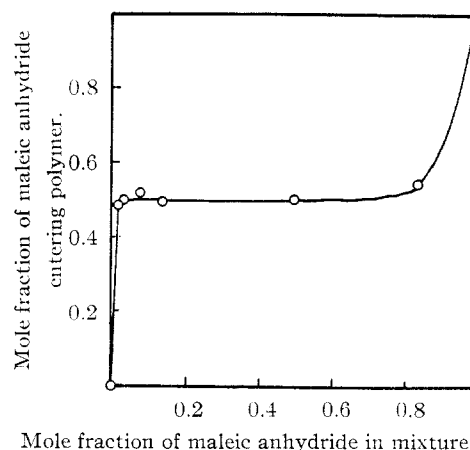


Fig. 3.—Wall diagram showing selectivity in copolymerization of maleic anhydride and allyl acetate.

**The Fate of the Peroxide.**—Polymer samples were prepared under three sets of conditions for study of end groups and the fate of the peroxide. Sample 1 was prepared with 4.58% of benzoyl peroxide; Sample 2 with 1.22% of *p*-chlorobenzoyl peroxide; and Sample 3 with 2.33% of *p*-chlorobenzoyl peroxide. Samples 1 and 2 were prepared at 30°, Sample 3 at 40°. Because of the insolubility of the copolymer, each sample consisted of two phases up to the point where the entire mass became solid. The final products were not homogeneous, having a distinct boundary between upper and lower layers. In the case of Sample 1, the upper and lower layers of the polymer were worked up separately; in the other two samples the polymer was worked up as a whole. The polymer was precipitated repeatedly by pouring its acetone solution into a non-polar solvent (chloroform for Sample 1, ether for Samples 2 and 3). The results indicated that the precipitation of the polymer produced in this way was complete within about 1.25%. The layers of Sample 1 were analyzed for polymer, maleic anhydride, benzoyl peroxide, and benzoic acid. The lower layer contained slightly more polymer, 70% more maleic anhydride, less benzoic acid, and less than one-third as much unchanged benzoyl per-

oxide in proportion as the upper layer. Table X shows the results of analyses on Samples 2 and 3, and Table XI on the residues from evaporation of the mother liquors from Sample 3.

TABLE X

ANALYSIS OF ALLYL ACETATE-MALEIC ANHYDRIDE COPOLYMERS PREPARED WITH *p*-CHLOROBENZOYL PEROXIDE

Sample no.	2	2	3	3
Initial weight, g.	10.0		11.15	
Initial weight, % peroxide	1.22		2.33	
Polymer sample taken for analysis, g.	1.5896	1.4930	1.5050	1.4950
Number of precipitations	3	6	3	3
Grams of AgCl obtained	0.00185	0.00130	0.00234	0.00238
% Chlorine	0.0288	0.0216	0.0384	0.0393
Monomer units per Cl atom	1245	1660	935	914
Total wt. of purified polymer, g.	6.3		8.0	
Wt. of attached chlorobenzoate, g.	<0.0080		<0.0138	
Wt. of unattached chlorobenzoic acid, g.	0.025		0.0229	
Wt. of unreacted peroxide, g.	0.075		0.217	
Total peroxide accounted for, g.	0.108		0.286	
% of peroxide accounted for	86.5		95.5	

TABLE XI

ANALYSIS OF RESIDUES FROM PRECIPITATIONS (SAMPLE 3)

Wt. of maleic anhydride, g.	0.99
Wt. of chlorobenzoyl peroxide, g.	.217
Wt. of chlorobenzoic acid, g.	.023
Total weight accounted for, g.	1.23
Actual wt. of residue, g.	1.33
Maximum wt. of polymer in residue, g.	0.10
Total purified polymer, g.	8.00
Maximum polymer loss, %	1.25

The analyses for chlorine were performed by an adaptation of Robertson's method.<sup>17</sup> This has the advantage over the Carius method of being well adapted to the examination of large samples of compounds with very low halogen content. The copolymer prepared with benzoyl peroxide was analyzed by this method and found to yield 1.7 mg. of silver chloride from a 1.5-g. sample. Assuming that this chlorine arose from impurities in the allyl acetate and maleic anhydride, we applied this as a correction to the results obtained with the use of *p*-chlorobenzoyl peroxide.

**Molecular Weight of Copolymer.**—Molecular weight determinations were made using a stainless steel osmometer of the type described by Fuoss and Mead.<sup>18</sup> The membranes used were partially denitrated collodion<sup>19</sup> except when water was the solvent, in which case thin collodion membranes proved more suitable. Great difficulty was encountered in finding a satisfactory solvent for the allyl acetate-maleic anhydride copolymer. Samples prepared with low initial peroxide concentrations were not sufficiently soluble in any organic solvent to permit an osmotic pressure measurement. Only the copolymer prepared with 4.58% benzoyl peroxide was sufficiently soluble in acetone, the best organic solvent found, to permit accurate measurements. Assuming that the anhydride

groups might be giving rise to some labile cross-links, we tried esterifying the copolymer with methanol or ethanol, with and without sulfuric acid as catalyst, but without success in increasing the solubility of the copolymer in organic solvents. The best solvent for the copolymers proved to be water, which hydrolyzed the anhydride groups to carboxyls. Table XII shows the results of the molecular weight studies of the several copolymer samples.

TABLE XII

MOLECULAR WEIGHTS OF ALLYL ACETATE-MALEIC ANHYDRIDE COPOLYMERS

Sample	Solvent	Temp., °C.	w	$\pi$	M
1, Upper layer	Acetone	19.4	2.00	1.52 1.57	41,500
1, Upper layer	Acetone	24.7	1.00	0.80 0.78	40,600
1, Upper layer	Water	21.2	1.00	4.9 4.9	5,160
1, Upper layer	Water	24.0	0.50	2.3 2.3	5,460
1, Lower layer	Acetone	20.2	2.0	1.26 1.35	49,200
1, Lower layer	Water	25.5	4.0	7.5	13,500
1, Lower layer	Water	23.1	2.0	6.3	7,970
1, Lower layer	Water	23.6	1.0	3.8 3.9	6,540
1, Lower layer	Water	24.0	0.50	2.15 2.10	5,940
3	Water	24.5	2.00 <sup>a</sup>	3.7 3.7	<13,650
3	Water	24.6	1.00 <sup>a</sup>	2.0	<12,630
3	Water	27.5	0.50 <sup>a</sup>	1.05	<12,170
2	Water	25.5	1.00 <sup>b</sup>	1.3 1.3	<19,500

<sup>a</sup> Less than  $\frac{9}{10}$  by weight of the polymer dissolved.

<sup>b</sup> Less than  $\frac{1}{2}$  by weight of the polymer dissolved.

That the molecular weight of Sample 1 in water is only about one-eighth of its molecular weight in acetone is not surprising in view of the large number of ionizable carboxyl groups in the hydrolyzed polymer. Although oxonium ions are normally too small and readily diffusible to contribute to the osmotic pressure across a membrane of this kind, in the present case the oxonium ions cannot cross the membrane in any numbers without building up a strong opposing potential, since the only anions in the system are too large to diffuse. The extra dissolved particles per molecule which appear in water may therefore be oxonium ions. Since in the most ionized sample only 2% of the carboxyl groups would need to be ionized to produce this effect, the assumption may be made that ionized carboxyl groups in the same polymer molecule are far enough apart not to influence one another appreciably. On this assumption we may compute an "average ionization constant" for these carboxyl groups in water from the data on Sample 1. This "average ionization constant," designated as  $\bar{K}_a$ , includes within it a factor for the number of ionizing groups per molecule and includes also the effect of diffusion of oxonium ions through the membrane. Table XIII shows the estimation of  $\bar{K}_a$  from the six measurements on Sample 1 in water at concentrations ranging from 0.5 to 4.0 g. per kilogram of solution. The calculation is based on the

TABLE XIII

IONIZATION OF ALLYL ACETATE-MALEIC ANHYDRIDE COPOLYMER IN AQUEOUS SOLUTION

Sample	w	Mol. wt.	$[H_3O^+] \times 10^4$	$\bar{K}_a \times 10^4$
1, Upper	1.00	41,000	1.68	2.8
1, Upper	0.50	41,000	0.79	1.3
1, Lower	4.0	49,200	2.15	1.15
1, Lower	2.0	49,200	2.10	2.21
1, Lower	1.0	49,200	1.32	1.75
1, Lower	0.50	49,200	0.74	1.10

Average 1.72

assumption that the results in acetone show the true molecular weight of the copolymer. Despite the roughness of the agreement among the samples, these results lend considerable support to the ionization hypothesis as

(17) Robertson, *J. Chem. Soc.*, **107**, 902 (1915)

(18) Fuoss and Mead, *J. Phys. Chem.*, **47**, 59 (1943). The apparatus was built by Mr. A. H. Geddes from working drawings kindly provided by Dr. Fuoss.

(19) Montonna and Jilk, *ibid.*, **45**, 1374 (1941); Fuoss and Mead, *ref.* 18.

opposed to the suggestion that water merely breaks certain intermolecular associations or cross-links formed by the anhydride groups in the anhydrous polymer. (In the latter case, the determined molecular weight should be independent of the dilution.)

The measurements on Samples 2 and 3 cannot be used to give an indication of their molecular weights, since the osmotic pressures in these solutions are less than would be expected from the oxonium ions alone. This is an indication that the incomplete solution of the samples, mentioned in the footnotes to Table II, is serious and probably of greater magnitude than was guessed by visual observation of the residue.

The osmotic measurements in acetone for Sample 1 indicate a degree of polymerization of 415 units for the upper phase and 497 units for the lower phase. The weighted average degree of polymerization for the copolymer made with 4.58% benzoyl peroxide is then 464 monomer units. In view of the limited use which can be made of these molecular weight values, no extrapolation to infinite dilution is attempted, although this would yield more reliable molecular weights than those employed in this discussion.

**The Copolymerization of Allyl Acetate with Other Monomers.**—The copolymerization of allyl acetate and maleic anhydride is notable for the speed, efficiency with respect to peroxide, and greater degree of polymerization as compared to the separate polymerization of the two monomers, and for the 1:1 ratio in which the monomers enter the polymer. A few other combinations of monomers were investigated without any being found which approached this pair in relative speed of copolymerization. Table XIV shows the results of some polymerizations of allyl acetate with other monomers which were carried out at 80° to the exhaustion of the peroxide. In each case the total monomer consumption in the copolymerization is compared with that in the polymerizations of the separate monomers. Very low degrees of polymerization, as with fumarodinitrile and quinone, are of doubtful significance in view of the amounts of peroxide decomposition products to be expected in these runs.

TABLE XIV

TOTAL RATE OF COPOLYMERIZATION OF ALLYL ACETATE WITH OTHER MONOMERS AT 80° IN THE PRESENCE OF BENZOYL PEROXIDE

Monomer	Mole % peroxide	Final % polym. alone	Mole % peroxide	Final % polym. in copolymerization with allyl acetate
Allyl acetate	1.95	38.0		..
Diethyl maleate	2.21	11	2.09	60.5
Diethyl fumarate	2.22	98.8	2.09	83.7
1,2-Dichloroethylene	2.14	49.0	2.13	53.2
Tetrachloroethylene	2.16	1.6	2.12	23.7
Fumarodinitrile	2.10			Slight
Crotonaldehyde	2.13	14.7		17.3
Quinone	2.13			4.0
Styrene	2.00	100.0	2.13	56.7

**The Copolymerization of Maleic Anhydride with Other Monomers.**—Table XV shows the results of a few tests on the copolymerization of maleic anhydride with other monomers. Although the fact is not apparent from the data in the table, styrene and maleic anhydride yield a true copolymer whose solubility behavior is different from that of polystyrene, polymaleic anhydride, or a mixture of the two.

**Attempted Correlation of Monomer Alternation with Physical Properties.**—One of the simplest explanations of the strong tendency for allyl acetate and maleic anhydride to enter the copolymer in a 1:1 ratio would be the existence of some preferential association between the dissimilar molecules, and a tendency for the resulting complex to enter the polymer as a single unit. There is no evidence

TABLE XV

TOTAL RATE OF COPOLYMERIZATION OF MALEIC ANHYDRIDE WITH OTHER MONOMERS AT 80° IN THE PRESENCE OF BENZOYL PEROXIDE

Monomer	Mole % peroxide	Final % polymerization Alone	With maleic anhydride
Maleic anhydride	1.90	47.8	
Tetramethylethylene	2.13	14.0	14.5
Styrene	2.00	100	
	1.92		99.7
Diisobutylene	2.16	6.7	
	2.13		<23.0
Crotyl alcohol	2.13	4.2	37.8

for this in the kinetics, but in view of the difficulties, previously cited, in the way of an exact interpretation of the kinetics we have also examined the vapor pressures, mutual solubilities, and viscosities of mixtures of monomers which do and do not show a tendency toward copolymerization in a 1:1 ratio. No characteristic abnormalities are observed in any of these properties of the allyl acetate-maleic anhydride mixture in comparison to related mixtures not showing this type of selectivity. The results of the measurements are summarized in Tables XVI, XVII, and XVIII. Of the pairs of monomers included in Table XVI only allyl acetate-maleic anhydride and allyl acetate-diethyl maleate show an active tendency toward accelerated copolymerization in a 1:1 ratio.<sup>20</sup>

**Vapor Pressure.**—The vapor pressure measurements were made with an all-glass apparatus consisting of a small sample tube connected to a mercury manometer and to an outlet with a stopcock. The sample tube was attached to the apparatus through a ground glass connection. A sample was placed in the tube, the tube was connected to the apparatus, the mixture was cooled in a Dry Ice-alcohol bath, and the apparatus was evacuated on an oil pump for five minutes. The stopcock was then closed and the mixture was warmed to room temperature, after which the cooling and evacuation were repeated. After the stopcock was closed and the oil pump disconnected the entire apparatus was immersed in a glass-walled thermostat bath. After about five minutes equilibrium was attained and the vapor pressure was read from the manometer. The entire procedure was repeated until checking results were obtained.

**The solubility determinations** were made by the successive addition of small known increments of solute to solvent until saturation was reached.

**Viscosity.**—Viscosity measurements were made using an Ostwald pipet immersed in a thermostat at 30°.

## Discussion

The appearance of a second phase early in all the copolymerization experiments precludes interpretation of the kinetics to the same extent as is possible with homogeneous experiments. We cannot, for example, draw conclusions from the exact shape of the curve of monomer concentration plotted against peroxide concentration, nor can we be sure that inhibition is absent. Certain conclusions can be drawn, however, from the facts at hand with regard to the mechanism of the copolymerization of allyl acetate and maleic anhydride.

**The Decomposition of Benzoyl Peroxide.**—One of the best evidences of a chain reaction is susceptibility to inhibition by small quantities of oxygen. In previously reported kinetic studies of the decomposition of benzoyl per-

(20) K. Nozaki, unpublished results.

TABLE XVI  
 THE VAPOR PRESSURES OF VARIOUS MONOMER MIXTURES AT 30°

Allyl Acetate-Maleic Anhydride							
Mole % M. A.		0.00	9.92	21.6	35.5	49.7	62.3
Vapor pressure, mm.	Obs.	46.0	41.1	36.8	31.4	27.0	25.2
	Ideal	46.0	41.4	36.1	29.7	23.1	17.3
Methyl Acrylate-Maleic Anhydride							
Mole % anhydride		0.00	8.33	18.5	31.2	44.9	57.9
Vapor pressure, mm.	Obs.	120.5	111.5	99.8	87.5	72.0	61.5
	Ideal	120.5	110.5	98.2	82.9	66.4	50.7
Vinyl Acetate-Acrylonitrile							
Mole % acrylonitrile		0.00	25.7	40.8	58.0	73.5	84.7
Vapor pressure, mm.	Obs.	148.0	152.3	151.0	148.3	144.5	140.5
	Ideal	148.0	144.4	142.3	139.9	137.7	136.1
Allyl Acetate-Diethyl Maleate							
Mole % D. M.		0.00	14.2	24.9	40.0	57.2	72.7
Vapor pressure, mm.	Obs.	46.0	39.2	34.8	29.4	21.8	16.0
	Ideal	46.0	39.8	35.1	28.5	20.9	14.2
n-Propyl Acetate-Diethyl Maleate							
Mole % D. M.		0.00	15.2	26.5	41.8	59.0	74.3
Vapor pressure, mm.	Obs.	57.3	50.2	44.8	37.3	28.3	20.0
	Ideal	57.3	48.9	42.7	34.3	24.8	16.4
Vinyl Acetate-Allyl Acetate							
Mole % A. A.		0.00	17.6	29.9	46.1	63.1	77.4
Vapor pressure, mm.	Obs.	148.0	130.0	116.4	98.3	82.2	69.0
	Ideal	148.0	130.0	117.5	99.9	83.6	69.0

 TABLE XVII  
 SOLUBILITY OF MALEIC AND SUCCINIC ANHYDRIDES IN  
 SEVERAL SOLVENTS AT 30°

Solvent	Solubility in grams/cc. of solvent	
	Maleic anhydride	Succinic anhydride
Styrene	0.47	0.011
Toluene	.45	.010
Ethylbenzene	.20	.008
Cumene	.10	.005

 TABLE XVIII  
 VISCOSITIES OF MIXTURES OF DIETHYL MALEATE AND  
 ALLYL ACETATE AT 30°

Mole % allyl acetate	Flow time, minutes		
	Observed	Ideal	Corrected for "Free Space" <sup>21</sup>
0.0	9.557		
42.8	5.055	6.35	5.99
60.0	3.880	5.05	4.705
100.0	2.068		

oxide<sup>22-24,1</sup> inhibition by oxygen has been found, or assumed, to be negligibly slight. It is slight in the decomposition of benzoyl peroxide in allyl acetate, but in the mixture of allyl acetate and maleic anhydride, as shown in the experiments reported here, such inhibition is substantial. It is clear that an important proportion of the decom-

position of benzoyl peroxide in such solutions when not inhibited is induced by free radicals of a kind different from, or at a concentration much greater than, those present in allyl acetate alone or in other solvents in which this decomposition has been studied. Since the rate of decomposition of benzoyl peroxide has not been found to vary more than about fourfold in a number of the common solvents, we may guess that the factor of 196 between the rate in allyl acetate-maleic anhydride solution and the rate in allyl acetate alone is due largely to radical-induced chain decomposition of benzoyl peroxide superposed upon the strictly thermal, unimolecular reaction. We have not been able to verify this by kinetic methods in the present case, but a reinvestigation of the kinetics of benzoyl peroxide decomposition in a number of solvents has revealed that such chain decomposition is always present to a greater or less degree.<sup>16</sup>

In our previous treatment of the polymerization of allyl acetate we have been able to make the assumption that the decomposition of benzoyl peroxide is a chain-initiating act, and that the rate of this decomposition comes close to measuring the rate of formation of new chain-propagating centers. In the present case, however, this cannot be so; for if the decomposition of a benzoyl peroxide molecule is induced by reaction with a free radical, this decomposition consumes one free radical while producing another. It is therefore not a chain initiating step at all, but a process of

(21) McLeod, *Trans. Faraday Soc.*, **30**, 482 (1934).

(22) D. J. Brown, *THIS JOURNAL*, **62**, 2657 (1940).

(23) Kamenskaya and Medvedev, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).

(24) McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

chain transfer which wastes a peroxide molecule as far as inducing polymerization is concerned. Were we to assume that the thermal, unimolecular decomposition of benzoyl peroxide in our mixed solvent proceeded at the same rate as in allyl acetate, the increase in the mixed solvent being due entirely to chain decomposition, we should conclude that only one out of 196 peroxide molecules decomposing is starting a chain, and that therefore the "kinetic chain length" in the copolymerization is equal to the  $dM/dP$  multiplied by 196. This would give kinetic chain lengths of 36,600 and 83,700 for the copolymerizations with 4.58 and 0.949% peroxide, respectively. All the peroxide which undergoes chain decomposition must therefore be acting to lower the molecular weight of the product by interrupting the growth of polymer molecules by means of chain transfer.

In pure maleic anhydride the rate of peroxide decomposition is markedly greater than in allyl acetate and deviates from the first order. This fact suggests that the radical terminating in a maleic anhydride unit is capable of inducing the decomposition of benzoyl peroxide to a greater extent than the radical terminating in an allyl acetate unit. A further factor contributing to the large proportion of induced peroxide decomposition in the copolymerization might well be the ability of the acetoxyallyl radical<sup>1</sup> to initiate copolymerization chains by reaction with maleic anhydride, which it can do only to a minor extent with allyl acetate in the polymerization of this substance by itself. A simple analysis of the kinetics shows that such a process would increase the concentration of growing-chain radicals relative to that of acetoxyallyl radicals.

**Estimation of  $\alpha$  and  $\mu$  for the Copolymerization.**—Adapting the notation of Mayo and Lewis to our monomers, let us define the monomer selectivity ratios

$$\alpha = k_{AA}/k_{AM}$$

and

$$\mu = k_{MM}/k_{MA}$$

where  $k_{AM}$  denotes the bimolecular reaction rate constant for reaction of a free radical ( $R_A$ ) ending in an allyl acetate unit with a maleic anhydride molecule, and correspondingly for the other symbols. We may obtain a rough idea of the values of  $\alpha$  and  $\mu$  by ignoring the temperature difference between the runs of Tables VIII and IX and applying the method of Mayo and Lewis (Equations 12 and 13 of Reference 7) to the seven-hour point in Table VIII and the 22-hour point in Table IX. (These equations are very sensitive to slight errors in the concentrations of monomers toward the end of the reaction, hence the earlier points give the most reliable results.) In applying the equations to the data of Table IX, it has been assumed that the initial ratio  $M/A = 5.09$  is held unchanged by precipitation of maleic anhydride instead of increasing as indicated by the over-all analyses. The effect of this assumption is

to yield the highest possible apparent values for  $\mu$ , *i.e.*, the lowest indicated selectivity of  $R_M$ . These points yield plots of  $\mu$  against  $\alpha$  which are nearly vertical for Table VIII and nearly horizontal for Table IX, and which intersect at  $\alpha = 0.005$ ,  $\mu = 0.018$ . We may obtain an idea of the possible effect of experimental errors upon the determined values of  $\alpha$  and  $\mu$  by setting  $dA/dM = r$  and throwing Equation 10 of Mayo and Lewis into the form (for our monomers)

$$\alpha = r \left( \frac{M}{A} \right)^2 \mu + (r - 1) \frac{M}{A}$$

Any assumed value of  $r$  at a given time then permits us to plot a straight line relating  $\mu$  to  $\alpha$ . The reproducibility of our monomer analyses, together with the self-consistency of the data, convinces us that the value of  $dA/dM = r$  as inferred from Tables VIII and IX cannot be in error by as much as  $\pm 20\%$ . In Table VIII, in which  $r$  appears equal to unity throughout, the assumption that it is equal to 1.2 at 41.2 hours yields an almost vertical plot of  $\mu$  vs.  $\alpha$ , in which the values of  $\alpha$  are higher than they would be for any smaller  $r$  which might be assumed. Likewise, an almost horizontal plot is obtained by setting  $r$  equal to the minimal value of 0.6 for the initial point of Table IX. This yields higher values of  $\mu$  than any higher assumed value of  $r$ . The intersection of these lines (the effect of the temperature difference being neglected) indicates 0.0075 as the upper limit of  $\alpha$ , and 0.13 as the upper limit of  $\mu$ .

**Attached Peroxide Fragments in Relation to Degree of Polymerization and Kinetic Chain Length.**—Table XIX summarizes the available information from different runs on the over-all number of monomer molecules polymerized per peroxide molecule decomposed ( $\Delta(M + A)/\Delta P$ ), the degree of polymerization ( $DP$ ) and the number of monomer units ( $E$ ) polymerized per attached peroxide fragment (per end group).

TABLE XIX

Table	Initial peroxide, wt. %	Temp., °C.	$\frac{M_0}{A_0}$	$\frac{\Delta(M + A)}{\Delta P}$	$E$	$DP$
VI	4.58	30	1	187		
XIV	4.58	30	1			464
XI	2.33 <sup>a</sup> (Cl)	40	1		924	
IX	1.64	30	5	148		
VIII	1.55	30	0.2	202		
XI	1.22 (Cl)	30	1		1660	
VII	0.949	30	1	427		

<sup>a</sup> Equivalent to 1.81% by weight of benzoyl peroxide.

The only molecular weight or  $DP$  figure that we have is for a run under conditions which yield  $\Delta(M + A)/\Delta P = 187$ ,  $DP = 464$ . These figures mean that during polymerization a chain is transferred to a peroxide molecule on an average once for every 187 monomer molecules polymerized. One might then expect  $DP$  to be no larger than 187. That  $DP$  is actually 2.5 times as great as  $\Delta(M + A)/\Delta P$  might mean (1) that polymer



chains, in inducing peroxide decomposition, are left with terminal unsaturation and then become involved in further polymerization; (2) that benzoate radicals frequently yield chain transfer to saturated polymer molecules by the capture of a hydrogen atom, rather than activating a new monomer molecule to start a chain; or (3) that a dienic end-product is formed in chain termination, as suggested for the polymerization of allyl acetate,<sup>1</sup> and enters into copolymerization with the monomers to yield partially cross-linked polymers. Assumption 1 describes a mechanism by which a growing free radical would induce the decomposition of a peroxide molecule without combining with a fragment of that molecule. Assumption 2, similarly, pictures the starting of a polymerization chain by a peroxide fragment which is simply converted into benzoic acid without becoming permanently attached to the polymer. A mechanism of each kind seems to be required by the facts in the last two lines of Table XIX; for here it appears that only one in 3.9 of the peroxide molecules undergoing decomposition yields any fragment attached to the polymer. This conclusion is reached by comparing  $E$  for a run with *p*-chlorobenzoyl peroxide with  $\Delta(M + A)/\Delta P$  for a run with the same mole per cent. of benzoyl peroxide. At least one of these mechanisms is also required by the fact (Table X) that half of the weight of the consumed peroxide is accounted for as free benzoic acid isolated from the polymer. However, the requirement of a mechanism whereby a benzoate radical can start a polymerization chain without becoming attached to that chain may be met in other ways than by attack on a polymer—for instance, a benzoate radical might take hydrogen from the  $\alpha$ -position of the allyl group in allyl acetate and the acetoxyallyl radical, though unable to initiate the polymerization of allyl acetate, might still vigorously attack maleic anhydride.

**The Kinetic Chain Length.**—If our estimate is correct that the kinetic chain length of the copolymerization is 36,600 with 4.58% initial peroxide concentration, compared with 36.4 for allyl acetate under the same conditions, then there is a factor of 1000 to be accounted for between these two processes. The kinetic chain length is equal to the ratio (Rate of chain propagating step)/(Rate of chain terminating step), and therefore an increase in this quotient may be brought about either by an increase in the rate of the chain propagating step or by a decrease in the rate of the chain terminating step, or both. Assuming, as is the case, that the kinetic chain length is of very similar magnitude for the separate polymerizations of allyl acetate and maleic anhydride, then if the rate of the chain terminating step were unchanged in the copolymerization, values of  $\alpha = \mu = 0.001$  would result in the observed multiplication of the kinetic chain length. Since  $\mu$  is almost certainly much larger than 0.001, it is

likely that the rate of the chain terminating step is also affected by the transition from separate polymerization to copolymerization.

If the disappearance of free radicals is slower in the copolymerization than in the polymerization of the pure monomers, it follows that the reaction which leads to chain termination in the polymerization of pure allyl acetate, although it must be capable of occurrence in the copolymerization, must in this case not lead to the termination of chains. A consideration of this conclusion and of other mechanisms of chain termination presents so many possible steps in the reaction on which we have no direct evidence that we refrain from any discussion of the details of chain termination in this copolymerization.

#### The Question of the Cause of the Selectivity.—

Our exploratory experiments on the copolymerization of other pairs of monomers indicate that maleic anhydride is the unique member of the pair rather than allyl acetate. The notable properties of maleic anhydride include a high dipole moment, a special type of conjugated unsaturation giving it a formal resemblance to quinone, and high activity in the Diels-Alder diene synthesis. The unfortunate circumstance that the quinones cannot be copolymerized with olefinic monomers, in development of this analogy, may be highly significant. The strong inhibitory properties of quinones toward polymerization indicate a tendency for the quinone to be selectively attacked by the free radical propagating the chain. The radical,  $R_Q$ , resulting from this attack, need be only slightly more stabilized by resonance<sup>25</sup> than the analogous radical  $R_M$ , to account for the qualitative difference between virtually total inhibition and selective copolymerization. In the complete absence of any evidence of selective association between allyl acetate and maleic anhydride in solution, we may turn attention to a little-understood physical property which comes nearer than the others to affording some correlation with copolymerization behavior. Stilbene and indene give strong yellow colors with maleic anhydride, while 1,1-diphenylethylene and styrene give light yellow. The colors usually deepen with rising temperature, and in the cases of stilbene and diphenylethylene the colors disappear upon cooling. Chloranil yields deeper colors, dark red with stilbene and indene, orange with styrene and 1,1-diphenylethylene. The polymerizing monomers without aromatic groups, including allyl acetate, yield no such colors, but those unsaturated substances which do yield the colors all show marked copolymerization with maleic anhydride. The electron-transfer theory of J. Weiss<sup>26</sup> has been successful in accounting for such colors and has been applied also<sup>27</sup> to a discussion by Woodward of the chemical behavior of qui-

(25) Price and Durham, *THIS JOURNAL*, **65**, 757 (1943); Price, *Ann. N. Y. Acad. Sci.*, **XLIV**, 367 (1943).

(26) Weiss, *J. Chem. Soc.*, 245 (1942).

(27) Woodward, *THIS JOURNAL*, **64**, 3058 (1942).

ones and maleic anhydride in the Diels-Alder reaction. It is not likely that the monomer units in copolymerization actually add to the growing chain as charged particles. However, any tendency of two monomers to act as electron donor and electron acceptor, respectively,<sup>28</sup> would be reflected in the contributions of corresponding resonance structures and resultant polarities, both in the monomers themselves and in the radicals terminating in them. Probably the explanation of the selectivity in copolymerization of allyl acetate and maleic anhydride is to be sought along these lines. The scarcity of monomers which behave like maleic anhydride would then be due to the fact that most substances with a similar ability to accept electrons (including the quinones) have enough additional resonance possibilities to make them chain inhibitors rather than copolymerizers. To be highly selective in the manner of maleic anhydride and yet not an inhibitor requires rather narrow limits of resonance stabilization in molecule and radical.

### Summary

Maleic anhydride is polymerized at 55° by benzoyl peroxide, about 29 monomer molecules being polymerized for each peroxide molecule decomposed.

Allyl acetate and maleic anhydride undergo rapid and highly selective copolymerization in the presence of benzoyl peroxide. The copolymerization is more rapid at 30° than the polymerization of either of the monomers separately at 80°. The peroxide decomposition under these conditions is largely induced by chain transfer, being 196 times

(28) Compare Gibson and Loeffler, *THIS JOURNAL*, **62**, 1324 (1940).

as rapid as in allyl acetate alone. For each peroxide molecule decomposed, 187–427 molecules of monomer are polymerized, compared with not over 36 for allyl acetate separately under the same conditions, and a similar figure for maleic anhydride.

The copolymer is insoluble in the mixture of monomers and shows only limited solubility in all solvents except water. The copolymer prepared with 4.58% by weight of benzoyl peroxide, a great excess of peroxide, has a molecular weight of about 40,000 in acetone; copolymers prepared with lower peroxide concentrations are too insoluble for osmotic pressure measurements. Measurements in water are difficult to interpret because of ionization of the carboxyl groups in the hydrolyzed polymer.

A study of copolymers prepared with *p*-chlorobenzoyl peroxide has been made and it is concluded that only about one out of four peroxide molecules decomposing leads to the attachment of a fragment to the polymer.

A survey of a few other copolymerizations shows none with the degree of tendency toward 1:1 copolymerization exhibited by this system, which yields a 1:1 copolymer even when the ratio of monomers is originally 1:5 and 5:1. This selectivity is not correlated with any abnormal vapor pressures, solubilities, or viscosities of the monomer mixtures.

The results are interpreted in terms of the mechanism of polymerization, as far as the experimental limitations permit.

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RECEIVED<sup>29</sup> APRIL 24, 1946

(29) Original manuscript received September 12, 1945.

[CONTRIBUTION FROM EASTERN REGIONAL RESEARCH LABORATORY<sup>1</sup>]

## Hydroxylation and Epoxidation of Some 1-Olefins with Per-acids

BY DANIEL SWERN, GERALDINE N. BILLEN AND JOHN T. SCANLAN

In previous publications from this Laboratory, the quantitative hydroxylation of mono-unsaturated fatty materials with hydrogen peroxide in formic acid solution<sup>2</sup> and epoxidation with peracetic acid in acetic acid solution,<sup>3</sup> respectively, were reported. The purpose of the present publication is to describe the results obtained when these reactions were applied to straight-chain, 1-olefins.

In our earlier paper,<sup>2</sup> it was tentatively concluded that the hydrogen peroxide-formic acid hydroxylation reaction, in which formic acid

serves the dual purpose of solvent and oxygen carrier (performic acid is the intermediate compound), is a general method for the hydroxylation of mono-unsaturated compounds with isolated ethylenic linkages. In seeking further confirmation of this conclusion, we have applied this reaction to 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene, and we have found that good yields of 1,2-glycols are obtained when only 1.025 to 1.05 moles of hydrogen peroxide is employed for each mole of olefin. The crude, saponified reaction products, obtained in yields of 70% or more, usually consisted of almost pure 1,2-glycols without further treatment. The pure glycols, obtained in yields ranging from 40 to 70%, were isolated either by fractional distillation or by recrystallization from

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Swern, Billen, Findley and Scanlan, *THIS JOURNAL*, **67**, 1786 (1945).

(3) Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).