and a slow stream of carbon dioxide-free, dry nitrogen (or oxygen) was bubbled through the liquid, passed from there through two Dry Ice traps into a Dehydrite tube and finally into an Ascarite tube, the open end of which was protected by a soda-lime tube. The reaction vessel was kept at the boiling point of benzene for sixteen to twenty hours, then the system was swept with nitrogen for several hours until the Ascarite tube ceased to gain weight. Constancy was always attained in less than two hours. The values are corrected for small fractions of peroxide remaining undecomposed in solution after the heating period.

Carbon dioxide was eliminated from the tank nitrogen by scrubbing with 50% aqueous potassium hydroxide in a spiral wash bottle and drying with calcium chloride.

Details of the kinetics of polymerization and of the molecular weight determinations will be presented in a paper immediately following.

Summary

Allyl acetate is polymerized by heating with acyl peroxides at 80° to a polymer whose molecules contain an average of about thirteen monomer units. The rate of polymerization is reproducible and is not affected strongly by oxygen unless the solution is vigorously agitated with oxygen or air during polymerization. Water, hydrogen chloride and pyridine in small amounts do not affect the rate.

When the polymerization is induced by 5.9% by weight of *p*-chlorobenzoyl peroxide, 72.5% of the chlorine originally present in the peroxide appears in end-groups permanently attached to the polymer, 16.8% appears as free, unattached benzoic acid, and 10.7% is unaccounted for. Out of the 72.5% in the form of end-groups, definitely 52% and probably 60.5% of the original chlorine is in the form of *p*-chlorobenzoate groups, 12% as *p*-chlorophenyl groups. Chain transfer occurs to the extent of 23%.

The amount of carbon dioxide evolution from the acyl peroxide depends upon the solvent, temperature, and presence of oxygen, but not upon the average concentration of monomer during polymerization.

CAMBRIDGE, MASS. RECEIVED DECEMBER 14, 1944

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Polymerization of Allyl Compounds. II. Preliminary Kinetic Study of the Peroxide-Induced Polymerization of Allyl Acetate

BY PAUL D. BARTLETT AND ROLF ALTSCHUL[1]

The conversion of a vinylic compound without solvent into high polymer would not necessarily be expected to obey the simple laws of classical kinetics. In the polymerization of pure styrene, for example, the reaction begins in a fluid hydrocarbon medium in which the reactant is also the solvent, and ends in a glassy solid containing the residual styrene molecules frozen at high dilution. It might be anticipated that the change of degree of saturation, molecular weight, and physical state of the solvent would so alter the rate constants of the steps involved as to make a kinetic analysis out of the question. That this is not the case is one of the most remarkable facts in this field. We have followed the thermal decomposition of benzoyl peroxide in a number of polymerizing solvents with no change in its rate constant from the beginning to the end of the reaction. Flory has shown that the changes in viscosity and in the molecular size of the reactants attending the polyesterifications of glycols with dibasic acids have no effect on the kinetics[2] in comparison with similar esterifications not leading to macromolecular products. The evidence clearly justifies kinetic studies under these unorthodox conditions with the reactant as the solvent In the polymerization of pure vinylic monomers we are presumably dealing with an example of the fact that the rate constants of free radical reactions are relatively insensitive to changes of environment which would profoundly affect reactions of polar type.[3]

In the present study the disappearance of unsaturation and of peroxide have been followed as a function of time during the polymerization of allyl acetate at 80° under nitrogen without solvent, in the presence of 5.90% by weight of *p*-chlorobenzoyl peroxide and of different amounts of benzoyl peroxide from 1.01 to 9.95% by weight. Unsaturation was determined as described in Part I of this series[4] and peroxide concentration was determined by iodometric titration as described in the Experimental Part. The results of the experiments are included in Tables I–V, the symbols having the following significance

P = peroxide concentration, moles/kilogram
M = monomer concentration, moles/kilogram

Units of Concentration.—When allyl acetate undergoes polymerization to the extent of 71%, as in the experiment of Table II, the volume of the system contracts by 22%. This means that the rate of a chemical reaction in such a sys-

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[1] Pittsburgh Plate Glass Fellow, 1941–1944; present address, Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pa.

[2] Flory, THIS JOURNAL, 61, 3334–3340 (1939).

[3] Ziegler, Orth and Weber, *Ann.*, 504, 131 (1933), measured the rate of dissociation of hexaphenylethane into triphenylmethyl radicals in sixteen solvents, finding an extreme variation of less than 2.6-fold. Within the same range of solvents Menschutkin had found a 742-fold variation in the rate of the triethylamine–ethyl iodide reaction.

[4] Bartlett and Altschul, THIS JOURNAL, 67, 812 (1945).

TABLE I

POLYMERIZATION OF ALLYL ACETATE AT 80.0 ± 0.3°
p-CHLOROBENZOYL PEROXIDE, 5.90%

Hours	*P*	*M*	% Polymer
0	0.185	9.41	0
1.00	.162	8.76	6.9
2.50	.122	7.83	16.8
6.00	.074	6.67	29.1
9.9	.037	5.71	39.3
46.5	...	4.68	50.3

TABLE II

POLYMERIZATION OF ALLYL ACETATE AT 80.0 ± 0.3°
BENZOYL PEROXIDE, 9.95%

Hours	*P*	*M*	% Polymer
0	0.413	8.91	0
0.50	.361	8.20	8.0
1.00	.323	7.47	16.2
2.50	.227	5.94	33.3
4.42	.140	4.76	46.6
7.50	.068	3.63	59.2
13.30	.036	2.89	67.6
45.1	...	2.59	70.9

TABLE III

POLYMERIZATION OF ALLYL ACETATE AT 80.0 ± 0.3°
BENZOYL PEROXIDE, 6.10%

Hours	*P*	*M*	% Polymer
0	0.248	9.34	0
0.50	.223	8.86	5.1
1.25	.187	8.28	11.3
2.50	.140	7.42	20.6
4.42	.089	6.48	30.6
7.52	.045	5.74	38.5
13.30	.023	5.15	44.9
48.0	...	4.76	49.0

TABLE IV

POLYMERIZATION OF ALLYL ACETATE AT 80.0 ± 0.3°
BENZOYL PEROXIDE, 2.14%

Hours	*P*	*M*	% Polymer
0	0.0887	9.79	0
1.51	.0658	9.28	5.2
2.50	.0522	8.99	8.2
4.42	.0356	8.62	12.0
7.50	.0205	8.17	16.5
13.0	.0061	7.82	20.1
47.5	....	7.33	25.2

TABLE V

POLYMERIZATION OF ALLYL ACETATE AT 80.0 ± 0.3°
BENZOYL PEROXIDE, 1.01%

Hours	*P*	*M*	% Polymer
0	0.0413	9.90	0
0.50	.0381	9.75	1.5
1.25	.0354	9.70	2.0
2.50	.0269	9.51	3.9
4.42	.0180	9.24	6.7
7.40	.0102	9.01	9.0
13.4	.0034	8.72	11.9
49.0	....	8.71	12.0

tem cannot be identified with the rate of change of the concentration of any chemical species in moles per liter. The following analysis shows the relationships between the different measures of concentration and reaction velocity in a system whose volume is not constant.

Let x and y be the concentrations of the species X and Y, expressed in moles per kilogram of solution (molality). Let x' and y' be the concentrations of these same species expressed in moles per liter (molarity). Let D represent the density of the solution, which changes with time. Consider first the unimolecular reaction

$$\mathrm{X} \longrightarrow \mathrm{Z}$$

The rate of change of x' may be regarded as the sum of a rate due to the chemical reaction, which converts X into Z, and a rate due to the expansion or contraction of the medium, so that

$$-\frac{\mathrm{d}x'}{\mathrm{d}t} = kx' - x'\frac{(\mathrm{d}D/\mathrm{d}t)}{D}$$

However, since $x' = Dx$ and

$$\frac{\mathrm{d}x'}{\mathrm{d}t} = D\frac{\mathrm{d}x}{\mathrm{d}t} + x\frac{\mathrm{d}D}{\mathrm{d}t}$$

the equation above becomes simply

$$-\mathrm{d}x/\mathrm{d}t = kx$$

In the bimolecular reaction

$$\mathrm{X} + \mathrm{Y} \longrightarrow \mathrm{Z}$$

the rate of change of volume concentration of X is

$$-\frac{\mathrm{d}x'}{\mathrm{d}t} = kx'y' - x'\frac{\mathrm{d}D/\mathrm{d}t}{D}$$

Making the same substitutions as above, this expression becomes

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = kxy' \; (= kx'y)$$

It is a consequence of this, as will appear in the discussion to follow, that in the reaction at hand weight concentration is the correct measure of concentration for kinetic purposes.

Graphical Summary of Data.—Figure 1 shows the logarithm of benzoyl peroxide concentration plotted against time for the experiments of Tables II–V, the curves being displaced vertically for convenience by an amount *a*, whose value is given for each curve. Figure 2 shows the concentration of monomer plotted against the concentration of peroxide for the same four experiments. The following facts are evident from the tables and graphs: (1) the decomposition of benzoyl peroxide in allyl acetate is nearly unimolecular, the rate constant varying from 0.191 to 0.235 hr.$^{-1}$ over a tenfold range of concentration. (2) In any run there is a linear relationship at all times between the amount of peroxide decomposed and the amount of allyl acetate polymerized. $\mathrm{d}M/\mathrm{d}P$ is constant in any run, and varies from 15.6 to 28.8 over the tenfold range of peroxide concentration. That this linear relationship between peroxide decomposed and monomer polymerized is real, and not due to a limited range of observation, is readily seen from the fact that

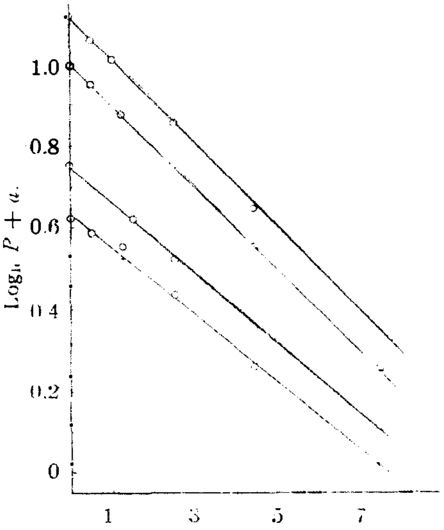

Fig. 1.—Rate of decomposition of benzoyl peroxide in polymerizing allyl acetate at 80°: left to right, data of Tables V (a = 2.0); IV (a = 1.9); III (a = 1.6); and II (a = 1.5).

each run is carried well beyond the point where no detectible peroxide remains. The remaining monomer decreases strictly in proportion to the disappearance of the peroxide.

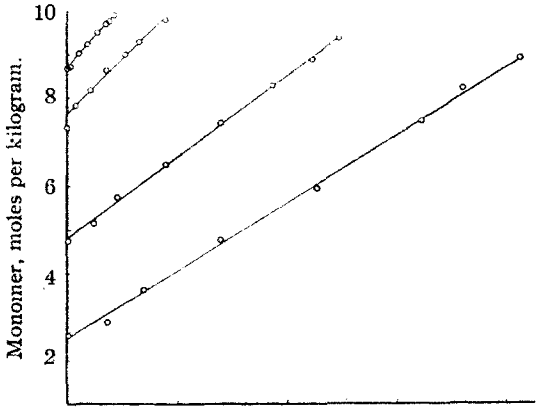

Fig. 2.—Monomer concentration plotted against peroxide concentration in the polymerization of allyl acetate. Bottom to top: data of Tables II, III, IV, and V.

Interpretation of the Constant dM/dP.—There is no reasonable doubt of the general correctness of the free-radical mechanism for peroxide-induced polymerization.[5] Nevertheless, there exists no case of such polymerization of which a complete description can now be given with any confidence. A recent tabulation in this Laboratory of unanswered questions concerning the peroxide-induced polymerization of styrene revealed that there were still at least 1500 mechanisms for this well-studied reaction, differing from one another in significant details, among which no decision as yet could be made. The majority of these mechanisms present great difficulties of mathematical formulation. One quickly recognizes the kinetic treatment of such reactions as a search for an approximation which will be amenable to mathematical handling and at the same time give as close an account of the experimental facts as possible. This is what we are trying to do in the following discussion.

First of all, it is clear that if dM/dP is constant, then *all molecular species whose concentrations change during the reaction must enter in the same order into the chain propagating and chain terminating steps.* This must mean that the chains are broken by the collision of a growing free radical with a monomer molecule. The possibility that a polymerization chain can be broken by collision with a monomer molecule has been considered in theoretical derivations,[6] but not to our knowledge demonstrated in any polymerization yet studied. At first it might seem to violate the principle[7] that free radicals can be formed or destroyed in pairs only. Numerous examples are known, however, of stable molecules acting as inhibitors of chain reactions, and it is necessary only to assume that, as in the case of inhibition of polymerization by nitro compounds,[8] the molecule is able to react with the radical to yield a new free radical with greater stability and lower reactivity than the old. If such a radical is incapable of carrying on the polymerization chain, it will eventually disappear through combination with one of its kind or with another growing free radical. We shall designate this mode of termination, involving the monomer in a part-time role of inhibitor, as "degradative chain transfer." It differs from ordinary chain transfer[7a] to the monomer in the degree to which chains may still be propagated following the transfer. If the radical resulting from interaction of a growing chain with a monomer molecule proceeds to carry on the chain, then the process is ordinary chain transfer; if not, it is degradative chain transfer. The kinetics of the two cases are quite different, but intermediate cases are both possible and likely. The amount of chain transfer indicated by our tracer experiments suggests that the "stable" final radicals in the case of allyl acetate may not be too stable to start new chains a minor fraction of the time.

Reactions Involved in Degradative Chain Transfer.—Is there any obvious way in which an allyl acetate molecule might react with a free radical and yield a new free radical with greate stability than the original one? There are two positions in allyl acetate from which hydrogen

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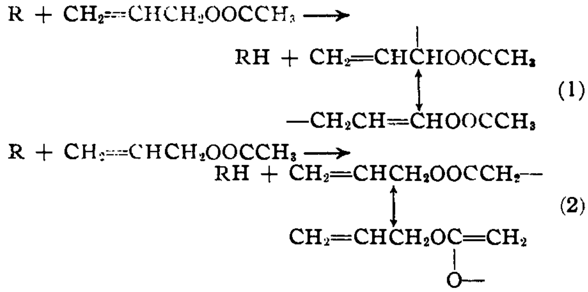
[5] See Price, *Ann. N. Y. Acad. Sci.*, **44**, 352 (1943).

[6] Branson and Simha, *J. Chem. Phys.*, 11, 297 (1943).

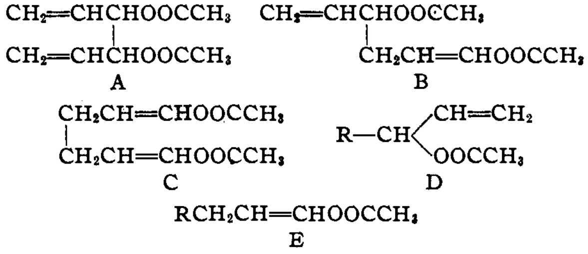
[7] Flory, This Journal, **59**, 242 (1937); (7a) *ibid.*, pp. 243, 251.

[8] Price and Durham, *ibid.*, **65**, 757 (1943).

atoms might be removed with somewhat less than normal input of energy.



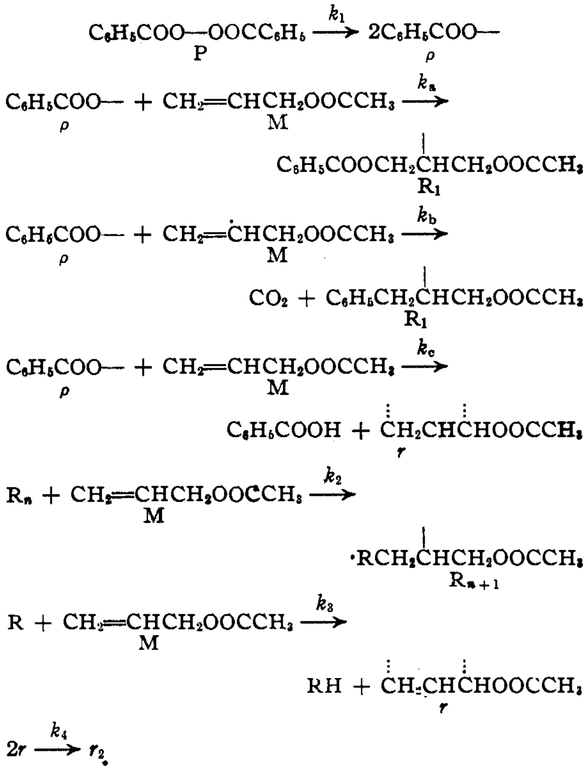
Both of these radicals are stabilized by resonance in such a way as to make them less reactive than the type of radical present as a chain carrier. We can decide in favor of Reaction 1 and reject Reaction 2 in view of the well-known fact that vinyl acetate polymerizes in long chains with no appearance of degradative chain trasnfer,[9] and the observation by Dr. S. G. Cohen[10] that the polymerization of allyl benzoate and allylpropyl carbonate, which cannot give Reaction 2, shows the same constant dM/dP characteristic of allyl acetate polymerization. There are two ways in which the acetoxyallyl radical, once formed, may disappear in conformity with the observed kinetics. One way is by dimerization, whose rate would be immaterial to the kinetics of the reaction provided that it were the exclusive mode of disappearance of the radical. The other way is by rapid combination with a growing radical, so that effectively each degradative chain transfer would arrest two chains. These modes of reaction raise the possibility of five products appearing in the polymer, as follows:



We have prepared Compound A, b. p. (2 mm.) 79-82°, and the related chloroacetate, by esterifying the dimolecular reduction product of acrolein. Experiments with these compounds, while not satisfactorily conclusive, are consistent with the prediction that they should copolymerize with allyl acetate if formed. B, C, and E, being enol acetates, should, if present, yield aldehydes on hydrolysis, but no aldehyde test could be obtained under these conditions. No model compounds were prepared to determine the extent to which these species would disappear by copolymerization. No specific test was devised for the terminal group D.

The formation of A, B, or C and their copolymerization with allyl acetate would yield a polymer having between 0 and 0.5 double bond per polymer molecule. If A, B, and C were formed, and remained in the polymer unpolymerized, there would be 0.67 double bond per product molecule. The mode of termination resulting in D or E calls for one double bond to each two polymer molecules, or 0.5 per molecule, which number might likewise be diminished by copolymerization. Determinations of unsaturation in the non-volatile polymers made with 9.95, 6.10 and 1.01% benzoyl peroxide by weight showed 0.16, 0.18 and 0.16 double bond per polymer molecule, respectively. The evidence allows no definite conclusions on the nature of the final products of degradative chain transfer.

Formulation of the Mechanism of Polymerization.—We are now ready to formulate a mechanism, acknowledging the existence of different kinds of radicals which differ greatly in their properties. Consider the steps



$$\underset{P}{C_6H_5COO{-}OOCC_6H_5} \xrightarrow{k_1} \underset{p}{2C_6H_5COO{-}}$$

$$\underset{p}{C_6H_5COO{-}} + \underset{M}{CH_2{=}CHCH_2OOCCH_3} \xrightarrow{k_a} \underset{R_1}{C_6H_5COOCH_2\overset{|}{C}HCH_2OOCCH_3}$$

$$\underset{p}{C_6H_5COO{-}} + \underset{M}{CH_2{=}CHCH_2OOCCH_3} \xrightarrow{k_b} CO_2 + \underset{R_1}{C_6H_5CH_2\overset{|}{C}HCH_2OOCCH_3}$$

$$\underset{p}{C_6H_5COO{-}} + \underset{M}{CH_2{=}CHCH_2OOCCH_3} \xrightarrow{k_c} C_6H_5COOH + \underset{r}{\overset{\vdots}{C}H_2C\overset{\vdots}{H}CHOOCCH_3}$$

$$R_n + \underset{M}{CH_2{=}CHCH_2OOCCH_3} \xrightarrow{k_2} \underset{R_{n+1}}{\cdot RCH_2\overset{|}{C}HCH_2OOCCH_3}$$

$$R + \underset{M}{CH_2{=}CHCH_2OOCCH_3} \xrightarrow{k_3} RH + \underset{r}{\overset{\vdots}{C}H_2C\overset{\vdots}{H}CHOOCCH_3}$$

$$2r \xrightarrow{k_4} r_2$$

This mechanism is probably an oversimplification, but one which may yield some correct answers nevertheless. It implies that every benzoate radical which is formed reacts by the path associated with k_a, k_b or k_c. This is based upon evidence presented in Part I. There it was shown, in the case of *p*-chlorobenzoyl peroxide as a chain initiator, that 27.5% of the benzoate radicals initially formed are never attached to polymer

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(9) Kamenskaya and Medvedev, *Acta Physicochim. U. R. S. S.*, 18, 565 (1940).

(10) S. G. Cohen, unpublished observations in this Laboratory.

chains; 61% of these, or 16.8% of the whole, appeared as chlorobenzoic acid, having apparently reacted by way of k_c. The present mechanism assumes that the 10.7% of the benzoate which is unaccounted for has also reacted by way of k_c.

We may now express the steady-state concentrations of the three types of radicals, ρ, R and r, as follows:

$$\mathrm{d}\rho/\mathrm{d}t = k_1P - (k_a + k_b + k_c)M'\rho = k_1P - k^*M\rho' \cong 0$$

$$\rho' = \frac{k_1P}{k^*M}$$

where $k^* = k_a + k_b + k_c$

$$\mathrm{d}R/\mathrm{d}t = (k_a + k_b)M\rho' - k_3MR' \cong 0$$

$$R' = \frac{k_a + k_b}{k_3}\rho' = \frac{k_1(k_a + k_b)P}{k^*k_3M}$$

Likewise

$$r' = \sqrt{\frac{k_1P'}{k_4}}$$

This mechanism yields for the rate of disappearance of monomer

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = \left(k_1 + \frac{k_1(k_2 + k_3)(k_a + k_b)}{k^*k_3}\right)P$$

$$\frac{\mathrm{d}M}{\mathrm{d}P} = 1 + \frac{(k_2 + k_3)(k_a + k_b)}{k^*k_3} = \text{constant}^{11}$$

Inadequacies of the Mechanism Proposed.—The correspondence of the above mechanism with the facts is close enough to indicate that degradative chain transfer must be the chief mode of termination of the polymerization chains. A complete description of the mechanism, however, must include some additional reactions to account for two facts: (1) that the unimolecular rate constant for peroxide decomposition shows a trend toward higher values at the higher initial peroxide concentrations, and (2) that dM/dP, constant in any run, is cut to 54% of its value when the initial peroxide concentration is multiplied by ten (Table VI). The interpretation of these two facts, involving some refinement in both experiment and theory, is reserved for a later paper.

Molecular Weight of Polyallyl Acetate.—The viscosities of solutions in benzene of the unfractionated polyallyl acetates prepared with different initial peroxide concentrations were determined. The intrinsic viscosities were all the same within an extreme variation of about 6%. The number-average molecular weights were determined cryoscopically for two polymer samples, and on the basis of these determinations the viscosities have been translated into average degree of polymerization $\bar{P}$ as shown in the last column of Table VI.

TABLE VI

SUMMARY OF CONSTANTS FOR THE POLYMERIZATION OF ALLYL ACETATE

Initial wt., %	Peroxide, moles/kg.	k_1 (dec. of Bz_2O_2)	dM/dP	$\bar{P}$
By Benzoyl Peroxide at 80°				
1.01	0.0413	0.191	28.8	13.5
2.14	.0887	.196	24.4	13.6
6.10	.248	.227	18.5	14.1
9.95	.413	.235	15.6	14.0
By p-Chlorobenzoyl Peroxide at 80°				
5.90	.185	163	25.3	13.3

Degree of Polymerization and dM/dP.—A comparison between Columns 4 and 5 of Table VI shows that the value of dM/dP, though constant throughout any run, varies significantly with the initial peroxide concentration while the degree of polymerization does not. Since each molecule of benzoyl peroxide, on decomposition, yields two free radicals, the quantity (dM/dP)/2 is a measure of the number of monomer molecules polymerized for each free radical produced. If the over-all mechanism of the polymerization outlined above were correct without amendment, and if each original free radical actually started a polymerization chain, we should expect (dM/dP)/2 to be exactly equal to $\bar{P}$.[12] Since in three of the four cases cited, (dM/dP)/2 is less than $\bar{P}$, it is clear that not every free radical starts a polymerization chain. The constancy of the average molecular weight of the polymer under all conditions is evidence that the conversion of growing polymer radicals into molecules must occur only by chain transfer to the monomer, as previously proposed. The value of dM/dP, however, may be affected by occurrences both before the initiation and after the termination of a polymerization chain. *Wastage of benzoate radicals*, through their interaction to yield carbon dioxide and phenyl benzoate or diphenyl before a polymerization chain is started, would lower dM/dP without changing $\bar{P}$ and would do this to a degree depending upon the concentration of peroxide. On the other hand, if the degraded allylic radical r (= CH_2CHCH-$OOCCH_3$) were capable of reacting with monomer to start a new polymerization chain (but with a rate constant unfavorable compared to that of reunion of two r's) this would amount to *chain transfer* and would *raise* dM/dP in comparison to $\bar{P}$. In one case—the tracer experiment described in Part I—we have enough evidence concerning the fate of the peroxide to show that a small amount (23%) of chain transfer was occurring. Of course, if chain transfer occurs in the present experiments it must be accompanied by wastage of peroxide fragments on a sufficient scale to keep (dM/dP)/2, as observed, below $\bar{P}$. Further study is being given to this point.

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(11) If, instead of the union of two r radicals, the reaction is terminated by a reaction between r and R

$$\frac{\mathrm{d}M}{\mathrm{d}P} = 1 + \frac{(k_2 + k_3)(k_a + k_b)}{2k_3k^*}$$

Although we do not know which of these modes of reaction of r prevails, we know that they are not both contributing to similar extents, for in this case their relative contributions would vary as R/r, or as $\sqrt{P'/M'}$, and dM/dP could not be constant.

(12) As pointed out by the Referee if diacetoxyhexadiene or an isomer is produced and is neither copolymerized nor removed by the evacuation procedure, then (dM/dP)/2 should equal $3\bar{P}/2$.

Chain Transfer in the Polymerization of Allyl Chloride.—When allyl chloride was polymerized exhaustively with 6.3% of its weight of benzoyl peroxide, the extent of polymerization was 80.6% by titration and 83.1% gravimetrically. Thus the polymerization showed an over-all $\Delta M/\Delta P$ of 36.4, somewhat higher than that for allyl acetate. At the same time the molecular weight of the product, determined cryoscopically, had the remarkably low values of 470 and 480, respectively, in two determinations, corresponding to $\bar{P} = 6.3$. This means that each peroxide fragment produced has given rise to not less than 2.9 molecules of polymer, and proportionately more as some of the peroxide fragments may have been wasted in reaction with one another.

The lower molecular weight of polyallyl chloride as compared to polyallyl acetate was predicted from the mechanism of degradative chain transfer coupled with the observation[13] that free radicals in polymerization react more rapidly to take chlorine from a carbon–chlorine bond than to take hydrogen from a carbon–hydrogen bond. The polymerization chains in the case of allyl chloride would be expected to terminate in the degradative transfer step whose relative fre-

$$R + CH_2{=}CHCH_2Cl \longrightarrow RCl + \overset{\vdots}{C}H_2CH\overset{\vdots}{C}H_2$$

quency should be greater than that of the corresponding step (involving hydrogen transfer) in the case of allyl acetate. At the same time it is reasonable that the resulting simple allyl radical, having only primary carbon atoms as seats for the unpaired electron, should be somewhat more reactive in initiating polymerization chains than the analogous radical from allyl acetate. In view of this consideration the increased chain transfer in the polymerization of alllyl chloride is not surprising.

Experimental

Purification of Materials.—Thiophene-free benzene was distilled through an all-glass apparatus under anhydrous conditions. The forerun was rejected and the second fraction was stored in a specially cleaned bottle over sodium wire.

Allyl acetate was purified as described in Part I.

Technical allyl chloride from the Eastman Kodak Co. was distilled twice through an all-glass distilling assembly with a Vigreux column, and the middle fraction, b. p. (759 mm.) 44.3–45.1°, n^{25}D 1.4122, was used.

The product from the exhaustive polymerization of allyl acetate was dissolved in about 4–5 times its weight of benzene and extracted with four portions of 35% ice-cold aqueous potassium carbonate solution. The last extract, after heating on the steam-bath and filtration, left no precipitate on acidification with hydrochloric acid, indicating complete removal of benzoic acid with the preceding extractions. After being dried with anhydrous potassium carbonate, the organic layer was stripped of the solvent with a slow stream of clean, dry air at room temperature and was then dried to constant weight at 100° under 1 mm. pressure and used for molecular weight determinations.

Determination of unsaturation was carried out as in Part I.[4] A further check of the method for unsaturation was provided in those runs in which the polymer was collected for molecular weight determination. This collecting was done by expelling all volatile material under a vacuum at room temperature; the weight of the residue, corrected for that of the peroxide and its decomposition products, was in close agreement with the amount of polymer inferred from the titrations.

Determination of Benzoyl Peroxide.—A sample of the allyl acetate solution (0.5 to 0.9 g.) was weighed to the nearest milligram in a tared 125 cc. g. s. Erlenmeyer flask. To it was then added 8–10 cc. of glacial acetic acid. A few lumps of Dry Ice were dropped into the flask, followed by 0.3 cc. of 50% aqueous potassium iodide solution (freshly prepared). The vessel was stoppered loosely and swirled for five minutes at room temperature. After addition of 50 cc. of distilled water, the iodine was titrated with thiosulfate to a starch end-point. The Dry Ice was renewed when necessary during the titration to prevent oxidation. In samples containing much polymer, the thiosulfate titration was carried near the end-point before the addition of the water.

3,4-Diacetoxy-1,5-hexadiene.—Conversion of hexadiene-(1,5)-diol-3,4[14] to the diacetate was accomplished with an excess of acetic anhydride at 150°.[15] The product was distilled under diminished pressure in a stream of dry nitrogen. The yield was 86.5% of a colorless oil having b. p. (2 mm.) 79–82°, nD 1.4390, d_{24} = 1.00; mol. wt. calculated 198.2; found 197.

3,4-Di-(chloroacetoxy)-1,5-hexadiene.—This compound was prepared as a close analog of Compound A (see section on reactions involved in degradative chain transfer) which should be easily traced in a test of its ability to copolymerize with allyl acetate. The diol (25 g.) was heated with a slight excess of chloroacetic anhydride for three hours at 150–155° in a stream of dry nitrogen. The yield on first distillation was 40 g. (69%) of material which on further distillation yielded a colorless oil, b. p. (2 mm.) 136–138°, n^{21}D 1.4809, d_{23} 1.24.

Analysis (by Miss Margaret Racich). Calcd. for $C_{10}H_{12}O_4Cl_2$: C, 44.96; H, 4.62. Found: C, 45.19; H, 4.82. The molecular weight was calculated as 267.1; found, 270. The molecular weights of these two esters were determined by saponification.

Polymerization of Allyl Acetate Containing Di-(chloroacetoxy)-hexadiene.—A number of experiments were performed to ascertain the extent to which the hexadienediol esters, under the conditions of polymerization, would enter into the polymer. They all suffer from uncertainty regarding the complete removal of volatile material. The following experiment, using the dichloroacetate, is representative. A mixture was prepared from 1.22 g. of the dichloroacetate and 9.28 g. of allyl acetate, and 10 cc. (9.55 g.) of this mixture was added to 0.605 g. of benzoyl peroxide. This solution was heated at 80° under nitrogen for forty-eight hours, a treatment which experience had shown to be adequate for the analytically complete destruction of the peroxide. A 2.535-g. sample of the resulting solution was freed of its volatile constituents, first under 1 mm. pressure at room temperature and then by heating to 150° at this pressure until no more distillation occurred. The polymer was rinsed with three 5-cc. portions of methanol, dissolved in C. P. benzene, and once more dried to constant weight *in vacuo*. A sample of this product was analyzed for its chlorine content by Dr. C. Tiedcke: Cl, 4.01. This corresponds to one molecule of dichloroacetoxyhexadiene present for every 15 molecules of allyl acetate in the polymer. The original molar ratio of the ester was 1:20.9.

Freezing Point Measurements.—A solution of the polymer was made up accurately by weight in benzene (15–20 cc.) and the solution placed in a large test-tube equipped with a stopper carrying a Beckmann thermometer, a short gas inlet tube through which a slow stream of dry nitrogen was admitted to pass over the surface of the solution, and a hand stirrer. The solution was partly

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[13] Suess and Springer, *Z. physik. Chem.*, **A181**, 81 (1937); see also Mayo, THIS JOURNAL, **65**, 2324 (1943).

[14] Kuhn and Rebel, *Ber.*, **60**, 1568 (1927).

[15] Griner, *Ann. chim.*, **26**, 371 (1892).

frozen in an ice-bath, then supported inside a transparent Dewar flask by a bored stopper and stirred. Temperature readings were taken after one-minute or half-minute intervals timed with a stop watch. The temperature readings were plotted against time and the "break" located by graphical extrapolation of the linear portions of the heating curves in the presence and absence of solid. The values of the freezing point depression thus obtained (Table VII) were in each case the result of at least two checking determinations.

TABLE VII

DETERMINATION OF K_m CONSTANT OF POLYALLYL ACETATE AND POLYALLYL CHLORIDE

Sample	Concn. in g./kg. C_6H_6	Depression of f. p., °C.	Mol. wt.	η_{sp}/c_{bm}[a] C_6H_6 soln., 27°	K_m
PAAc 197	34.8	0.20°	890	0.289	3.2×10^{-4}.
PAAc 197	47.0	.28	860	.289	3.4×10^{-4}
PAAc 208	54.0	.24	1150	.376	3.3×10^{-4}
PA Chloride	49.9	.53	480	.168	3.5×10^{-4}
	39.5	.43	470		

[a] c_{bm} = concentration in basal moles per liter.[15]

Viscometric Determinations.—The viscosities were measured in benzene as solvent, in a thermostat operating at 27.0 ± 0.15°. A modified Ostwald pipet was used. In orienting experiments it was established that no disturbances were created by vibration of the bath nor by slight disorientation of the viscometer, and that for solutions up to 3% polymer the time of flow was reproducible as closely as the stop watch could be read (0.2%), and varied by about one per cent. per degree centigrade. It was also established that the specific viscosity was a linear function of concentration up to a solute concentration of 34 g. per liter. The results are expressed in terms of the constant K_m of the Staudinger equation,[16]

$$K_m = \eta_{sp}/c_{bm} \times M$$

where c_{bm} = concentration in basal moles per liter, M = molecular weight of the polymer, and

$$\eta_{sp} = (\eta_2 - \eta_1)/\eta_1$$

Here η_1 and η_2 are the viscosities of the solvent and of the solution, respectively.

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[16] Staudinger, "Die Hochmolekulare organische Verbindungen," Berlin, 1932, p. 56.

Summary

The decomposition of benzoyl peroxide in allyl acetate as solvent is very nearly unimolecular, the rate constant at 80° varying from 0.191 to 0.235 hr.$^{-1}$ over a tenfold range of initial peroxide concentration. The concentration of monomer is a linear function of the concentration of peroxide over the entire course of a polymerization, *i. e.*, dM/dP is constant throughout. The value of dM/dP shows some dependence upon the initial peroxide concentration, changing from 28.8 with 1.01% by weight of peroxide to 15.6 with 9.95% by weight of peroxide, but the average degree of polymerization of the polymer is 13.7 ± 0.4 in all cases.

The constancy of dM/dP during a polymerization is interpreted as meaning that the polymerization chain is broken by collision of a growing free radical with a monomer molecule to yield a new, stabler free radical which is usually incapable of propagating the chain. This process is designated as "degradative chain transfer."

A discussion is presented showing that unimolecular reactions in an expanding or contracting medium are best treated in terms of concentrations per unit weight, and not per unit volume of the medium. In the present case it is also convenient to treat certain bimolecular reactions in terms of weight-concentrations of the species whose change in concentration is being considered.

Further work is in progress directed toward a fuller interpretation of the polymerization of allyl acetate by peroxides.

The polymerization of allyl chloride at 80° by benzoyl peroxide yields a polymer containing an average of 6.3 monomer units per molecule. On an average 5.8 such molecules are produced by each peroxide molecule decomposing.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Certain Compounds Related to Tryptophan

BY LEE IRVIN SMITH AND A. WALTER SOGN[1]

Recently, new and convenient syntheses for *dl*-tryptophan, starting with gramine, have been published.[2] In this paper work is reported which deals with a different approach to the synthesis of the amino acid. The synthesis was successful insofar as the tryptophan nucleus was concerned, but amination of the final product, ethyl α-carbethoxy-β-(3-indole)-propionate (VIII) could not be achieved.

In the synthesis, IV was the key compound. This substance was prepared from ethyl α-ketocyclopentanone carboxylate I, which was coupled with diazotized aniline to obtain II. The azo compound was subjected to hydrolytic cleavage whereby the phenylhydrazone of ethyl hydrogen α-ketoadipate, III, resulted and action of acid upon III caused a Fischer indole synthesis to occur with production of IV.

This series of reactions was first reported by Kalb, Schweizer and Schimpf,[3] but the procedure

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[1] Abstracted from a thesis by A. W. Sogn, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the M.S. degree, November, 1942.

[2] (a) Snyder, Smith and Stewart, THIS JOURNAL, **66**, 200 (1944); (b) Snyder and Smith, *ibid.*, **66**, 350 (1944); (c) Albertson, Archer and Suter, *ibid.*, **66**, 500 (1944); (d) **67**, 36 (1945); (e) Howe, Zambito, Snyder and Tishler, *ibid.*, **67**, 38 (1945); (f) Elks, Elliott and Hems, *J. Chem. Soc.*, 624 (1944); (g) 626 (1944); (h) 629 (1944).

[3] Kalb, Schweizer and Schimpf, *Ber.*, **59**, 1858 (1926).