# Kinetics of Polymerization of Allyl Compounds*

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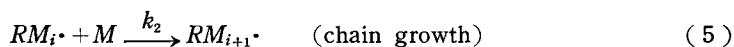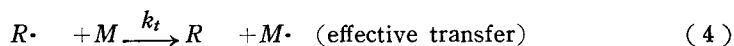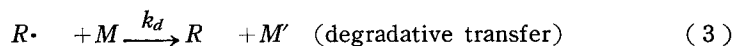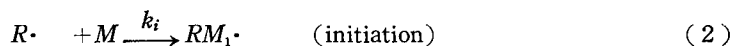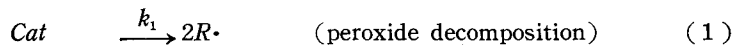
Kinetics of polymerization of allyl esters may be regarded in its essential part to have been established through the works of Bartlett[1] and Gaylord[2].

The benzoyl peroxide catalyzed bulk polymerization of allyl esters yields a polymer with a relatively low degree of polymerization. As for example the degree of polymerization of a polymer of allyl acetate is about 13. In any given polymerization, the concentration of monomer polymerized is a linear function of peroxide decomposition, i. e. $d[M]/d[Cat]$ is constant. The constancy of $d[M]/d[Cat]$ is attributed to degradative chain transfer, wherein active radicals, as in growing chains, yield stabilized radicals with much lowered reactivity.
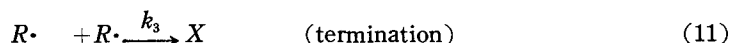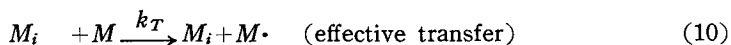
The mechanism proposed by Bartlett is, as mentioned by himself, inadequate to explain why $d[M]/d[Cat]$, which is constant in any run, changes with varying initial concentrations of benzoyl peroxide. The first point, with which the present investigation is concerned, is to find a quantitative explanation for the change. The second point is to present mathematical functions which permit quantitative distinction between effective and degradative chain transfer.

## A proposed kinetic scheme

We consider the following steps of reactions.

$$Cat \xrightarrow{k_1} 2R\cdot \qquad \text{(peroxide decomposition)} \qquad (1)$$

$$R\cdot + M \xrightarrow{k_i} RM_1\cdot \qquad \text{(initiation)} \qquad (2)$$

$$R\cdot + M \xrightarrow{k_d} R + M' \quad \text{(degradative transfer)} \qquad (3)$$

$$R\cdot + M \xrightarrow{k_t} R + M\cdot \quad \text{(effective transfer)} \qquad (4)$$

$$RM_i\cdot + M \xrightarrow{k_2} RM_{i+1}\cdot \quad \text{(chain growth)} \qquad (5)$$

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* Based upon papers published in Chem. High Polymers, Japan **11**, 255, 260, 266 (1954).

$$RM_i\cdot + M \xrightarrow{k_D} RM_i + M' \quad \text{(degradative transfer)} \qquad (6)$$

$$RM_i\cdot + M \xrightarrow{k_T} RM_i + M_1\cdot \quad \text{(effective transfer)} \qquad (7)$$

$$M_i\cdot \ + M \xrightarrow{k_2} M_{i+1}\cdot \quad \text{(chain growth)} \qquad (8)$$

$$M_i\cdot \ + M \xrightarrow{k_D} M_i + M' \quad \text{(degradative transfer)} \qquad (9)$$

$$M_i \ + M \xrightarrow{k_T} M_i + M\cdot \quad \text{(effective transfer)} \qquad (10)$$

$$R\cdot \ + R\cdot \xrightarrow{k_3} X \qquad \text{(termination)} \qquad (11)$$
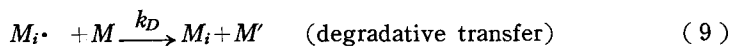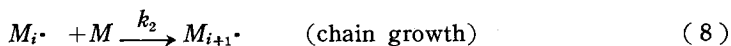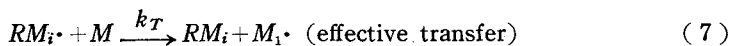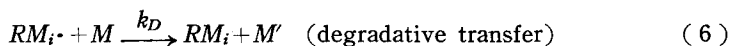
where $R\cdot$ is a radical formed by the decomposition of benzoyl peroxide, $M$ is a monomer, $M'$ is an inactive radical produced by a degradative transfer, $RM_i\cdot$ or $RM_i$ is a growing radical or a stable polymer molecule on which a catalyzer fragment is attached, $M_i\cdot$ or $M_i$ is a growing radical or a stable polymer molecule without a catalyzer fragment. To accout for the change of $d[M]/d[Cat]$ with the variation of initial peroxide concentration, eq. (11) is introduced. The product $X$ or at least its main part seems to be phenyl benzoate, which was isolated and identified in our experiment. Chain termination by a reaction between two growing radicals and between a growing radical and $R\cdot$ is neglected while no or only a very small change of degree of polymerization has been observed with a variation of the initial catalyzer concentration.

For the purpose of deduction of $d[M]/d[Cat]$ it is not necessary to make any differentiation between $RM_i\cdot$ and $M_i\cdot$, so the two radicals are denoted simply by $M_i\cdot$. By steady state assumptions we have

$$\frac{d[R\cdot]}{dt} = 2k_1[Cat] - (k_i+k_d+k_t)[R\cdot][M] - k_3[R\cdot]^2 = 0$$

$$[R\cdot] = \frac{1}{2k_3}\{-(k_i+k_d+k_t)[M] + [(k_i+k_d+k_t)^2[M]^2 + 8k_1k_3[Cat]]^{1/2}\} \qquad (12)$$

$$\frac{d[M_i\cdot]}{dt} = (k_i+k_t)[R\cdot][M] - k_D[M_i\cdot][M] = 0$$

$$[M_i\cdot] = \frac{k_i+k_t}{k_D}[R\cdot]$$

$$= \frac{k_i+k_t}{2k_3k_D}\{-(k_i+k_d+k_t)[M] + [(k_i+k_d+k_t)^2[M]^2 + 8k_1k_3[Cat])]^{1/2}\} \qquad (13)$$

$$-\frac{d[M]}{dt} = (k_2+k_T)[M_i\cdot][M] + (k_1+k_t)[R\cdot][M] \qquad (14)$$

In the above equation monomer consumption through chain transfer is omitted, for the inactive radical $M'$ do not combine with polymer molecules and escapes as volatile material by the gravimetric determination of the extent of polymerization.

The rate of the decomposition of benzoyl peroxide may be given by

$$-\frac{d[Cat]}{dt} = k_1[Cat] \tag{15}$$

From the above equations $d[M]/d[Cat]$ may be calculated and after an appropriate transformation we obtain

$$\left(\frac{d[M]}{d[Cat]}\right)^2 \frac{[Cat]}{[M]^2} = A^2 C - 2AB\frac{d[M]}{d[Cat]} \tag{16}$$

$A$, $B$ and $C$ are constants.

As will be shown later, the above equation can express quantitatively the dependency of $d[M]/d[Cat]$ on the initial catalyst concentration $[Cat]$, but it does not follow from the equation that $d[M]/d[Cat]$ is constant in the course of a given polymerization. When the initial catalyst concentration is very low the eq. (16) reduces to

$$\left[\frac{d[M]}{d[Cat]}\right]_0 = \frac{AC}{2B} = 2\frac{(k_i+k_t)(k_2+k_T+k_D)}{(k_i+k_d+k_t)k_D} = \text{constant} \tag{17}$$

If we assume the following relations

$$\frac{k_i}{k_2} = \frac{k_d}{k_D} = \frac{k_t}{k_T} \tag{18}$$

we obtain

$$\left[\frac{d[M]}{d[Cat]}\right]_0 = \frac{2(k_2+k_T)}{k_D} \tag{19}$$

Degree of polymerization $\bar{P}$ may be written as:

$$\bar{P} - 1 = \frac{k_2[M][M\cdot]}{k_D[M][M\cdot]+k_T[M][M\cdot]} = \frac{k_2}{k_D+k_T} = \text{constant} \tag{20}$$

Substituting equation (19) in (18) we obtain:

$$\frac{k_D}{k_D+k_T} = \frac{2\bar{P}}{\left[\dfrac{d[M]}{d[Cat]}\right]_0 + 2} \tag{21}$$

$\bar{P}$ and $[d[M]/d[Cat]]_{\to 0}$ are measurable quantities, so that we can find not only $k_D/(k_D+k_T)$ but also $k_2/k_D$, $k_2/k_T$ and $k_D/k_T$.

The number of polymer molecules with and without a catalyst fragment should be calculated. Under assumptions of steady state we have

$$k_i[R\cdot][M] = (k_D+k_T)[RM_i\cdot][M]$$

$$[RM_i\cdot] = \frac{k_i}{k_D+k_T}[R\cdot] \tag{22}$$

$$k_t[R\cdot][M]+k_T[RM_i\cdot][M] = k_D[M_i\cdot][M]$$

$$[M_i\cdot] = \left(\frac{k_t}{k_D} + \frac{k_i k_T}{k_D+k_T}\right)[R\cdot] \tag{23}$$

The rate of formation of stable $RM_i$ and $M_i$ molecules is given by:

$$\frac{d[RM_i]}{dt} = (k_D + k_T)[RM_i \cdot][M] \tag{24}$$

$$\frac{d[M_i]}{dt} = (k_D + k_T)[M_i \cdot][M] \tag{25}$$

From equations (22), (23), (24) and (25) we obtain:

$$\frac{d[M_i]}{d[RM_i]} = \frac{[M_i \cdot]}{[RM_i \cdot]} = \frac{k_t(k_D + k_T)}{k_i k_D} + \frac{k_T}{k_D} = \text{constant} \tag{26}$$

After integration we have:

$$\frac{[M_i]}{[RM_i]} = \frac{k_t(k_D + k_T)}{k_i k_D} + \frac{k_T}{k_D} = \text{constant} \tag{27}$$

Equation (27) means that the ratio of the number of polymer molecules without a catalyst fragment to that with a catalyst fragment is not influenced by the catalyst concentration. Under assumptions of the relations of equation (18) and introduction of (20) the following relation is obtained:

$$\frac{[M_i]}{[RM_i]} = \frac{k_T}{k_D}\frac{\bar{P}}{\bar{P}-1} \tag{28}$$

For $\bar{P}$ sufficiently larger than 1, the above equation reduces to

$$\frac{[M_i]}{[RM_i]} = \frac{k_T}{k_D} \tag{29}$$

Equation (29) may be rewritten as:

$$\frac{k_D}{k_D + k_T} = \frac{[RM_i]}{[RM_i]+[M_i]} \tag{30}$$

The right hand side of the above equation is the number fraction of polymer molecules with a catalyst fragment in the total polymer molecules, and may be analytically found.

By comparison of $k_D/(k_D + k_T)$ values obtained from kinetic data $[d[M]/d[Cat]]_0$ by equation (21) and that obtained from analytical data $[RM_i]/([RM_i]+[M_i])$ by equation (30), it is able to test the adequacy of the preposed kinetic scheme.

### Experimental Results and Discussions.

The bulk polymerization of several allyl compounds was carried out at 80°C, in the presence of varying initial concentrations of benzoyl peroxide (BPO) or 0, 0'– dichlorobenzoyl peroxide (OCBPO). In most cases, the course of polymerization and the catalyst decomposition were not followed as a function of time, but the ammount of polymer formed by any given amount of the catalyst after extensively

long polymerization time (15—20 hrs.) was determined, and this value was regarded to be equal to $d[M]/d[Cat]$. That the relation:

$$\frac{[M]}{[Cat]} = \frac{d[M]}{d[Cat]} \tag{31}$$

holds for allyl compounds is according to the polymerization scheme here presented not a theoretical consequence but an experimental evidence found by allyl acetate and various other allyl esters.

By the polymerization of allyl monomers, which do not contain halogen, OCBPO was used as a catalyst and Cl determination was carried out with a purified polymer to find the number of polymer molecules, to which catalyst fragment is combined as an end-group.  Otherwise BPO was used as a catalyst and benzoyl group was determined by saponification of a purified polymer.

The data of our experiment with allyl acetate are given in Table I.

Table I.  Polymerization of allyl acetate with OCBPO at $80\pm0.3°C$.

| Time hrs. | Catalyst init. conc. % | Polymer yield % | $\dfrac{d[M]}{d[Cat]}$ | Molec. wt. of Polymer | $\bar{P}$* | Cl cont. of polym. in % | $\dfrac{[RM_i]}{[RM_i]+[M_i]}$ |
|---|---|---|---|---|---|---|---|
| 15.0 | 0.5 | 5.58 | 35.3 | 1520 | 15.2 | 1.26 | 0.54 |
| ,, | 1.0 | 9.65 | 30.5 | 1400 | 14.0 | 1.45 | 0.57 |
| ,, | 2.0 | 16.40 | 25.9 | 1340 | 13.4 | 1.51 | 0.57 |
| ,, | 4.0 | 28.45 | 22.6 | 1260 | 12.6 | 2.04 | 0.72 |
| 0.2 | 5.0 | 9.77 | — | 980 | 9.8 | 1.95 | 0.54 |
| 0.5 | ,, | 19.10 | — | 1030 | 10.3 | 1.91 | 0.56 |
| 1.0 | ,, | 28.66 | — | 1190 | 11.9 | 1.93 | 0.64 |
| 15.0 | ,, | 34.35 | 21.7 | 1210 | 12.1 | 1.93 | 0.66 |

* Calculated under neglection of the end–group.

$\bar{P}=$(Molec. wt. of polymer)/(mole. wt. of monomer)

It is seen from Table I that $\bar{P}$ is strictly speaking, not constant but decreases somewhat with the increasing catalyst concentration, which means that chain termination through collision of two growing chains may occur.  But for the purpose of simplification this termination mechanismus was not taken into account.

Figure 1 shows variation of $d[M]/d[Cat]$ with $[Cat]$ according to equation (16) ; the plot may be approximated by a straight line as theory requires.  Figure 2 shows the same relation for BPO catalyzed bulk polymerization of allyl acetate at 80°C. For comparison with our results, those of Bartlett and Gaylord are also shown in the figure.  The points from three different sources can be plotted by a single straight line.  From these figures it is clear that the above presented kinetic scheme, in which chain termination by a reaction of two primary radicals $R\cdot$ is considered,
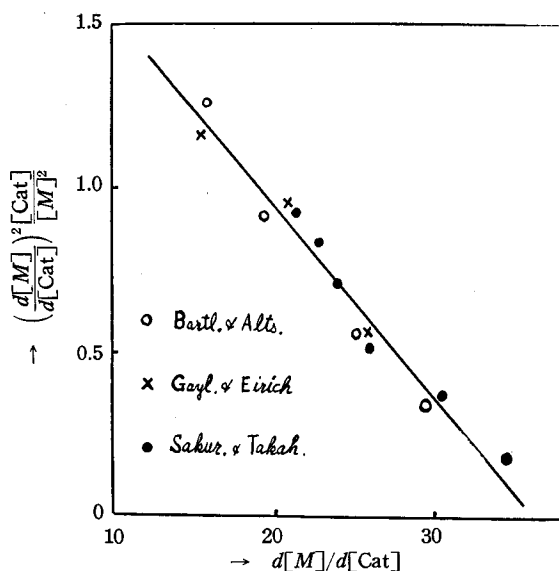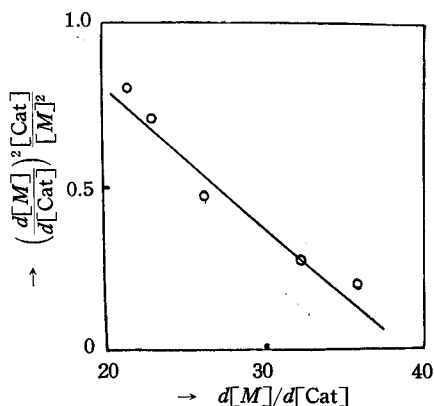
Fig. 1. Polymerization of Allylacetate by BPO



Fig. 2. Polymerization of Allylacetate by OCBPO

gives a quantitative explanation of the dependency of $d[M]/d[Cat]$ on the initial catalyst concentration. But here we meet an apparent contradiction, that $d[M]/d[Cat]$ is constant throughout the entire course of polymerization. The constancy of $d[M]/d[Cat]$ was the chief reason for Bartlett and Altschul presenting a new type of chain termination i. e. " degradative chain transfer ". It is true that the degradative chain transfer is the most remarkable feature of the allyl polymerization but the constancy of $d[M]/d[Cat]$ is not, except for a very low initial catalyst concentration, a necessary theoretical consequence. According to our calculation from data of Bartlett and Altschul $[Cat]/[M]^2$ is *nearly* constant in the main part of the course of polymerization. As can be easily seen from equation (16) this is the reason for the constancy of $d[M]/d[Cat]$ in the course of polymerization. Of course it can not be regarded as accidental and we hope that the integration of equation (16) will throw light upon it.

When $d[M]/d[Cat]$ at various initial catalyst concentration is known, we can find easily by extrapolation the value of $[d[M]/d[Cat]]_0$; through combination with the value of $\bar{P}$, $k_D/(k_D+k_T)$ can be calculated by equation (21). $k_D/(k_D+k_T)$ gives nothing other than the fraction of degradative chain transfer in the total transfer reactions.

A summary of constants obtained in the bulk polymerization of several allyl esters is given in Table II along with some of the data of Bartlett and Gaylord. The results indicate that the order of the $k_D/(k_D+k_T)$ value is trimethylacetate $<$

propionate $<$ acetate $<$ ethyl carbonate. This is the same as the order of $\bar{P}$ found by Gaylord and Eirich and the theoretical equation (21) also indicates that a larger $\bar{P}$ results in a higher $k_D/(k_D+k_T)$ value so long as $[d[M]/d[Cat]]_0$ has the same value.

Table II.  Summary of constants for the polymerization of allyl esters
by benzoly peroxide at 80°C.

| Monomer | $\left[\dfrac{d[M]}{d[\text{Cat}]}\right]_0$ | $\bar{P}$[d] | $\dfrac{k_D}{k_D+k_T}$ |
|---|---|---|---|
| Allyl acetate[c] | 30.2 | 12.3 | 0.764 |
| Allyl acetate[a] | 40.0 | 15.2 | 0.719 |
| Allyl acetate[b] | 32.2 | 13.7 | 0.796 |
| Allyl acetate | 34.4 | 13.8 | 0.754 |
| Allyl propionate[c] | 34.4 | 10.3 | 0.566 |
| Allyl ethyl carbonate[c] | 31.2 | 14.3 | 0.862 |
| Allyl trimethyl acetate[c] | 21.8 | 5.45 | 0.458 |

a. OCBPO was used instead of BPO
b. Data from Bartlett and Altschul, ref. 1.
c. Data from Gaylord and Eirich, ref. 2.
d. Calculated under neglection of endgroup

In the case of the polymerization of allyl acetate by OCBPO the values of $[RM_i]/([RM_i]+[M_i])$ are already shown in Table I and the mean is 0.60. According to equation (30) $[RM_i]/([RM_i]+[M_i])$ should be equal to $k_D/(k_D+k_T)$. Agreement of the analytical value 0.60 and the kinetic one 0.754 is not excellent but may be regarded as satisfactory when we consider simplification by the theoretical treatment.

Further experiments were carried out with allyl laurate, allyl benzoate, allyl chloroacetate, allyl chloride and allyl ether to compare the values of $k_D/(k_D+k_T)$ and $[RM_i]/([RM_i]+[M_i])$. The results are summarized in Table III.

It can be seen from Table III that $[RM_i]/([RM_i]+[M_i])$ and $k_D/(k_D+k_T)$ have, in agreement with the theory, nearly the same value. The order of the rate of

Table III.  Summary of constants for the polymerization of several allyl
compounds at 80°C.

| Monomer | Catalyst | $\left[\dfrac{d[M]}{d[\text{Cat}]}\right]_0$ | $\bar{P}$ | $\dfrac{[RM_i]}{[RM_i]+[M_i]}$ | $\dfrac{k_D}{k_D+k_T}$ |
|---|---|---|---|---|---|
| Allyl laurate | OCBPO | 56 | 7.1 | 0.206 | 0.245 |
| Allyl benzoate | ,, | 103 | 9.3 | 0.210 | 0.177 |
| Allyl chloroacetae | BPO | 108 | 8.0 | 0.082 | 0.145 |
| Allyl chloride | ,, | 46.5 | 8.6[a] | 0.270 | 0.355 |
| Allyl ethyl ether | OCBPO | 6.3 | 4.04[a] | 0.700 | 0.971 |

a. By the calculation the influence of end-group on the molec. wt. was
taken into account.

degradative transfer of allylesters of aliphatic acid is laurate $<$ propionate $<$ acetate. Degradative chain transfer is the most remarkable by allyl ethyl ether while effective chain transfer predominates by aromatic (benzoate) and halogen containing compounds such as chloroacetate and chloride.

## Experimental

*Materials*—All allyl compounds except allyl chloride and peroxides were prepared in this laboratory. The details will be reported elswhere.

*Experimental Procedure*—Polymerizations were carried out in sealed tubes in the presence of about 1 volume of air to 10 volumes of monomer. The tubes were immersed in the thermostatt for a measured length of time. For each point one tube was opened, the entire sample was withdrawn and subjected to vacuum distillation at room temperature. Almost all monomer residues and volatile materials were distilled off in two to three minutes. Then it was dried at 100°C to constant weight. The initial weight of the peroxide was subtracted from the weight of the dried distillation residue and this was regarded to be the ammount of polymer.

*Purification of Polymer for determination of molecular weight and end-groups*—Raw polymer isolated as above was dissolved in benzene, extracted with aqueous potassium carbonate, dried and isolated as described by Bartlett and Altschul.

*Molecular weight determinations*—All molecular weights were determined cryoscopically using benzene as a solvent.

*Determination of catalyst fragment*—When OCBPO was used as a catalyst combined chlorine was determined.

In the case of BPO catalyst, the purified polymer was dissolved in methanol, saponified with methanolic KOH, acidified with sulfuric acid and finally benzoic acid was extracted with ether. The method for the determination of benzoic acid is similar to that applied by Bartllet and Altschul for the determination of attached chlorobenzoate radical. It may be that a small part of the catalyst is attached to the polymer molecule as phenyl groups. The latter was neglected in this work. The reason that by the polymerization of allyl chloroacetate and allyl chloride $[RM_i]/([RM_i]+[M_i])$ is smaller than $k_D/(k_D+k_T)$ might be attributed to this neglection.

## References

1) P. D. Bartlett and R. Altschul: J. Amer. Chem. Soc., **67**, 816 (1945).
2) N. G. Gaylord and F. R. Eirich: J. Amer. Chem. Soc., **74**, 334 (1952).