

# Homopolymerization of *N*-Allylacetamide and *N*-Allylstearamide\*

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## Synopsis

When benzoyl peroxide was decomposed at 90°C. in *N*-allylacetamide and in *N*-allylstearamide,  $d[M]/d[P]$  was about 2 and  $\overline{DP}$  was between 9 and 10, because of a wastage of benzoyloxy radicals. These radicals formed benzoic acid and benzene as a consequence of hydrogen abstraction from the amide, and the resulting amide radicals became substituted with ester and phenyl groups from the initiator. *N*-butylstearamide, a saturated model for *N*-allylstearamide, gave corresponding products. Rates of peroxide decomposition indicated strong induced effects, decreasing in the order: *N*-allylacetamide, *N*-allylstearamide, *N*-butylstearamide. Slopes of the linear plots of the four products (in moles per kilogram) against initiator (in equivalents per kilogram) in the three amides in the above order were: benzoic 0.521, 0.570, 0.575; benzene 0.027, 0.086, 0.168; amide substituted by benzoate 0.459, 0.320, 0.106; amide substituted by phenyl 0.087, 0.087, 0.142. Transfer, compared to substitution, increased with chain length and decrease in unsaturation, and induced peroxide decomposition was correspondingly lowered. Thus, kinetic chain decreased with acyl chain length and decrease in unsaturation. A mechanism that postulates polar species in the transition state when amides were solvents accounted for both transfer and aromatic substitution and helped explain the difference in behavior of *N*-allylamides and allyl esters. Plots of amide entering polymer (in moles per kilogram) against initiator concentration (in equivalents per kilogram) were curves; plots of  $\log(a - x)$  for amide disappearance against the same coordinate were linear. Slopes were: *N*-allylacetamide  $-0.0742$ ; *N*-allylstearamide  $-0.1771$ .

Although the homopolymerization of allyl esters has been extensively studied,<sup>1</sup> few publications have described that of *N*-allylamides. The information available<sup>2</sup> suggested that *N*-allylamides were unpolymerizable, although polymers of unspecified conversion have been prepared from methallylamides.<sup>2,3</sup> Diallyl cyanamide<sup>4,5</sup> and certain allyl phosphonamides<sup>6</sup> failed to homopolymerize, suggesting that a nitrogen atom, existing in certain relationships to allylic functionality, might be rate-retarding. The possibility also existed that *N*-allylamides might resemble the difficultly polymerizable allyl bromide<sup>7</sup> and allyl alcohol,<sup>7-10</sup> the latter found to polymerize only when very large amounts of initiator were used.<sup>8-10</sup> However,

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even the most difficultly polymerizable allylic monomers,<sup>1,4,11-23</sup> including *N*-allylamides,<sup>24-26</sup> have been copolymerized readily with many vinyl monomers. This suggested that *N*-allylamides could also be homopolymerized if proper initiator concentrations were used.

A large consumption of initiator is one of the characteristics of the polymerization of allyl monomers.<sup>1,7,27-36</sup> In accordance with the mechanism of degradative chain transfer, the ratio of the rate of propagation to the rate of allylic hydrogen transfer is low (14-25 for allyl acetate<sup>27,32</sup>), and this effects a corresponding reduction in  $d[M]/d[P]$  (14-50 for allyl acetate<sup>27,32</sup>) compared with normal vinyl polymerization. Preliminary experiments showed that the polymerization behavior of *N*-allylamides differed from that of most allyl esters in one important respect. Massive amounts of benzoyl peroxide had to be used to effect appreciable polymerization ( $d[M]/d[P]$  ca. 2), even though the molecular weights of the polymers were similar to those found for many allyl esters ( $\overline{DP}$  ca.  $10^{31}$ ), which suggested that chain termination was still degradative. It could therefore be concluded that a considerable wastage of benzoyloxy radicals must have occurred to form low molecular weight reaction products.

This investigation was undertaken primarily to determine the path of attack on *N*-allylamides by the radicals formed as a result of the thermal fission of the peroxide. *N*-Allylacetamide and *N*-allylstearamide were selected as homolog extremes, and the saturated *N*-butylstearamide was chosen as an approximate model for the long-chain *N*-allylamide. Benzoyl peroxide, the initiator most extensively investigated in allyl ester polymerization, was used in this study. Since long-chain amides melt at about 85°C., the polymerizations were carried out at 90°C. Emphasis was placed on the quantitative determination of the products of peroxide decomposition, while kinetic studies were used to support the analytical evidence obtained. The results obtained for *N*-allylamides were compared with those reported for allyl acetate and other allyl esters, and a mechanism was proposed rationalizing the differences observed.

## PROCEDURE

Benzoyl peroxide was decomposed in small portions in the amide, maintained in a closed system at 90°C. under nitrogen for at least two lifetimes of the peroxide; the volatiles were trapped and the other reaction products determined by chemical means. The volatiles consisted of benzene (obtained uncontaminated in a cold trap and identified by infrared spectrum) and carbon dioxide, determined gravimetrically on ascarite. The balance of the reaction mixture consisted of essentially five products: (1) benzoic acid, determined by acid number and, after semiquantitative isolation, identified by a mixed melting point; (2) a benzoate ester of the amide, determined by ester number and identified in the infrared; (3) a nonpolymeric phenyl derivative of the amide; (4) polymer, determined by decrease in total unsaturation; and (5) unreacted amide. The amount of the phenyl derivative was determined indirectly as the difference between benzene and

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carbon dioxide found, since both phenyl substitution and benzene formation are accompanied by the evolution of a mole of carbon dioxide from a benzoyloxy radical. Volatile, nonacidic, purely aromatic compounds, such as phenyl benzoate and diphenyl, usually found when benzoyl peroxide is decomposed in solvents,<sup>35,37</sup> were not found in any of the reaction products by gas-liquid chromatography. Thus, all aryl substitution was considered to be on the amide substrate. The foregoing analyses were independently verified by column chromatography of selected crude reaction products of two of the amides studied, *N*-allylstearamide and *N*-butylstearamide. By this means isolation of the pure phenyl and aryl substitution products was sought and fractionation of poly-*N*-allylstearamide attempted. Kinetic studies were used to indicate the relative rate enhancement, caused by any induced decomposition reaction, over normal rates of benzoyl peroxide decomposition in "slow" solvents.<sup>37</sup>

## RESULTS AND DISCUSSION

### Composition, Kinetics, and Reaction Path

The crude reaction product compositions of the three amides studied are listed in Table I, and the overall results are plotted in Figures 1-3. The most striking feature of these results is the unusually large proportion of benzoic acid and of nonpolymeric substitution products relative to polymer formed.  $\overline{DP}$  values of about 10 for the polymer, together with the extremely low  $d[M]/d[P]$  ratio of about 2, indicate that much of the peroxide must have formed nonpolymeric substitution products. The proportion of products varied with the amide "solvent" employed. For any given amide, formation of each nonpolymeric compound was a linear function of the benzoyl peroxide concentration. Polymer formation decreased with in-

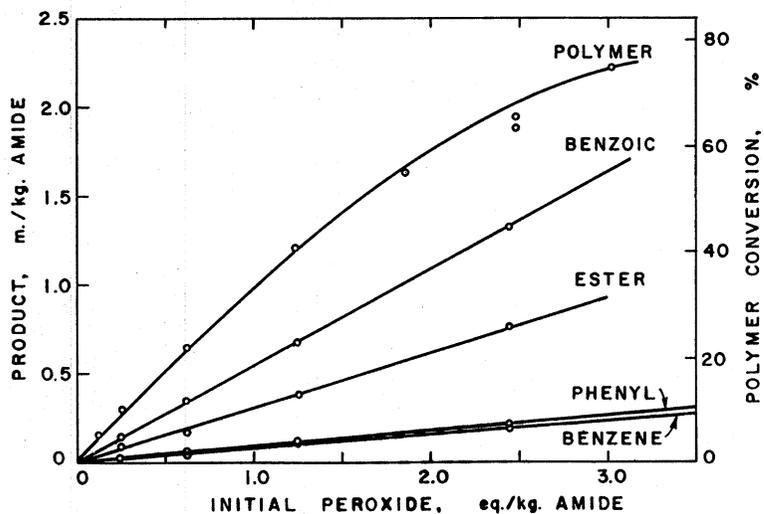


Fig. 1. Decomposition of benzoyl peroxide in *N*-allylstearamide at 90°C.

TABLE I  
Products of the Decomposition of Benzoyl Peroxide in *N*-Allylamides and in *N*-Butylstearamide at 90°C.

Product	Product concentration, moles/kg. amide, at various initial peroxide concentrations <sup>a,b</sup>								
	<i>N</i> -Allylstearamide		<i>N</i> -Allylacetaimide		<i>N</i> -Butylstearamide				
	0.247	0.617	1.249	2.438	1.983	4.122	6.035	1.168	2.344
	equiv./kg.	equiv./kg.	equiv./kg.	equiv./kg.	equiv./kg.	equiv./kg.	equiv./kg.	equiv./kg.	equiv./kg.
Benzoic acid	0.140	0.348	0.683	1.333	1.082	2.202	3.192	0.699	1.375
Benzene	0.020	0.050	0.108	0.207	0.050	0.102	0.160	0.243	0.440
Benzoate-substituted amide	0.077	0.173	0.388	0.769	0.804	1.653	2.669	0.098	0.222
Phenyl-substituted amide	0.024	0.054	0.109	0.214	0.156	0.378	0.508	0.116	0.284
Total	0.261	0.625	1.289	2.523	2.091	4.335	6.528	1.156	2.321
Amide entering polymer <sup>c</sup>	0.300	0.674	1.035	1.881	2.766	4.781	6.428	—	—
$d[M]/d[P]$	2.43	2.18	1.66	1.54	2.79	2.32	2.13	—	—
DP			10.17	9.05	9.12	9.66	7.86	—	—

<sup>a</sup> Initial benzoyl peroxide concentration equalled one half these concentrations.

<sup>b</sup> Approximate mole-% peroxide concentrations, based on amide, corresponding to the values in the table are: *N*-Allylstearamide; 4, 10, 20, 40; *N*-allylacetaimide, 10, 20, 30; *N*-butylstearamide, 20, 40.

<sup>c</sup> Based on total reduction in unsaturation. Other values, experimentally determined for *N*-allylstearamide and reported in Figs. 1 and 4 and not listed above are for initial peroxide and amide in polymer respectively: 0.1236 equiv./kg., 0.1613 mole/kg., 0.6180 equiv./kg., 0.6447 mole/kg., 1.2360 equiv./kg., 1.2017 mole/kg.; 1.8538 equiv./kg., 1.6260 mole/kg., 2.4718 equiv./kg., 1.9484 mole/kg.; 3.0920 equiv./kg., 2.2367 mole/kg.

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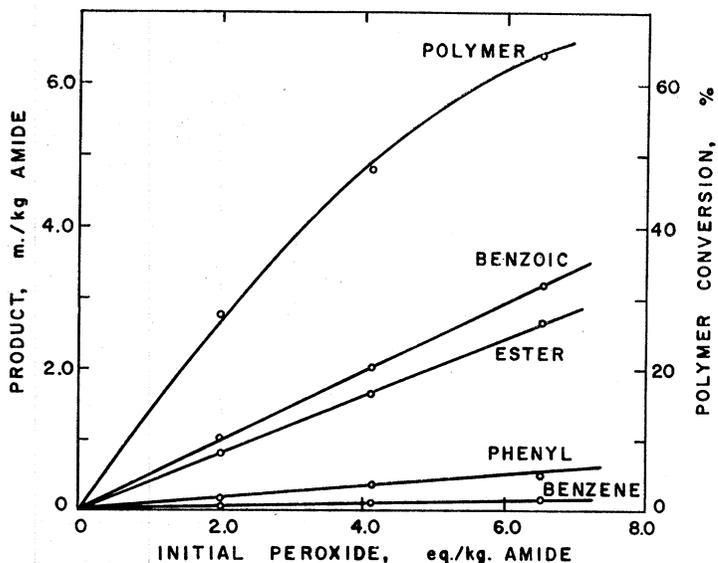


Fig. 2. Decomposition of benzoyl peroxide in *N*-allylacetamide at 90°C.

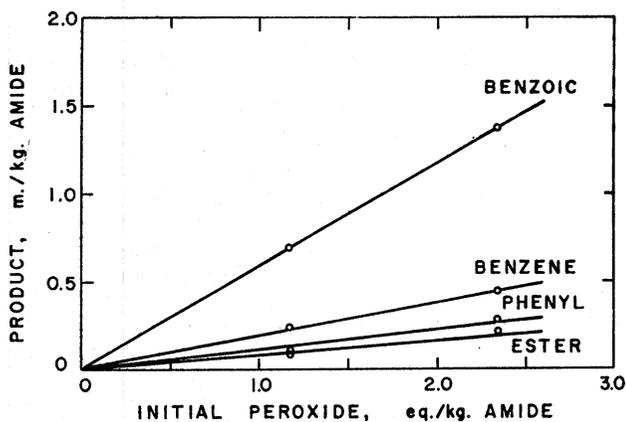


Fig. 3. Decomposition of benzoyl peroxide in *N*-butylstearamide at 90°C.

crease in initiator concentration in the polymerizable amides. However,  $\log(a - x)$  for both *N*-allylamides depended linearly on initiator concentration, as seen in Figure 4 for *N*-allylstearamide. The slopes, calculated as log mole fraction amide surviving versus initiator concentration (in equivalents/kilogram) were: *N*-allylstearamide  $-0.1771$ ; *N*-allylacetamide  $-0.0742$ .

First-order benzoyl peroxide decomposition rates in the three amides at 90°C. are listed in Table II. The values shown may be subject to some uncertainty, since solution rates approached reaction rates in the *N*-allylamides. The rate data could be obtained only after considerable peroxide had already been destroyed, so that extrapolation of the relationship to

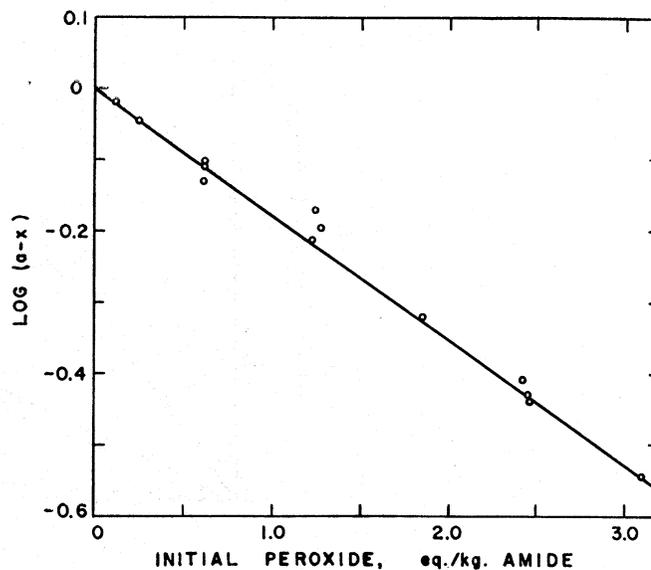
Fig. 4. Polymerization of *N*-allylstearamide at 90°C.

TABLE II  
Rates of Decomposition of Benzoyl Peroxide  
in Certain Amides and Other Solvents at 90°C.

Solvent	Peroxide, mole/kg.	$k_1 \times 10^2$ , min. <sup>-1</sup>
<i>N</i> -Allylacetamide	1.0101	Immeasurably fast <sup>a</sup>
<i>N</i> -Allylstearamide	0.6491	9.07 ± 0.023
<i>N</i> -Butylstearamide	0.6182	3.24 ± 0.002
Allyl acetate	0.413	0.78 <sup>b</sup>
Benzene	0.5861	0.776 <sup>b</sup>

<sup>a</sup> At 70°C.

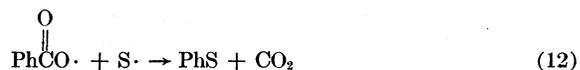
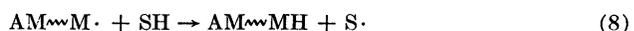
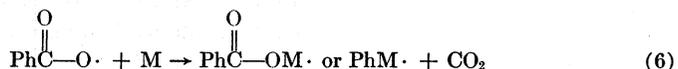
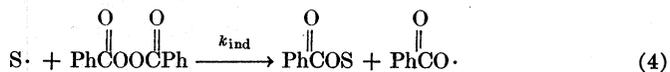
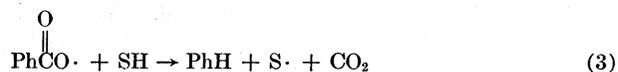
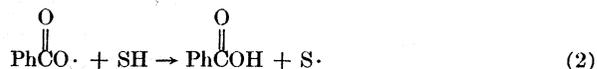
<sup>b</sup> Estimated as  $2 \times k_{80}^\circ$  from data of Bartlett and Altschul<sup>27</sup> and Barnett and Vaughan.<sup>46</sup>

initial amide concentration might be subject to error. In addition, precision was adversely affected by the high frequency of sampling required. However, since relative reaction rates are probably adequately expressed by these rate constants, investigation of decomposition kinetics at different concentrations and temperatures was considered unnecessary. Because of the experimental difficulties, amide monomer disappearance was not determined as a function of time,<sup>1,27-33</sup> and only overall  $d[M]/d[P]$  values were reported in Table I.

In Table II, the 90°C. rate constants for allyl acetate and benzene are estimated as  $0.78 \times 10^{-2}$  min.<sup>-1</sup> from literature values determined at 80°C. at concentrations in the range of the present investigation.<sup>27</sup> At 90°C. a concentration-dependent increase in induced decomposition

of benzoyl peroxide in allyl acetate has been noted by Litt and Eirich.<sup>32</sup> By extrapolation of these data a value of  $3.5 \times 10^{-2} \text{ min.}^{-1}$  may be estimated for an initial peroxide concentration of 0.6 mole/kg., similar to that used in this study. However, the absolute value, independent of induced effects, was found by these authors to be  $0.62 \times 10^{-2} \text{ min.}^{-1}$ . Thus the overall results illustrate the marked effect of induced decomposition on rate in the three amides. The same reaction order and similar rates were found when benzoyl peroxide was decomposed in dimethylformamide,<sup>38</sup> *n*-butyl ether,<sup>39</sup> and *n*-butyl alcohol,<sup>39</sup> solvent classes which exert abnormally high induced effects on benzoyl peroxide and give rise to similar reaction products.

These results are in harmony with the reaction eqs. (1)–(13).



where SH is amide functioning as solvent; S·, the solvent radical; M, *N*-allylamide functioning as monomer; M·, the vinyl radical; and A, aromatic end group.

Reactions (2) and (3), involving transfer of a hydrogen atom from the amide solvent to form either benzene or benzoic acid, may be classified as transfer reactions. Reactions (4), (5), (11), and (12) are aromatic-substitu-

tion reactions, forming the corresponding ester or phenyl substitution product, depending on whether or not carbon dioxide is expelled. Reaction (13) is the dimer-forming reaction, while reactions (6)–(10) produce polymer. Of special interest are the reactions of induced decomposition, eqs. (4), (5), (9), and (10). Also pertinent is the fact that dimer and substitution products are monomers capable of entering reaction (7).

### Relative Proportion of Products Formed

In Table III slopes of the lines formed in Figures 1, 2, and 3 compare the relative proportions of the individual transfer and substitution reactions. Ratios of transfer ( $T$ ) and substitution ( $S$ ), together with ratios of ester formation ( $E$ ) to phenyl substitution ( $P$ ) are also compared. The relationship  $T - S = D$  represents the slope for excess amide radical ( $S\cdot$ ) which terminated, presumably, as dimer [reaction (13)] but does not include dimer formed as a consequence of reaction (8). Total transfer relative to total substitution ( $T/S$ ) increased in the order  $N$ -allylacetamide  $< N$ -allylstearamide  $< N$ -butylstearamide,<sup>40</sup> the reverse of the order of induced decomposition of peroxide (Table II), as would be expected. The lower the  $T/S$  ratio the longer was the kinetic chain and the larger the observed rate constant. As can be seen from the equations, the kinetic chain includes polymer formation in the case of the two polymerizable amides.

The  $N$ -butylstearamide radical was apparently terminated to a large extent by dimerization, or by other means discussed later. Evidence for this is seen (Table III) in its high  $D/S$  ratio, compared to the two polymerizable amides. Analytically about one third of the benzoyloxy radicals formed substitution products in this solvent. Aryl substitution receives additional support from the magnitude of the corresponding peroxide decomposition rate (Table II).

TABLE III  
Slopes and Ratio of Slopes for the Products of Decomposition of Benzoyl Peroxide in  $N$ -Allyl- and  $N$ -Butylamides at 90°C.

Product formed	Formed by equation number	Ratio of slopes <sup>a</sup>	Slope $m^b$		
			$N$ -Allyl-acetamide	$N$ -Allyl-stearamide	$N$ -Butyl-stearamide
Benzoic acid	(2)	—	0.521	0.570	0.575
Benzene	(3)	—	0.027	0.086	0.168
Amide substituted by benzoate	(4) + (11)	—	0.459	0.320	0.106
Amide substituted by phenyl	(5) + (12)	—	0.087	0.087	0.142
		$T/S$	1.00	1.61	2.99
		$D/S$	0.0003	0.614	1.99
		$E/P$	5.26	3.67	0.745

<sup>a</sup>  $m_{\text{benzoic acid}} + m_{\text{benzene}} = T$ ;  $m_{\text{ester formation}} = E$ ;  $m_{\text{phenyl substitution}} = P$ ;  $E + P = S$ ;  $T - S = D$ , slope for formation of amide radicals that either terminated by dimerization or entered chains by effective chain transfer.

<sup>b</sup>  $m = [\text{Product}]/[\text{Peroxide equivalents}]$ , calculated by least squares method.

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Two additional points emerge from the data of Table III. In *N*-allylacetamide, the equal occurrence of transfer and substitution limits termination to the union of a solvent radical and a benzoyloxy or phenyl radical. This suggests that first-order kinetics apply to peroxide decomposition in this amide as well as in the other two (see Table II). When union of a solvent radical and an initiator radical is the only mode of termination, unimolecular kinetics are always observed.<sup>37,38</sup> The second point of interest is the decline in the ratio of ester to phenyl substitution (*E/P*) in going from *N*-allylacetamide to *N*-butylstearamide (Table III), which parallels the decline in the magnitude of the respective rate constants (Table II). Apparently, decrease in the induced reactions favored longer-lived benzoyloxy radicals, and thus promoted carbon dioxide evolution.<sup>37</sup>

### Comparison with Allyl Acetate Polymerization

The ratio of consumption of allylamide in forming polymer to the total amount consumed in forming nonpolymeric aromatic substitution products decreased from 4.2 to 2.4 for *N*-allylstearamide and from 3.5 to 2.5 for *N*-allylacetamide with increase in peroxide concentration. (The calculation assumes one aromatic endgroup). These values compare with a ratio of >100 found when benzoyl peroxide was decomposed in allyl acetate.<sup>27</sup> In view of the predominance of hydrogen transfer found, the *N*-allylamides were either more labile than allyl esters toward abstraction of allylic hydrogen or significantly less reactive as monomers toward addition of initiator radicals. The latter situation seemed very unlikely, because *Q* and *e* values of *N*-allylamides<sup>26</sup> were similar to those of allyl acetate. With *N*-allylamides, transition-state stabilization through resonance, by the formation of polar structures such as I and II



first proposed by Bamford for the decomposition of benzoyl peroxide in dimethylformamide<sup>38</sup>, would provide a mechanism accounting for both transfer and aromatic substitution. Greater electron release by nitrogen than by oxygen should make such polar contributions more important in amides than in esters. Polymerization, then, would be the consequence of a competition for initiator radicals between addition and aromatic substitution. Polymer chain termination via attack on the peroxide by the very active vinyl radicals<sup>41</sup> [reactions(9) and (10)] would continue the kinetic chain and account partly for the greater induced decomposition found in *N*-allylstearamide than in *N*-butylstearamide.

If reactions (9) and (10) had predominated, there should have been two aromatic endgroups per polymer chain. To check this point, the polymer benzoate ester groups were determined. The results are listed in Table IV together with two sets of calculated values. Both calculations assume the

same  $E/P$  ratio for the polymer as was found for the whole system (Table III). Calculation I assumes that esterified monomer was not copolymerized, while calculation II assumes that it was copolymerized to the extent available. Since there was opportunity for other reactions, these calculated values are only approximate. Although the results are not conclusive, they do support a polymer chain termination via reactions (9) and (10), which would account for the higher induced decomposition found in *N*-allylamides than in *N*-butylstearamide.

TABLE IV  
Mole Ratio of Ester to Polymer<sup>a</sup>

Polyamide	Ester/polymer at various initial benzoyl peroxide concentrations <sup>b</sup>			
	10 mole-%	20 mole-%	30 mole-%	40 mole-%
<i>N</i> -Allylacetamide				
Found	2.21	2.40	1.60	—
Calculation I	1.68	1.63	1.68	—
Calculation II	2.01	2.49	3.26	—
<i>N</i> -Allylstearamide				
Found	—	1.35	—	1.53
Calculation I	—	1.56	—	1.57
Calculation II	—	2.21	—	3.10

<sup>a</sup> Calculated values based on  $\overline{DP} = 10$ .

<sup>b</sup> Based on weight of amide.

### Results of Column Chromatography

Selected crude reaction products, obtained when benzoyl peroxide was decomposed in both *N*-butylstearamide and in *N*-allylstearamide, were chromatographed on a Florisil column, and fraction purity was monitored by thin-layer chromatography. Results for *N*-allylstearamide are listed in Table V and compared with results calculated from the data of Table I. Agreement is fairly good in view of the uncertainties involved in the calcu-

TABLE V  
Comparison of Composition Results by Column  
Chromatography and by Calculation from the Data in Table I

Fate of initial amide after radical attack	Initial benzoyl peroxide, equiv./kg. amide	Composition, mole-%	
		By column chromatography	Calculated from data of Table I
In polymer <sup>a</sup>	1.249	36.14	44.58 <sup>b</sup>
"  "	2.438	60.10	70.36 <sup>b</sup>
As aromatic-substituted monomer	1.249	12.04	9.60
"  "	2.438	18.23	10.56
As unreacted amide	1.249	52.26	45.80
"  "  "	2.438	21.77	19.08

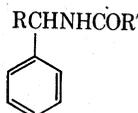
<sup>a</sup> Includes aromatic-substituted polymer.

<sup>b</sup> Includes all dimer amide.

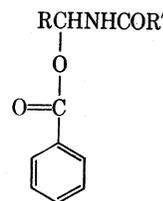
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lations, which assume proportional copolymerization of the nonpolymeric aromatic substitution products and that all of the dimerized amide entered the polymer fraction. The latter assumption was made because no dimer was separated from the polymer fraction by chromatography.

Chromatography separated the reaction mixture into three main fractions, two of which, the unreacted amide and the polymer fraction, were obtained in a pure form. The middle fraction was a mixture of essentially two nonpolymeric compounds, which, on the basis of infrared spectra, were assigned the structures III and IV where R is either *n*-propyl or vinyl.



III



IV

These were the phenyl and ester derivatives formed as a result of reactions (4), (5), (11), and (12), and reported in Table I. No substitution on nitrogen was observed. From *N*-butylstearamide, III was obtained in almost pure form, as judged by thin-layer chromatography, m.p. 106–107°C.; from *N*-allylstearamide, IV was obtained in 90% purity as indicated by thin-layer chromatography and infrared examination of a single small fraction. Compound IV is similar to the ester formed when benzoyl peroxide was decomposed in dimethylformamide.<sup>38</sup>

The fractionation of poly-*N*-allylstearamide on Florisil is reported in Table VI. No dimer was found in spite of the prediction of the *D/S* ratio in Table III. Either the column was unable to separate dimer from higher molecular weight species, or hydrogen abstraction from the acyl portion

TABLE VI  
Molecular Weight Distribution of Poly-*N*-allylstearamide

Fraction number	Initial benzoyl peroxide = 1.249 equiv./kg. amide			Initial benzoyl peroxide = 2.438 equiv./kg. amide		
	$w_i$	$\bar{M}_n$	Ester number	$w_i$	$\bar{M}_n$	Ester number
1	0.43	2703	29.2	0.10	1647	39.4
2	0.13	3340	25.0	0.22	2182	31.4
3	0.10	3076	19.1	0.29	3000	23.0
4	0.10	3455		0.15	3691	21.0
5	0.14	4093	15.0	0.14	4771	18.2
6	0.07	4523		0.05	4425	—
7	0.33	2561	—	—	—	—
Whole polymer	—	3292 <sup>a</sup>	23.5 <sup>b</sup>	—	2927 <sup>a</sup>	29.4 <sup>b</sup>

$$^a \sum w_i \bar{M}_n.$$

$$^b \sum w_i (\text{ester no.}).$$

had generated radicals that were consumed in initiating polymers via effective chain transfer.<sup>31</sup>

Column chromatography of *N*-butylstearamide yielded about one third of the amount of products predicted by Table I, even though the unreacted amide fraction was separated in a pure state, as shown by thin-layer chromatography and melting point. Again, no dimer was isolated in a pure form, in spite of the large amount that was predicted by the results in Table III. In addition to the aromatic substitution products already discussed, about 35–45% of the reacted amide was polymer of unknown composition; the molecular weights, which were between 900 and 3000, increased with the peroxide content of the system. Even when the proportion of reacted amide was corrected for two transfers per amide unit, as required for polymer, only 50% of the predicted reacted amide was accounted for. It may be that a considerable portion of the polymer found was formed by radical attack on aromatic residues as has been observed in certain unreactive solvents.<sup>42</sup> However, infrared spectra of the polymer showed amide peaks.

## EXPERIMENTAL

### Preparation of Amides

*N*-Allylacetamide, *N*-allylstearamide, and *N*-butylstearamide were prepared by ester aminolysis at 30°C.,<sup>43</sup> and the long-chain amides were purified by the reference procedure. The preparation of *N*-allylacetamide was modified by the use of a ratio of amine to ester of 1.1/1 and a 24-hr. reaction time. After two precipitations in benzene (4 ml./ml. reaction product) to remove unused catalyst, and evaporation of the aromatic solvent from each filtrate, the crude *N*-allylacetamide was distilled (b.p. 104–104.5°C./10 mm.) to give the amide in 76% yield. The three amides were 99% pure by elementary analysis and by gas-liquid chromatography.

### Benzoyl Peroxide

Benzoyl peroxide was Eastman Kodak White Label and was 99% pure by peroxide determination.<sup>44</sup> The peroxide value was checked frequently during this investigation.

### Reaction Procedure

Weights of amide were taken in the range of 10–100 g. so that the initial weight of benzoyl peroxide did not fall below 2.9 g. nor exceed 6.0 g. in any experiment involving the long-chain amides. When *N*-allylacetamide was used, the peroxide weight range was between 4.8 and 7.3 g. for an amide weight range of 10–20 g. To the amide, in a flask containing a gas inlet, placed in a thermostatted bath at  $90 \pm 0.1^\circ\text{C}$ ., the benzoyl peroxide was added in small increments (0.2–0.4 g.), over a period of 30–90 min., by means of a small tube connected by rubber tubing to a neck of the reaction flask. The small tube was removed to receive the next increment, without opening the system to the outside, by clamping off the rubber tubing before

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disconnecting. Gaseous reaction products were carried by Ascarite-treated nitrogen through a small Vigreux column, over solid anhydrous calcium sulfate, to an analytically tared Dry-Ice trap and then through two Ascarite tubes connected in series. Reaction was always continued for 3 hrs. after the addition of the last increment of initiator. The application of moderate vacuum for 1 hr. at 90°C. was necessary in those *N*-allylstearamide experiments in which 4 and 10 mole-% of initial benzoyl peroxide were used, in order to remove all of the benzene from the crude reaction mixture; vacuum applied in the other experiments removed no additional benzene. From the results of acid number, saponification number (0.2*N* alcoholic KOH, 1 hr. reflux), Wijs iodine number, and a peroxide number (the last was always zero), the data in Table I were calculated. The saponification did not hydrolyze any of the amides used; the blank titration was obtained when each of the amides was treated alone.

### Kinetic Procedure

The peroxide was added and dissolved as described in the preceding section except that the addition was done as quickly as possible. Addition and solution times were 30 min. for *N*-butylstearamide, 15 min. for *N*-allylstearamide, and 14 min. for *N*-allylacetamide, the last at 70°C. It was qualitatively observed that the accumulation of aromatic products shortened solution time. Initial samples were removed after 5 min. from *N*-butylstearamide, after 1 min. from *N*-allylstearamide (by quickly immersing and withdrawing short pieces of glass tubing, which were tared with the analytical flask), and after 15 sec. from *N*-allylacetamide (by use of a pipet). Because solution rates approached reaction rates, the first sample withdrawn showed that peroxide was destroyed in the three amides to the following extents: 36.8% in *N*-butylstearamide, 86.7% in *N*-allylstearamide, and 100% in *N*-allylacetamide. The balance of each decomposition followed good first-order kinetics. Benzoyl peroxide was only slightly soluble in *N*-allylacetamide at 60°C., so that a lower-temperature kinetic study was not practical.

### Benzoic Acid

The reaction mixtures used to obtain the data in columns 3, 4, 8, and 9 of Table I were dissolved in benzene (10–20 ml./g.) washed with three equal volumes of 10% sodium carbonate solution at 30–40°C., washed free of alkali, washed once with 10% HCl solution, and freed of acid. The aqueous layers were extracted twice with ethyl ether (equal volumes) and the ether evaporated. Mixed melting points showed that the residue was pure benzoic acid, and recovery was 86–96% of that calculated from acid number.

### Column Chromatography

The crude reaction mixture, after benzoic acid removal, was chromatographed from benzene solution on a Florisil column. Unreacted amide was eluted with pure benzene and 10% chloroform, the aromatic fraction

with 20–50% chloroform; the polymer was fractionated (Table VI) with 2–20% ethanol. The polymer found when *N*-butylstearamide was the reaction solvent required 5% acetic acid (followed by Florisil removal) for complete elution. Overall recovery was 93–96%. Thin-layer chromatography of selected fractions from column chromatography was used to monitor the column separations. Thin-layer results and melting points showed that the unreacted amide was very pure.

The aromatic fractions were shown by thin-layer chromatography to be a complex mixture in which two compounds, one high melting and one low melting, predominated. The low melting compound (isolated from one fraction of *N*-allylstearamide in 90% purity) had distinct infrared absorption peaks (carbon tetrachloride) at 1275 and 1117  $\text{cm}^{-1}$ , characteristic of benzoate C—O stretching modes and at 1720  $\text{cm}^{-1}$ , reflecting C=O stretching. The high melting compounds (melting range, 100–110°C.) showed distinct phenyl adsorptions at 1640–1650  $\text{cm}^{-1}$ , ascribed to phenyl shifted to higher wave number from the normal 1600  $\text{cm}^{-1}$  region by proximity to the —CONH— grouping. The typical secondary amide NH stretching adsorptions at 3460–3500  $\text{cm}^{-1}$ , present in the pure amides, were retained and the maxima intensified in all of the products obtained, including the polymer, although the peak was shifted to as low as 3300  $\text{cm}^{-1}$  in some of the polymer fractions. The amide II bands at 1500  $\text{cm}^{-1}$ , present in the pure amides, were generally broadened and shortened with increase in aromatic substitution. Since this was especially pronounced with the phenyl substitution product, in which interaction with the amide group is possible, the allylic carbon was considered the site of the major amount of aromatic substitution, although substitution at acyl carbon atoms may have contributed to the complexity of products. Qualitative agreement was obtained between the intensity of infrared maxima and the amounts of products shown by thin-layer chromatography.

### Amide Polymers

Poly-*N*-allylstearamide was obtained from column chromatography as described above; poly-*N*-allylacetamide was isolated from the crude reaction mixtures as the residue from repeated aqueous extractions at room temperature. All molecular weights were found by a thermistor method.<sup>45</sup> The molecular weights of poly-*N*-allylstearamide samples were determined in carbon tetrachloride, in which the correct value was found for the monomer. Those of poly-*N*-allylacetamide were measured in chloroform, since this polymer was insoluble in carbon tetrachloride; a single sample checked in methyl ethyl ketone gave the same result. Micro acid and saponification determinations were made on the polymer and reported in Table VI as ester numbers. Unsaturation (Wijs iodine number) was low in poly-*N*-allylacetamide (ca. 0.5 double bond per chain) but higher in poly-*N*-allylstearamide (ca. 2 double bonds per chain), in which amide dimer could have copolymerized, because  $T/S > 1$ , (Table III). Poly-*N*-allylacetamide was a viscous semisolid at room temperature; poly-*N*-allylstearamide a soft wax melting at 70–80°C.

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### Résumé

Lorsque le peroxyde de benzoyle est décomposé à 90°C dans le *N*-allylacétamide et le *N*-allylstéaramide,  $d[M]/d[P]$  est environ égal à 2 et  $\overline{DP}$  se situe entre 9 et 10, à cause d'une perte en radicaux oxybenzoyles. Ces radicaux forment de l'acide benzoïque et du benzène par arrachement d'hydrogène de l'amide, et les radicaux amides qui en résultent deviennent substitués avec les groupes esters et phényles à partir de l'initiateur. Le *N*-butylstéaramide, modèle saturé du *N*-allylstéaramide, fournit les produits correspondants. Les vitesses de décomposition du peroxyde montrent d'importants effets d'induction, dans l'ordre décroissant: *N*-allylacétamide, *N*-allylstéaramide, *N*-butylstéaramide. Les pentes des droites dans le graphique des quatre produits (en moles par kilo) en fonction de l'initiateur (en équivalents par kilo) dans les trois amides dans l'ordre ci-dessus sont: benzoïque 0,521, 0,570, 0,575; benzène 0,027, 0,086, 0,168; amide substitué par le benzoate 0,459, 0,320, 0,106; amide substitué par le phényle 0,087, 0,087, 0,142. Le transfert, comparé à la substitution, augmente avec la longueur de la chaîne et une diminution d'insaturation, et la décomposition induite du peroxyde est abaissée d'une valeur correspondante. Donc, la chaîne cinétique diminue avec la longueur de la chaîne acyle et une diminution d'insaturation. Un mécanisme faisant appel à des espèces polaires dans l'état de transition lorsque les amides jouent le rôle de solvants tient compte du transfert et de la substitution aromatique et aide à expliquer la différence dans le comportement des *N*-allylamides et des esters allyliques. Le graphique représentant l'amide engagée dans le polymère (en moles par kilo) en fonction de la concentration en initiateur (en équivalents par kilo) sont des courbes. Les graphiques de  $\log(a - x)$  pour la disparition de l'amide en fonction de la même coordonnée sont linéaires. Les pentes sont: *N*-allylacétamide  $-0,0742$ ; *N*-allylstéaramide  $-0,1771$ .

### Zusammenfassung

Bei der Zersetzung von Benzoylperoxyd bei 90°C in *N*-Allylacetamid und *N*-Allylstearamid betrug wegen Nebenreaktionen der Benzoyloxyradikale  $d[M]/a[P]$  etwa 2 und  $\overline{DP}$  lag zwischen 9 und 10. Die Benzoyloxyradikale bildeten durch Wasserstoffabspaltung aus dem Amid Benzoesäure und Benzol, und die entstehenden Amidradikale erhielten Ester- und Phenylgruppen des Starters als Substituenten. *N*-Butylstearamid, ein gesättigtes Modell für *N*-Allylstearamid, lieferte analoge Produkte. Die Geschwindigkeit der Peroxydzersetzung liess starke induzierte Effekte erkennen, die in der Reihenfolge: *N*-Allylacetamid, *N*-Allylstearamid, *N*-Butylstearamid abnahmen. Die Neigung der linearen Abhängigkeit der vier Produkte (in Molen pro Kilogramm) vom Starter (in Äquivalenten pro Kilogramm) bei den drei Amididen in der angegebenen Reihenfolge betrug: Benzoesäure 0,521, 0,570, 0,575; Benzol 0,027, 0,086, 0,168; benzoatsubstituiertes Amid 0,459, 0,320, 0,106; phenylsubstituiertes Amid 0,087, 0,087, 0,142. Die Übertragung nahm im Vergleich zur Substitution mit der Kettenlänge und mit abnehmender Unsättigung zu. Ein Mechanismus mit polarem Übergangszustand bei Amidlösungsmitteln konnte Übertragung und aromatische Substitution erklären und liess auch den Unterschied im Verhalten von *N*-Allylamiden und Allylestern verstehen. Beim Auftragen des polymergebundenen Amids (in Molen pro Kilogramm) gegen die Starterkonzentration (in Äquivalenten pro Kilogramm) ergaben sich Kurven; das Diagramm von  $\log(a - x)$  für den Amidumsatz gegen die gleiche Grösse war linear. Die Neigungen betruge für *N*-Allylacetamid  $-0,0742$  und für *N*-Allylstearamid  $-0,1771$ .