TABLE I (*Concluded*)

R			$R' = OCOCH_3$ $R' = NHCOCH_3$				
Acetyl	Alcohol	Orange	Prisms	100[a] 85[b]	198–199	9.88	9.95
2-Pyridyl	Acetone	Yellow-orange	Prisms	100	203.5	12.17	12.00
2-Thiazolyl	Acet. + alc.	Red-orange	Cluster of heavy plates	100	207	12.01	12 14
2-Pyrimidyl	Acetone	Yellow-orange	Fine needles	100	195–196	15.18	15.46
Acetylguanyl	Acetone	Orange	Needles	67	205–206	14.99	15.14
Acetyl	Acet. + alc.	Orange	Prisms	64[c] 90[d]	213.5–214.5	13.21	13.34
2-Pyridyl	Acetone	Orange	Cluster of needles	91	149–150	15.25	15.28
2-Thiazolyl	Acet. + alc.	Orange-red	Clusters of needles	100	160–161[e]	15.05	15.12
2-Pyrimidyl	Acet. + alc.	Yellow-orange	Cluster of prisms	99	208–209[f]	18.26	18.36
Acetylguanyl	Alc. + petr. ether	Orange	Fine needles	87	246	18.02	18.14

[a] Acetylation of 4-(3'-methyl-4'-hydroxynaphthylazo)-benzenesulfonamide. [b] Acetylation of 4-(3'-methyl-4'-hydroxynaphthylazo)-N-acetylbenzenesulfonamide. [c] Acetylation of 4-(3'-methyl-4'-aminonaphthylazo)-benzenesulfonamide. [d] Acetylation of 4-(3'-methyl-4'-aminonaphthylazo)-N-acetylbenzenesulfonamide. [e] Two polymorphic forms m. p. 280° and m. p. 218° yielded the same acetyl derivative. [f] Two polymorphic forms m. p. 283° and m. p. 248–249° yielded the same acetyl derivative.

procedure of Lesser[5] with slight modification. The yield was about 80–90%.

2-Methyl-1-naphthylamine hydrochloride and 2-methyl-1-naphthol were, respectively, coupled with sulfanilamide. The hydrochloride of 4-(3'-methyl-4'-aminonaphthylazo)-benzenesulfonamide thus obtained was treated with a 10% sodium hydroxide solution to liberate the free amine. The analogs from albucid, sulfapyridine, sulfathiazole, sulfadiazine and sulfaguanidine were similarly prepared. The yields and properties of these compounds are listed in Table I.

Acetyl Derivatives of 4-(3'-Methyl-4'-aminonaphthylazo)-benzenesulfonamide, 4-(3'-Methyl-4'-hydroxynaphthylazo)-benzenesulfonamide and Analogs.—A sample of 0.001 g. mole of 4-(3'-methyl-4'-aminonaphthylazo)-benzenesulfonamide was refluxed with 1 cc. of acetic anhydride and about 3 drops of pyridine for an hour. It was poured into cold water and then filtered. The precipitate was recrystallized from a suitable solvent. This was identified as the diacetyl derivative by analysis and mix-melting point with the acetyl derivative obtained by acetylation of 4-(3'-methyl-4'-aminonaphthylazo)-N-acetylbenzenesulfonamide. 4-(3'-Methyl-4'-aminonaphthylazo)-sulfanilylguanidine also forms diacetyl derivative which occludes acetic acid tenaciously and has to be stirred with a 10% NaOH before recrystallization. Acetyl derivatives of 4-(3'-methyl-4'-hydroxynaphthylazo)-benzenesulfonamide and analogs were similarly prepared. 4-(3'-Methyl-4'-hydroxynaphthylazo)-benzenesulfonamide and 4-(3'-methyl-4'-hydroxynaphthylazo)-sulfanilylguanidine yielded diacetyl derivatives, respectively. The properties of these acetyl derivatives are listed in Table I.

Summary

4-(3'-Methyl-4'-aminonaphthylazo)-benzenesulfonamide, 4-(3'-methyl-4'-hydroxynaphthylazo)-benzenesulfonamide and their analogs derived from albucid, sulfapyridine, sulfathiazole, sulfadiazine and sulfaguanidine have been respectively synthesized. Also corresponding acetyl derivatives have been prepared.

A preliminary test has shown that 4-(3'-methyl-4'-hydroxynaphthylazo)-benzenesulfonamide possesses an antihemorrhagic activity almost equal to that of 2-methyl-1,4-naphthoquinone. An extensive study of antihemorrhagic activities of these compounds is in progress.

2-Methyl-1-naphthylamine has been prepared by refluxing 2-methyl-1-nitronaphthalene with Raney nickel only, in a yield of 96%.

AUSTIN, TEXAS RECEIVED FEBRUARY 10, 1945

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Polymerization of Allyl Compounds. I. Factors Governing the Acyl Peroxide-Induced Polymerization of Allyl Acetate, and the Fate of the Peroxide

BY PAUL D. BARTLETT AND ROLF ALTSCHUL[1]

If pure allyl acetate is heated at 80° with 6% of its weight of benzoyl peroxide, the slow decomposition of the peroxide induces polymerization of the ester. The peroxide is 90% decomposed after thirteen hours; only an undetectable amount remains after forty-eight hours, at which time about 50% of the original allyl acetate has polymerized. The soft, transparent polymer is obtained by distillation of the volatile monomer. It is soluble in a number of organic solvents and has an average molecular weight of about 1300, hence an average degree of polymerization of 13. This low degree of polymerization and high requirement of initiating peroxide makes allyl acetate a favorable material for studying the mechanism of polymerization, especially with regard to the fate of the peroxide.

Different samples of allyl acetate, prepared with care to remove free alcohol and acid and distilled in the absence of air, yielded reproducible results. The polymerizations described in this paper were followed by bromometric titration of

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weighed samples of the monomer–polymer mixture. At times we also made use of two other methods, the dilatometric and the gravimetric, for following the polymerizations. All three methods checked closely when applied to the same reaction. Table I shows the reproducibility of the polymerization using three samples of allyl acetate prepared at different times, and also adding to one of these samples substances which might occur as impurities from the preparation and treatment of the ester.

Oxygen is capable of retarding the polymerization of allyl acetate, but the effect of simple exposure to air is not great. In order to demonstrate it, a sample undergoing polymerization must be agitated vigorously with air or oxygen. A solution containing 6.10% of benzoyl peroxide in allyl acetate, sealed under nitrogen, was 20.5% polymerized after 2.5 hours at 80°; a similar solution, sealed in air and spun mechanically during polymerization, contained 8.3% polymer after the same length of time. Comparable tests showed that a series of evacuations and nitrogen flushings using a water-pump at 0° was as effective in eliminating air inhibition as the most careful series of freezings with liquid nitrogen and exhaustions with a diffusion pump; the effect of any of these precautions was about a 10% increase in rate over that observed in air without agitation (Table II).

TABLE I

REPRODUCIBILITY OF POLYMERIZATION OF ALLYL ACETATE AT 80.0 ± 0.2° IN THE PRESENCE OF ADDED SUBSTANCES AND 4.58% BENZOYL PEROXIDE

Batch of monomer	Substance added and moles %	% Polymerization after 6.00 hours
1	None	31.0
2	None	31.1
3	None	30.4
3	H_2O (15)	31.1
3	HCl (2) + H_2O (5)	31.1
3	Pyridine (tr.)	30.3

TABLE II

EFFECT OF DEGASSING PROCEDURE ON RATE OF POLYMERIZATION OF ALLYL ACETATE AT 80.0 ± 0.2°; BENZOYL PEROXIDE, 1.12%

For a description of the procedures, see the Experimental Part.

Procedure	% Polymerization after twelve hours
Air, no agitation	11.2
A	12.5
B	12.2
C	12.4
D	12.5

Determination of Fate of Peroxide.—It has been shown in a number of cases that when polymerization is induced by the decomposition of acyl peroxide, fragments of the peroxide are permanently attached to the polymer.[2] Table III shows the chlorine balance for a polymerization of allyl acetate containing 5.90% of *p*-chlorobenzoyl peroxide, which was carried out to total decomposition of the peroxide, and followed by recovery of the free and extractable chlorobenzoic acid, determination of the bound and saponifiable chlorobenzoate groups, and finally an estimation of the bound and unsaponifiable chlorophenyl groups.

TABLE III

DISTRIBUTION OF CHLORINE AFTER POLYMERIZATION OF ALLYL ACETATE WITH 5.90% BY WEIGHT OF *p*-CHLOROBENZOYL PEROXIDE AT 80°

	Mg.	%
Polymer sample, 0.765 g.		
Chlorine present in original peroxide	21.73	100
Chlorine in free chlorobenzoic acid isolated	3.66	16.8
Chlorine bound to polymer, by analysis	15.76	72.5
Chlorine unbound and unaccounted for	2.31	10.7
Chlorine in pure chlorobenzoic acid hydrolyzed from polymer	11.32	52.1

During a run similar to this the carbon dioxide evolved was swept through with nitrogen and collected quantitatively in an ascarite tube. It amounted to 0.24 mole per mole of initial peroxide, or 12% of the maximum carbon dioxide possible if each *p*-chlorobenzoate radical formed had undergone decarboxylation.

The Evolution of Carbon Dioxide from Benzoyl Peroxide.—The form in which peroxide fragments are attached to the polymer—whether as benzoate or as phenyl groups—is related to the evolution of carbon dioxide during the polymerization, since for each phenyl group attached to the polymer one carbon dioxide molecule must have appeared. The reactions have been written[3]

$$C_6H_5COO{-}OOCC_6H_5 \longrightarrow 2C_6H_5COO^-$$
$$C_6H_5COO^- \longrightarrow CO_2 + C_6H_5^-$$
$$C_6H_5COO^- + CH_2{=}CHR \longrightarrow C_6H_5COOCH_2CHR{-}$$
$$C_6H_5^- + CH_2{=}CHR \longrightarrow C_6H_5CH_2CHR{-}$$

We have determined the amount of carbon dioxide evolved during the polymerization of allyl acetate with concentrations of benzoyl peroxide varying from 2.68 to 10% by weight, with the results shown in Table IV. The total amount of carbon dioxide produced by a given amount of peroxide is seen to be independent of the initial peroxide concentration in the absence of oxygen, but to

TABLE IV

CARBON DIOXIDE EVOLUTION DURING BENZOYL PEROXIDE-CATALYZED POLYMERIZATION OF ALLYL ACETATE AT 80.5 ± 0.5°

Peroxide wt. %	Peroxide moles/l.	Atmosphere	% Polymerization attained	Moles CO_2/mole peroxide
10.0	0.389	N_2	71	0.64, 0.60, 0.65
6.13	.233	N_2	48	0.64
2.68	.103	N_2	25	.70
10.0	.389	O_2, slow stream	44.5	.83
10.0	.389	O_2, fast stream	25.0	1.58
2.68	.103	O_2, fast stream	19	1.75

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[2] Price, Kell and Krebs, THIS JOURNAL, 64, 1103 (1942); Price and Durham, *ibid.*, p. 2508; Kern and Kämmerer, *J. prakt. Chem.*, 161, 181 (1942); Price and Tate, THIS JOURNAL, 65, 517 (1943); Bartlett and Cohen, *ibid.*, p. 543.

[3] Price and Kell, *ibid.*, 63, 2800 (1941).

be much increased by the passage of a rapid stream of oxygen through the polymerizing solution. This effect of oxygen is seen again when benzoyl peroxide is decomposed in solution in toluene at 100° or in nitrobenzene at 80° (Table V). In these solvents a mole of peroxide yields almost twice as much carbon dioxide as in allyl acetate under comparable conditions.

TABLE V

CARBON DIOXIDE EVOLUTION DURING DECOMPOSITION OF BENZOYL PEROXIDE IN TOLUENE AT 100 ± 0.5° AND NITROBENZENE AT 80.5 ± 0.5°

Peroxide, moles/l.	Solvent	Atmosphere	Temp., °C.	k (hr.$^{-1}$)	Moles CO_2/mole peroxide
0.208	Toluene	N_2	100	1.38	1.285
.208	Toluene	O_2	100	...	1.45
.126	Nitrobenzene	N_2	80	0.175	1.015
.126	Nitrobenzene	O_2	80	.130	1.272

Discussion.—Of the 16.8% of free *p*-chlorobenzoic acid isolated from the polymerization, not more than one-fourteenth, or 1.2%, can possibly have been present as an impurity in the original peroxide, for this peroxide showed 98.8% purity by iodometric titration. This indicates that the most important path by which peroxide fragments are lost in allyl acetate, without giving rise to polymer, is the taking of hydrogen from somewhere by benzoate radicals. The source of this hydrogen is considered in a later discussion.[4]

The molecular weight of the polymer produced by the chlorobenzoyl peroxide was 1330, and therefore the 0.765-g. sample of this polymer described in Table III contained 0.575 millimole. The amount of chlorine found in it was 15.76/35.46 = 0.444 milligram-atom. Hence, on an average, only 77% of the polymer molecules contain fragments from the peroxide. The growth of at least 23% of the polymer molecules must have been initiated otherwise than by the attachment of a chlorine-containing radical. If any of the chains were terminated by union with chlorobenzoate or chlorophenyl radicals, thus having two peroxide fragments per molecule, it would mean a corresponding increase in the number of polymer molecules having no peroxide fragment attached. Presumably, then, at least 23% of all the growing chains in this experiment were initiated (while others were terminated) by chain transfer.[5] Since 52.1% of all the initial chlorine was isolated as purified *p*-chlorobenzoic acid from the hydrolysis of the polymer, at least 52.1/72.5 or 72%, of the end-groups were *p*-chlorobenzoate groups. This is a minimal figure, since there was some loss in recrystallizing the acid.

An attempt was made to determine the *p*-chlorophenyl groups by reacetylating the polyallyl alcohol resulting from the previous hydrolysis and determining the chlorine content of this reconstituted polymer. The loss in this process was so great, due to solubility of the polyallyl alcohol in water, that the result is of little significance. Were we to assume that the small amount of reacetylated polymer isolated was typical of the whole, then the *p*-chlorophenyl groups in the polymer would account for 1.7 × 0.758/0.16 = 8% of the original chlorine (correction being made for that part of the 0.765-g. sample removed as benzoic acid by hydrolysis). This is a minimal figure for *p*-chlorophenyl groups, since there would be more loss of the lower-molecular-weight components of the polyallyl alcohol than of the higher. However, there cannot have been more chlorophenyl groups attached to the polymer than there was carbon dioxide eliminated, and this sets an upper limit of 12%. All the measurements are therefore consistent with the estimate that of the chlorine in the original peroxide, 60.5% is attached to the polymer as *p*-chlorobenzoate groups, 12% as *p*-chlorophenyl groups, 16.8% appears as free *p*-chlorobenzoic acid, and 10.7% is converted into this or other unattached products not isolated.

A comparison of the amount of carbon dioxide evolved from benzoyl peroxide with that from *p*-chlorobenzoyl peroxide shows that the figures arrived at above are no guide to the nature of the end-groups in polyallyl acetate prepared with unsubstituted benzoyl peroxide. The unchlorinated peroxide evolves nearly three times as much carbon dioxide (30–35% instead of 12%) as does *p*-chlorobenzoyl peroxide under the same conditions.

The assumption that carbon dioxide is evolved by unimolecular decomposition of a benzoate radical leads to the prediction that less carbon dioxide should be evolved, the greater the concentration of monomer molecules at hand to react with the benzoate radicals and shorten their free lifetime. The figures contradict this prediction, since in a run in which 71% polymerization occurred the evolution of gas was not proportionately greater than in a run reaching only 25% polymerization. This seems to indicate that the carbon dioxide does not issue from a unimolecular decomposition of benzoate radicals. The facts would be in accord with either of two interpretations: either that all the carbon dioxide evolved is produced spontaneously by decomposition of benzoyl peroxide at once into phenyl radical, carbon dioxide, and possibly benzoate radical[6]

$$\begin{aligned} C_6H_5COO{-}OOCC_6H_5 \longrightarrow\ & C_6H_5COO + CO_2 + C_6H_5 \\ & 2C_6H_5 + 2CO_2 \end{aligned}$$

or alternatively that carbon dioxide is eliminated from benzoate radicals only at the moment of reaction with another molecule, as for example

$$C_6H_5COO + CH_2{=}CHR \longrightarrow CO_2 + C_6H_5CH_2CHR$$

or

$$C_6H_5COO + O_2 \longrightarrow CO_2 + C_6H_5OO$$

(the last radical above being possibly involved in

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[4] Part II of this series: THIS JOURNAL, **67**, 816 (1945).

[5] Flory, *ibid.*, **59**, 251 (1937).

[6] Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

the obscure series of reactions attending oxygen inhibition of polymerization).

Experimental

Allyl acetate was prepared by heating under reflux for two hours a mixture of 1.5 moles (102 cc.) of allyl alcohol, 0.75 mole (71 cc.) of acetic anhydride, and 1.5 moles (86 cc.) of acetic acid, to which 5 cc. of concentrated sulfuric acid had been added. The resulting mixture was poured slowly with stirring into ice water, and extracted with ice-cold sodium carbonate and cold saturated calcium chloride solutions. After drying with 12 g. of anhydrous potassium carbonate, the ester was distilled twice through an all-glass apparatus in a stream of pure dry nitrogen. The middle fractions only were collected, b. p. (124–126 mm.) 53.2–54°, n^{24}_{D} 1.3985. This product showed no active hydrogen when examined in the Zerewitinoff apparatus.

Measurements of Rate of Polymerization.—All experiments were carried out in an oil thermostat, the temperature being 80 ± 0.3° unless otherwise noted. A solution of the peroxide in the monomer was made up by weight and portions sealed in glass tubes under nitrogen. The tubes were immersed in the thermostat for measured lengths of time. For each point one tube was opened and a weighed sample (about 500 mg.) was withdrawn and titrated for unsaturation.

Determination of Unsaturation.—To the weighed allyl acetate solution in a constricted test-tube, 5 cc. of 4.3 *N* sodium methoxide in 90% methanol was added at once. After sealing, the mixture was allowed to stand at room temperature for an hour with frequent shaking and was then heated at 100° for one to two hours. The mixture was cooled to ice temperature, transferred quantitatively to a volumetric flask, and diluted with water to 250 cc. Portions (10 cc.) were withdrawn by pipet and added to measured amounts of standard (0.05 *N*) bromide–bromate solution. Twenty-five cc. of 10% sulfuric acid was added and, when the bromine color became noticeable after about three to five minutes, 0.5 cc. of 30% aqueous potassium iodide solution was run into the flask. This was followed immediately by thiosulfate titration.

This method proved entirely reproducible, and was checked when applied to pure allyl acetate. For a freshly prepared solution of 4.58% benzoyl peroxide in allyl acetate the calculated concentration of monomer, in moles/l., is: $(1.00 - 0.458) \times 930/100 = 8.87$ moles/l. Found: 8.87. (For allyl acetate, $d_{22} = 0.928$, mol. wt. 100. For a 4.6% solution of benzoyl peroxide in allyl acetate, $d_{22} = 0.930$.)

The Effect of Oxygen upon the Polymerization of Allyl Acetate.—Four procedures, representing different degrees of completeness, were tried for eliminating oxygen prior to polymerization of allyl acetate. The procedures were:

A. A constricted test-tube, containing the monomer sample, was chilled in an ice-bath and, at that temperature, was evacuated with an aspirator five times to 15–20 mm. of mercury. The vessel was flushed each time with dry nitrogen (purified by passage through two wash bottles containing Fieser's solution,[7] then through a saturated lead acetate solution, and drying with calcium chloride) and was finally sealed off under an atmosphere of nitrogen.

B. The same procedure was followed, except that a bath of Dry Ice and alcohol and an oil pump were used, the evacuation being carried to 1–2 mm.

C. Procedure B was followed, but with the inclusion of a warming and rechilling step following each evacuation, the system being isolated.

D. Procedure C was modified by chilling with a liquid nitrogen bath and exhausting to less than 10^{-4} mm. with a diffusion pump.

In view of the results in Table II, Method A was used in the kinetic experiments upon which our interpretation of the mechanism is based.

Determination of End-Groups and Fate of Peroxide.—A sample of a solution of allyl acetate containing 5.90% by weight of *p*-chlorobenzoyl peroxide (0.603 g. of peroxide to 9.61 g. of ester) was polymerized at 80° under nitrogen until complete destruction of the catalyst was assured (46.5 hours). Then 4.024 g. of this product, 50.3% polymerized, was dissolved in 40 cc. of c. p. benzene and extracted with three portions of 9% aqueous sodium carbonate, the last extract giving no precipitate on acidification. After brief boiling of the combined aqueous layers to eliminate benzene from the solution and after filtration, the chlorobenzoic acid was precipitated by careful acidification with hydrochloric acid. The suspension was kept at ice temperature for twenty-four hours, filtered with suction, and the solid washed with a little ice-cold dilute hydrochloric acid. The weight of crude *p*-chlorobenzoic acid, dried to constant weight in a vacuum desiccator over concentrated sulfuric acid, was 0.040 g., m. p. 228–232°, mixed m. p. 230–233°. This corresponded to 0.34 mole of free *p*-chlorobenzoic acid per mole of *p*-chlorobenzoyl peroxide.

The benzene solution of allyl and polyallyl acetates was dried with anhydrous potassium carbonate, carefully boiled to dryness, and heated *in vacuo* at 100°. This sample contained 2.06% chlorine (analysis by Miss Margaret Racich). To determine the attached chlorobenzoate groups, 0.765 g. of the polymer was allowed to dissolve in 3 cc. of methanol and was kept at 50° for forty-five hours after addition of 6 cc. of 4.3 *N* sodium methoxide in 90% methanol. After the solution had refluxed for one-half hour, 20 cc. of distilled water was added and the solution acidified with 1 cc. of concd. sulfuric acid, followed by 50 cc. of distilled water. Extraction with seven portions of c. p. ether afforded quantitative separation of chlorobenzoic acid, the last extract leaving no residue on evaporation to dryness. After drying with anhydrous sodium sulfate, the combined ether solutions were carefully boiled to dryness and dried in a vacuum desiccator to constant weight over sodium hydroxide. The resulting 67 mg. of crude *p*-chlorobenzoic acid was purified by solution in 15 cc. of cold 7% aqueous sodium bicarbonate, filtration, careful acidification of the filtrate with concentrated hydrochloric acid, collection of the precipitate by suction filtration after allowing the suspension to stand at 0° for twenty-four hours. The solid was washed with a little cold dilute hydrochloric acid and dried to constant weight *in vacuo* over sodium hydroxide. The purified *p*-chlorobenzoic acid thus isolated weighed 50 mg., m. p. 238–240°, mixed m. p. 240–241°.

From the original dilute sulfuric acid solution, after the ether extractions, the polyallyl alcohol was isolated by neutralization with dilute sodium hydroxide solution and evaporation to dryness under reduced pressure, followed by washings with two portions of cold distilled water and subsequent decantations. This product was acetylated by heating in acetic anhydride and potassium acetate. The reconstituted polyallyl acetate weighed 0.16 g. and contained 0.22% chlorine (analysis by Miss Margaret Racich).

For the calculations summarized in Table III, the sample of purified polymer (0.765 g.) was taken as the base of reference. On the basis of strict proportionality with the actual initial amounts of material taken, and the analytically determined fraction of polymerization (50.3%), this amount of polymer is considered to have come from $0.765/(0.503 \times 9.61) = 15.8\%$ of the original monomer and this same fraction of the original benzoyl peroxide is therefore taken as that to be accounted for. The unattached benzoic acid was isolated from a sample of reaction product weighing 4.024 g. and representing $4.024/(9.61 + 0.60)$ or 39.4% of the original material. The figure in Table III is therefore obtained by multiplying the actual amount of chlorine in the isolated chlorobenzoic acid by the fraction $15.8/39.4 = 0.401$ to bring it to the same base of reference as the other quantities in the table.

Carbon Dioxide Determinations.—As a reaction vessel we employed a 20 × 150 mm. Pyrex test-tube carrying a side-arm reflux condenser the open end of which was connected to the absorption train. Ten cc. of the test solution of peroxide was placed in the test-tube, which was surrounded by a vapor bath of boiling benzene (80.5 + 0.5°).

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(7) Fieser, This Journal, 46, 2689 (1924).

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.

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[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).