in water," and they do not consider these solubilities worth reporting.

The solubility here reported, of 0.204% at 25°, is not claimed to be final and accurate, and is to be compared with the following literature values (recalculated into units of weight per cent.)

Longi (1883)[9]	0.166 at 25°
Noyes (1890)[5]	.192 at 24.5°
Böttger (1903)[10]	.159 at 25°
Whitby (1910)[11]	.171 at 27°
Hill (1917)[1]	.195 at 25°
Reedy (1921)[2]	.196 at 25°
Dalton, Pomeroy and Weymouth (1924)[3]	.189-0.191 at 25°
Owen (1933)[6]	.192 at 25°
Neuman (1934)[7]	.192 at 25°

The highest values reported are those of Hill and of Reedy. The latter apparently took the greatest pains in purifying the salt by recrystallization. The present investigation shows that the presence of even small amounts of sodium bromate reduces considerably the solubility of silver bromate.

Reedy found that the purity of his silver bromate tended to be low, 99.6 to 99.8%, and he attributed this deviation from purity to the presence of air occluded in the crystals during precipitation. He even recommended the salt as a standard in iodimetry. But in view of the formation of a solid solution with sodium bromate, such use of silver bromate should obviously be undertaken only with serious precautions. The only other analysis of the silver bromate used for solubility work is given by Hill, who reported, without comment, that his salt gave 44.97 and 45.00% of silver (determined as silver chloride) as compared to the theoretical 45.75%. His sample was made by precipitation from potassium bromate and silver nitrate; the same reaction was used for the preparation of the material used in References 9, 10, 11, in which no analysis is given.

Summary

1. The system silver bromate–sodium bromate–water has been studied in detail at 25°, and, partially, at 50° and 5°.

2. The salts form a definite compound, $AgBrO_3 \cdot NaBrO_3$, which forms a continuous solid solution with silver bromate. Sodium bromate also forms a solid solution containing up to 2.5–3.0% of silver bromate.

3. Some implications of these results on analytical procedures involving silver bromate are discussed. Precipitation of silver bromate from solutions containing sodium ion must result in an impure salt which can be purified by recrystallization only with difficulty.

4. The results may explain the great variation in the values of the solubility of silver bromate reported in the literature, and suggest that the samples of the salt used in various theoretical studies may have been contaminated with sodium bromate.

NEW YORK, N. Y.

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[9] Longi, *Gazz. chim. ital.*, **13**, 87 (1883).

[10] Böttger, *ibid.*, **46**, 603 (1903).

[11] Whitby, *Z. anorg. Chem.*, **67**, 108 (1910).

[CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY AND POLYTECHNIC INSTITUTE OF BROOKLYN]

Mechanism of Peroxide Initiated Styrene Polymerization

BY HARRY F. PFANN[1] D. J. SALLEY[1a] AND H. MARK

Recent publications of Price and his co-workers[2] and of Kern and Kammerer[3] have succeeded in clarifying the mechanism of the peroxide initiated polymerization of styrene. Their results confirm and extend proposals advanced by Norrish,[4] Schulz[5] and others that the active centers for chain propagation are free radicals resulting from the decomposition of the peroxide as such or an addition compound between peroxide and styrene. As there appears to be continued interest[6,7,8] in this problem, the writers wish to present the following data obtained from experiments[9] in progress from 1940 to 1942, which were not published at that time due to the outbreak of the war.

In this work, halogen-containing polymer was prepared from styrene and *m*-bromobenzoyl peroxide. Non-combined initiator was removed by repeated extraction, and the presence of bromine in the polymer was demonstrated by combustion of the sample followed by determination of the halogen, as well as by measurement of the radioactivity of the polymer samples after neutron bombardment.

Experimental Procedure

Polymer samples were prepared by heating commercially pure styrene (Dow Chemical Company, 1941, n^{25}_D 1.5432, d^{24} 0.9025) with *m*-bromobenzoyl peroxide (m. p. 127–128°, 99% of theoretical active oxygen) in sealed glass tubes 38 mm. × 180 mm. immersed in an oil-bath at

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[1] (a) American Cyanamid Company, Stamford, Connecticut.

[1] (b) Present address: Koppers United Company, Butadiene Division, Kobuta (Monaca), Pennsylvania.

[2] Charles C. Price, *et al.*, THIS JOURNAL, **63**, 2798 (1941); **64**, 1103, 2508 (1942): **65**, 517 (1943).

[3] W. Kern and H. Kammerer, *J. prakt. Chem.*, **161**, 81–112 (1942); *C. A.*, **37**, 5381 (1943).

[4] Norrish and Brockman, *Proc. Roy. Soc.*, **A171**, 147–71 (1939); Norrish, *Trans. Faraday Soc.*, **35**, 1082 (1939).

[5] G. V. Schulz, *Naturwissenschaften*, **27**, 387, 456, 659 (1939).

[6] (a) Abere, Goldfinger, Mark and Naidus, *J. Chem. Phys.*, **11**, 379 (1943); (b) *Ann. N. Y. Acad. Sci.*, **44**, 267 (1943).

[7] Compare also Mayo, THIS JOURNAL, **65**, 2324 (1943).

[8] Bartlett and Cohen, *ibid.*, **65**, 543 (1943).

[9] Taken in part from the Thesis for the Degree of Master of Science by Harry F. Pfann, Polytechnic Institute of Brooklyn, June, 1942.

140 ± 2°. Each tube was sealed off under vacuum (except Sample No. 100). The temperature of reactants was followed by use of a thermocouple placed in a well extending into the center of the reaction mixture. Heating was continued until *ca.* 50% of the styrene was polymerized, after which the reaction was quenched by sudden cooling.

Polymer was isolated by precipitation from benzene solution with methanol. A 5% solution of polymer in benzene was extracted three times by agitation with 15% aqueous sodium hydroxide at *ca.* 50° during one hour. The extracted polymer, precipitated with methanol, was digested in methanol on the steam-bath, and dried in a vacuum oven.

Chemical determination of the bromine content of the polymer was carried out by combustion in a macro combustion tube over a platinum gauze catalyst, absorption of the halogen in an alkaline sodium bisulfite solution, and gravimetric determination of silver bromide by a modification of the Pregl micro technique.[10] Combustion of the non-volatile polymer was attended by considerable difficulty, but the results tabulated represent fairly successful determinations.

Physical determination of the bromine content was carried out by measuring the intensity of the radioactive isotopes of bromine produced by irradiation with neutrons. Cast films of the polymer 1.0 sq. cm. by 1 mm. were subjected to neutron bombardment in the Columbia University cyclotron. Measurements of the resulting intensities were carried out with a mica-window type of Geiger counter tube. All counts were corrected for decay and for slight variation in the thickness of the specimens. The ratio of the corrected intensities gave the relative amounts of bromine present, and the absolute amount was obtained using one of the samples as the basis.

TABLE I

PREPARATION OF POLYSTYRENE SAMPLES

Initiator: *m*-bromobenzoyl peroxide; bath temperature, 140 ± 2°.

Sample	Initiator concentration, mg./g./styrene	Heating period, minutes	Reaction temp. maximum, °C.	Polymerized, %
100	Oxygen[a]	41	191	50.8
101	Evacuated	41	...	53.5
104	1.54	31	164	51.8
111	7.68	14	187	50.2
115	12.84	7	220	59.0
116	12.84	4	217	48.0

[a] Tube evacuated and filled with oxygen at 760 mm. before sealing.

TABLE II

PROPERTIES OF EXTRACTED POLYMER SAMPLES

			Bromine content of sample (mg. Br per 1 g. polymer)			
				Determined		
Sample	Relative viscosity[a]	Viscosity average molecular weight[b]	Original reaction mixture	Gravimetric	Radioactive	Calculated:[c] 2 Br atoms per polymer molecule
104-E-1	1.77	155,000	0.61	0.8 ± 0.1 (3)[d]	0.6	1.04
111-E-1	1.43	86,500	3.05	3.5 ± .4 (5)	3.4	1.86
116-E-1	1.24	48,800	5.12	5.4 ± .5 (3)	5.4	3.28
116-E-3	..	..	5.12	5.2 ± .5 (3)	..	..

[a] Relative viscosity of 1% solution of dried polymer in toluene at 20°. [b] Viscosimetric molecular weight calculated from equation $M = \eta\,\mathrm{sp}/K_\mathrm{m} \times \mathrm{Concn.}$, using $K_\mathrm{m} = 0.50 \times 10^{-4}$ given for thermal polymerization at 135°. Compare H. Staudinger and G. V. Schulz, *Ber.*, **68**, 2332 (1935). [c] Based on viscosimetric molecular weight. [d] Number of determinations averaged.

Experimental Results

Table I gives the conditions for preparation of the polymer samples. "Reaction Temperature Maximum" indicates the highest temperature indicated by the thermocouple, showing that there was a marked deviation from the isothermal condition of the heating bath. Comparison of samples 100 and 101 suggests that oxygen may act initially as an inhibitor, as it does, *e. g.*, in certain emulsion polymerizations.

In Table II are given the properties observed for the several polymer preparations. Sample 116-E-3 differed from 116-E-1 in that it was given three standard extractions and precipitations after polymerization. The essential constancy of the bromine content indicates that the halogen determined represents chemically bound, not associated or adsorbed, catalyst fragments. The agreement between the chemical and radioactive determinations appears quite satisfactory.

The analytically determined bromine content does not agree well with the value calculated from the viscosity average molecular weight, which calculation is based on the assumption of two initiator fragments per polymer molecule. This would be the case if chain termination is only effected through mutual saturation of two growing chains.[11,12]

Perhaps of more significance is the variation shown under "Comparison of Values." Polymer sample 104 was prepared with the smallest peroxide concentration at the lowest temperature, and it was found to have only 58% of the halogen calculated from viscosity measurements. Sample 116, prepared with greatest peroxide concentration and highest temperature, was found to have 166% of the calculated halogen content. Sample 104-E-1, of highest molecular weight, would be expected to have been subject to the greatest degree of chain transfer. A high incidence of chain transfer would result in a low concentration of initiator per polymer molecule.[13]

It must also be borne in mind that the viscosity average as contained in column three of Table II places less emphasis on the short chains than the counting of the bromine end-atoms does. If the low molecular fractions of the polymer are initiated by the brominated peroxide while the high molecular weight fractions are produced after the consumption of the initiator by thermal activa-

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(10) F. Pregl, "Quantitative Organic Microanalysis," Blakiston Co., Philadelphia, Pa., 1930.

(11) See reference 6a, p. 383; 6b, p. 296.

(12) Compare also Price, *Ann. N. Y. Acad. Sci.*, **44**, 365 (1943).

(13) Reference 12, p. 366.

tion, the viscosity average is bound to give distinctly larger molecular weights than the counting of the end-groups. This may explain the high bromine content of the polymer prepared at 217° (sample 116-E) where the decomposition of the catalyst should be expected to be very fast and at the same time thermal activation would be most efficient.

Acknowledgment

The authors are anxious to express appreciation to the directors of the Stamford Research Laboratories of the American Cyanamid Company for extending to the junior author the use of the laboratories' facilities. Thanks are also extended to the staff of the Columbia University cyclotron for bombardment of the samples.

Summary

1. Styrene has been polymerized in the pure liquid phase at various temperatures and with various amounts of *p*-bromobenzoyl peroxide.

2. The bromine content of the polymer was determined gravimetrically and with the aid of a radioactive bromine isotope. The values obtained by the two methods agreed reasonably well with each other.

3. The polymers contain on the average between one and three bromine atoms per chain, if the viscosity average chain length is compared with the analytical bromine content.

4. It is shown that the radioactive tracer method can be fairly easily applied to this problem of polymer chemistry.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Rearrangement of Alkyl Halides[1]

BY FRANK R. MAYO[2a] AND ARTHUR A. DOLNICK[2b]

The addition of hydrogen bromide to a 1-alkene may yield either of two products, depending on the mechanism of addition.[3] The normal addition, giving a secondary or tertiary bromide, proceeds by an ionic or molecular mechanism. The abnormal addition, which is accelerated by oxygen and peroxides and is inhibited by certain antioxidants, proceeds by an atom-chain mechanism, giving a primary bromide. On the assumption that the rearrangement of an alkyl bromide proceeds by loss and readdition of hydrogen bromide, it was concluded that the rate of rearrangement should be affected by the same catalysts which influence the addition of hydrogen bromide. This paper describes the effects of such catalysts on the rearrangement of normal and isopropyl bromides to an equilibrium mixture. These readily available bromides were chosen because the carbon skeleton cannot rearrange and because a mixture of the halides is easily analyzed. For comparison with a representative pair of alkyl chlorides, experiments were made with *i*- and *t*-butyl chlorides. Data were also obtained on the two dibromoethanes.

Previous Work

When an alkyl bromide is strongly heated, it rearranges to give an equilibrium mixture of all the isomeric bromides which can be formed without rearrangement of the carbon skeleton. In spite of considerable work in the field, there is marked disagreement on the composition of some equilibrium mixtures, on the factors which influence the rate of approach to equilibrium, and on the mechanism of rearrangement.

In the liquid phase at 250°, normal and isopropyl bromides rearrange to give a mixture containing 30 and 70%, respectively, of these bromides.[4a] The proportion of primary bromide increases with the temperature[4a] and is smaller in the vapor phase.[4b] Equilibria between tertiary and isobutyl bromides have been more extensively investigated[5] in both the liquid and the vapor phase, but although the tertiary bromide always predominates, wide discrepancies in the composition of the equilibrium mixture have been reported; secondary butyl bromide (with rearrangement of the carbon skeleton) has also been detected.[5g] Equilibria between the four bromoisopentanes and between some isomeric dibromoalkanes have received less attention.[5a,6]

The rearrangement of the bromoisobutanes is retarded by the corresponding alcohols and by di-isobutylene.[5b] Michael has recently suggested[7]

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(1) Presented before the Division of Organic Chemistry at the St. Louis meeting of the American Chemical Society, April 9, 1941. This paper is a condensation of a thesis submitted by Arthur A. Dolnick in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

(2) Present addresses: (a) General Laboratories, United States Rubber Company, Passaic, N. J.; (b) Publicker Commercial Alcohol Company, Philadelphia, Pa.

(3) Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

(4) (a) Brouwer and Wibaut, *Rec. trav. chim.*, **53**, 1001 (1934); (b) Brunel and Rafsky, *Science*, **60**, 23 (1924).

(5) (a) Michael and Leupold, *Ann.*, **379**, 263 (1911); (b) Michael, Scharf, and Voigt, THIS JOURNAL, **38**, 653 (1916); (c) Brunel, *Ber.*, **44**, 1000 (1911); (d) Brunel, *Ann.*, **384**, 245 (1911); (e) Brunel, THIS JOURNAL, **39**, 1978 (1917); (f) Dienger, *Z. physik. Chem.*, **136**, 93 (1928); (g) Hückel and Ackermann, *J. prakt. Chem.*, [2] **136**, 15 (1933).

(6) (a) Gustavson, *J. prakt. Chem.*, [2] **36**, 303 (1887); (b) Faworsky, *et al.*, *Ann.*, **354**, 325 (1907); (c) Michael and Zeidler, *ibid.*, **385**, 227 (1911).

(7) Michael, *J. Org. Chem.*, **4**, 521 (1939), footnote 9.