group. The increase would be expected to be less than by a factor of 5 (as with anilinium ion[31]) but appears to be by a factor of forty if the constant 4.3×10^{-9} is attributed to the hydroxy group. The ionization constant of phenol[33] is 1.1×10^{-10}. This large increase may be due to salt effects on the doubly charged ion. The value of $\sigma\rho_2$ for the arsonic acid group is then -1.6 but this is due to the O^- group rather than the hydroxy group. It would be expected that the O^- group would decrease the ionization of the arsonic acid much more than do the hydroxy or carboxylate groups.

It is quite interesting that the group AsO_3H^- para to a carboxy group has hardly any effect on the ionization of the carboxy group: the ionization constant of benzoic acid[21] is 6.3×10^{-5}.

The effects of a nitro or an amino group in the 4-position on the dissociation constants of α-naphthylarsonic acid are the same as for phenylarsonic acid.

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Summary

An investigation was made of the first and second ionization constants of nineteen substituted phenylarsonic acids in water at 22°. It was observed that in general a given substituent changes the first and second ionization constants by the same factor. In the case of a substituent in the meta and para positions the effect is similar to that for benzoic acid and in the ortho position to that for phenylboric acid.

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[33] J. Kendall, This Journal, **39**, 7 (1917).

[Contribution from the Converse Memorial Laboratory of Harvard University]

The Ester Groups in Polystyrene Made with Chloro- and Bromobenzoyl Peroxides

By Paul D. Bartlett and Saul G. Cohen[1]

There is good evidence that the polymerization of an olefinic monomer catalyzed by an acyl peroxide is neither "polymerization" nor "catalysis" in the narrow meanings of these terms. It involves the attachment of fragments from the peroxide to the double bond of the monomer with the emergence of a free radical which propagates the chain reaction by successive additions of the monomer. Although this proposition has been much debated, it yields the only satisfactory interpretation of the kinetics of polymerization.[2] There is little evidence to date as to the nature of the terminal groups which must be present in polymers prepared by acyl peroxides if this mechanism is correct. Kamenskaja and Medwedew point out that the breakdown of benzoyl peroxide can lead to both benzoate and phenyl radicals, either one of which might initiate the polymerization. They quote an unpublished observation indicating that there are benzoate fragments in polystyrene. Schulz and Husemann[3] concluded that with polystyrene of molecular weights in the usual range, the concentration of terminal groups would be so small as to escape detection readily. Price, Kell, and Krebs,[4] however, showed that a dilute solution of styrene in benzene could be polymerized at the boiling point by a relatively large amount of *p*-bromobenzoyl peroxide to a low-molecular-weight polymer containing 5.72% of bromine permanently bound.

We have utilized these conditions and have shown by suitable methods of hydrolysis that the greater part (53–64%) of the halogen permanently bound to the polymer is in the form of *p*-bromobenzoate groups, while the rest of it is evidently in the form of *p*-bromophenyl groups which cannot be removed by saponification. This substantiates the original suggestion of Kamenskaja and Medwedew and also the findings of Price and co-workers[4] to the extent that catalyst fragments are incorporated in the structure of the polymer. However, the latter authors concluded that their polystyrene contained no ester groups, since (a) the analysis for carbon, hydrogen, and halogen left no room for oxygen, and (b) boiling with 20% aqueous potassium hydroxide effected no saponification. In com-

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[1] Pittsburgh Plate Glass Fellow.

[2] Kamenskaja and Medwedew, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).

[3] Schulz and Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

[4] Price, Kell and Krebs, This Journal, **64**, 1103 (1942).

position our sample evidently differed from that of Price, Kell and Krebs. However, even our sample was completely unaffected by 20% aqueous potassium hydroxide, being extremely insoluble in this reagent. This is, therefore, no evidence of the nature of the terminal groups.

Table I summarizes the quantitative information obtained under two sets of conditions. Expt. 1 was carried out using the concentrations, temperature, time, and solvent of Price, Kell and Krebs, with *p*-bromobenzoyl peroxide; Expt. 2 was made without solvent, using an amount of *p*-chlorobenzoyl peroxide equal to less than 1% of the weight of the styrene. The polymer was purified by repeated solution in dioxane or benzene and precipitation with methanol. The purified polymer was analyzed for halogen by the Carius method. In Expt. 1 it was confirmed that long boiling with aqueous potassium hydroxide produced no change in the polymer. The saponification of the benzoate groups was accomplished in Expt. 1 by repeated long boiling with sodium ethoxide in ethanol, followed by the addition of water, and in Expt. 2 by using sodium ethoxide in a mixture of ethanol and toluene, which yielded a completely homogeneous solution, and later adding water to this.

TABLE I

TERMINAL GROUPS IN LOW-MOLECULAR-WEIGHT POLYSTYRENES

		Expt. 1 *p*-Bromobenzoyl peroxide in benzene	Expt. 2 *p*-Chlorobenzoyl peroxide
Initial mole fraction of styrene		0.023	0.997
Initial mole fraction of peroxide		.0027	.003
Halogen in monomer, %		.015	.015
Halogen in purified polymer, %		10.7	.096
Halogen in hydrolyzed polymer, %		3.87	.021
Halogen in control polymer, % (after saponification)		0.011	.011
Halogen from catalyst in purified polymer, %		10.7	.081
Polymer halogen accounted for as XC_6H_4COOH isolated from alkaline hydrolysis, %		5.7	.079
Percentage of terminal groups which are benzoate	by isolation	53	97.5
	by analysis	64	88
Percentage of terminal groups which are phenyl (by analysis)		36	12

Bromo- and chlorobenzoic acids were isolated, respectively, from the alkaline hydrolyzate and identified by mixed melting points. The percentage of the terminal groups which are bromo- and chlorobenzoate groups, as calculated from the solid acid isolated, is not too discordant with the estimate of the same quantity made on the basis of the halogen analysis of the polymer before and after the alkaline treatment. Of the two sets of conditions used, the one with the larger amount of peroxide, leading to the polymer of lower molecular weight, has the higher fraction of non-ester-bound phenyl groups.

The experiment with the chlorobenzoyl peroxide, leading to one terminal group for every 420 styrene units, presents analytical difficulties of the kind envisaged by Schulz and Husemann. The chlorine content of the monomer, 0.015%, is appreciable compared to that of the polymer, 0.096%, and is an important part of the chlorine content, 0.021%, found for the polymer from which all ester groups had been removed. Our conclusions regarding the possible number of *p*-chlorophenyl groups in the polymer depend upon whether or not the chlorene present in the original styrene becomes removable by sodium ethoxide when the styrene is converted into polymer. To settle this we ran the experiment described in the table as the "control," in which styrene was polymerized by benzoyl peroxide, the polymer was treated with sodium ethoxide in ethanol–toluene solution as in the isolation of the chlorobenzoic acid, and the recovered polymer was analyzed for chlorine. Its chlorine content was found to be 0.011%, indicating a loss of about one-third of the original halogen of the styrene by this alkaline treatment. In making the calculations it was assumed that the same occurred in the run with chlorobenzoyl peroxide, and that the halogen in the final polymer due to chlorophenyl groups could be taken as 0.021–0.011 = 0.010%. A few thousandths of a per cent. error in this figure would greatly affect the last figure in Table I. On the other hand, it is unlikely that the per cent. of chlorobenzoate groups based upon the acid actually isolated can be very much too high. We therefore place more reliance on this figure than on the other, and conclude that under these conditions of polymerization the terminal groups are almost all of ester character.

Experimental

Styrene.—Eastman Kodak Co. practical grade was redistilled and a fraction boiling sharply at 52.4° (31 mm.), was used in the polymerizations.

Anal. For halogen: sample, 149.90 mg.; AgCl, 0.09 mg.; Cl, 0.015%.

p-Bromobenzoyl peroxide was prepared in 79% yield by adding an ether solution of p-bromobenzoyl chloride to a stirred cold aqueous sodium peroxide solution. The product was crystallized from chloroform–methanol and dried in a vacuum desiccator. It explodes violently at 148°.

p-Chlorobenzoyl peroxide was prepared and purified in the same way as the bromo compound. It was obtained in 87% yield and decomposed at 138°.

Polymerization of Styrene with Bromobenzoyl Peroxide.—A solution of 1.2 g. of bromobenzoyl peroxide and 2.7 g. of styrene in 100 cc. of benzene was boiled under reflux for five hours, the conditions of the experiment of Price, Kell and Krebs. The benzene was boiled off on the water-bath, and the residue was four times dissolved in dioxane and precipitated with methyl alcohol. The product obtained after these four precipitations weighed 0.625 g. The mother liquors were worked up further, yielding 1.40 g. more of the polymer. These two fractions, suspected of being non-identical, were kept separate and analyzed for bromine by the Carius procedure. The first and smaller fraction contained 10.7% bromine and the second and larger fraction 11.5%. Although this is much more bromine than was present in the sample of Price, Kell and Krebs (5.72%), the similarity of our two fractions to each other, the number of reprecipitations, and the parallel evidence obtained in the later polymerization convince us that the polymer had been effectively freed of extractable by-products of the polymerization. The disparity between our two fractions with regard to bromine analysis is in the direction to be expected of an inhomogeneous product so fractionated as to separate the higher molecular weight components preferentially by their lower solubility. The lower polymers must contain a higher fraction of terminal groups than the higher polymers. Actually the two samples are much closer together in bromine analysis than would be possible on the basis of mechanical contamination with benzoic acid or its simple esters.

Hydrolysis of Polystyrene Made with p-Bromobenzoyl Peroxide.—The 0.426-g. portion was boiled under reflux for seventeen hours in a solution of 7 g. of potassium hydroxide in 28 cc. of water. The mixture was cooled and filtered, the polystyrene (0.426 g., 100% recovery) was collected, washed and dried in vacuum. Ether extraction of the alkaline solution yielded 8 mg. of oil and solid, from which no bromobenzoic acid could be isolated. An ether extraction of the acidified aqueous solution yielded 2 mg. of yellow oil only.

The recovered polystyrene, 0.426 g., was suspended in a solution of 1.8 g. of sodium in 50 cc. of absolute alcohol and boiled under reflux for eighteen hours. The alcohol was boiled off and replaced with water, the mixture was cooled and filtered, and the polystyrene was washed with water and dried in the vacuum, the recovery being 0.387 g. The alkaline filtrate and washings were combined, acidified with 12 cc. of concentrated hydrochloric acid, and extracted with ether. A white solid was precipitated by the acidification and dissolved by the ether. The ether extracts were combined, dried, and concentrated, leaving a white solid, 0.149 g. This was taken up in sodium bicarbonate, filtered, and acidified, yielding 0.050 g. of p-bromobenzoic acid, m. p. 253–254°. This represents 43.4% of the bromine content determined for this fraction of the polymer.

This extraction process was repeated twice more, using the same quantities of sodium and alcohol, and periods of boiling of forty-six and one-half and forty-seven hours, respectively. Further portions of p-bromobenzoic acid were isolated amounting to 7 mg., m. p. 245–247°, mixed m. p. 248–250°, and 4 mg., m. p. 247–249, mixed m. p. 248–250°. This raised the bromine accounted for as p-bromobenzoic acid to 53% of that present in the original polymer. A Carius analysis was performed on the polymer between these two last extractions: 0.0401 g. of polymer gave 0.00459 g. of silver bromide, corresponding to 4.87% bromine.

The remaining polystyrene, 0.31 g., was dissolved in 10 cc. of toluene and boiled under reflux with 20% aqueous potassium hydroxide for twenty-three hours. Although no bromobenzoic acid was isolated by this procedure, 99 mg. of oily material was extracted from the acidified aqueous solution by ether, and the bromine content of the recovered polystyrene was reduced. *Anal.* Sample, 36.6 mg.; AgBr, 3.35 mg.; Br, 3.9%. From this analysis it follows that not more than 3.9/10.7, or 36.4%, of the bromine originally present in the polystyrene sample can have been due to p-bromophenyl groups attached through C–C linkages.

Homogeneous Treatment with Alkali of Polystyrene Made with Bromobenzoyl Peroxide.—The polystyrene (0.224 g.) was dissolved in 6 cc. of toluene, and to it was added a solution of 0.1 g. of sodium in 3 cc. of ethanol and 3 cc. of toluene. A homogeneous solution resulted. This was boiled under reflux for twenty-five hours; 0.5 cc. of water was then added and the boiling was continued for fourteen hours further. Finally 5 cc. of water was added, the mixture was boiled for two hours and then the organic solvents were boiled out over a period of one hour. The polymer was collected, washed with water and dried in vacuum. The amount recovered was 0.222 g., 99%. Working up the filtrate and washings as before yielded only 8 mg. of oil from which no p-bromobenzoic acid could be isolated. Final Carius analysis of the polymer: sample, 49.2 mg.; AgBr, 4.47 mg.; Br, 3.87%.

Polymerization of Styrene with 0.88% Benzoyl Peroxide (control).—A solution of 0.0132 g. of benzoyl peroxide in 1.503 g. of styrene was sealed in an ampoule and heated at 80–82° for 22.5 hours and at 99–101° for twenty-three and one-half hours. The polymer was obtained as a hard, slightly yellow solid, 1.460 g. (96% yield). The polystyrene was dissolved in 10 cc. of benzene and precipitated by the addition, by drops, of 20 cc. of methanol to the stirred solution. This precipitation was repeated five times; the polymer was dried in vacuum at 100°, 1.272 g. being recovered (87% yield).

Hydrolysis of the Polystyrene.—A solution of 0.22 g. of sodium in 7 cc. of absolute ethanol and 7 cc. of toluene was added to a solution of 0.827 g. of the polystyrene in 20 cc. of toluene. The solution was heated under reflux for fifty-three hours, 3 cc. of water was added and the boiling was continued for twenty-four hours. Two 10-cc. portions of water were added as the alcohol and toluene were boiled off.

The polymer was collected, washed repeatedly with distilled water and dried in vacuum; 0.811 g. was recovered: halogen analysis (Carius): sample, 161.3 mg.; AgCl, 0.07 mg.; Cl, 0.011%.

Polymerization of Styrene by 1% Chlorobenzoyl Peroxide.—A solution of 0.1918 g. of *p*-chlorobenzoyl peroxide in 20.13 g. of styrene (a 0.943% solution) was sealed in ampoules which were heated at 81–84° for twenty-three and one-half hours and at 100–103° for twenty-nine and one-half hours. When the ampoules were removed from the heating bath, they soon shattered, leaving the polystyrene as pieces of a hard, transparent, slightly colored solid, 20.04 g. (99% yield).

Purification of the Polystyrene.—Preliminary experiments showed that the polystyrene was equally well purified by repeated solution in toluene, benzene, or dioxane, followed by precipitation with methanol. In 100 cc. of benzene, 17.76 g. of the polystyrene was dissolved and was precipitated by the addition, by drops, of 200 cc. of methanol to the stirred solution. Because this polystyrene was of higher molecular weight than the sample prepared with the higher concentration of bromobenzoyl peroxide, the precipitation by the methanol was practically quantitative. The polymer was dissolved and reprecipitated six times in this way, and the amounts of material removed were ascertained by examination of the mother liquors. The liquors from the first three precipitations were combined and concentrated, yielding 0.216 g. of oil and solid. The residue from the combined fourth and fifth precipitations amounted to 0.062 g., and that from the sixth precipitation was 0.039 g. The purified polystyrene, dried in vacuum at 100°, weighed 17.42 g.

Products Extracted from the Polymer During Purification.—The residue from the first three precipitations was washed with benzene, leaving a fine crystalline residue, 0.0155 g., m. p. 238–239° alone and when mixed with *p*-chlorobenzoic acid. The benzene washings were extracted with sodium bicarbonate, the solution acidified and extracted with ether. Evaporation of the ether led to a solid residue, 0.0105 g. Purification through the sodium salt yielded a further 0.005 g. of *p*-chlorobenzoic acid, m. p. and mixed m. p. 237–239°. This acid, of course, represents decomposition of the peroxide without utilization of the fragments in promoting polymerization. The benzene solution of the material insoluble in bicarbonate was evaporated to dryness and boiled for 3.5 hours in a solution of 1 g. of potassium hydroxide in 10 cc. of ethyl alcohol. The alcohol was replaced by water and the mixture was filtered and acidified. The slightly yellow solid collected was impure *p*-chlorobenzoic acid, 0.021 g., m. p. 230–232°, mixed m. p. 234–237°. The breakdown products of the peroxide not attached to the polymer thus included both *p*-chlorobenzoic acid and its esters.

Similar treatment of the mother liquors from the fourth and fifth precipitations yielded 6 mg. of alkali-soluble oil from which no *p*-chlorobenzoic acid was obtained. The sixth precipitation yielded no weighable amount of alkali-soluble material either before or after alkaline hydrolysis. This is the evidence that *p*-chlorobenzoic acid and its esters of low molecular weight were effectively removed by the procedure we employed.

Hydrolysis of the Polystyrene.—The polymer, 5.76 g., was dissolved in 60 cc. of toluene. To it was added a solution of sodium ethoxide made from 1 g. of sodium, 30 cc. of absolute ethyl alcohol and 30 cc. of toluene. A homogeneous solution resulted. This solution was heated at 100° for fifty-three hours, 1.5 cc. of water was added and the heating was continued for a further twelve hours. Then 20 cc. of water was added and the alcohol and toluene were slowly distilled out. Finally 50 cc. of water was added and 25 cc. of it distilled off. The mixture was filtered and the polymer was washed with several portions of water. The combined filtrates were acidified. A white precipitate was extracted by ether, the ether dried and evaporated. An oily residue was left which, on reprecipitation from solution in sodium bicarbonate, weighed 20 mg. and melted at 237–239°, mixed m. p. with *p*-chlorobenzoic acid, 238–239°. Halogen analyses (Carius). Polystyrene purified by six precipitations: sample, 188.2 mg.; AgCl, 0.73 mg.; Cl, 0.096%. Polystyrene after homogeneous hydrolysis: sample, 207.3 mg.; AgCl, 0.18 mg.; Cl, 0.021%.

Summary

Styrene has been polymerized by halogenbenzoyl peroxides under different conditions of concentration and evidence has been obtained that both halogenbenzoate and halogenphenyl radicals from the peroxide are permanently attached to the polymer. Of these terminal groups under two sets of conditions, 53 and 97.5%, respectively, are indicated to be ester groups by the isolation of *p*-bromo- and *p*-chlorobenzoic acid from vigorous alkaline hydrolysis of the purified polystyrene. The halogen analyses of the hydrolyzed and unhydrolyzed polymers indicate 64% bromobenzoate and 36% bromophenyl in the one case, and 88% chlorobenzoate and 12% chlorophenyl in the other.

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