Polymerization of Styrene in Heavy Alcohol and Heavy Benzene and the Same Reaction Catalyzed by Heavy Benzoyl Peroxide[1]

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The author has previously found[2] that a certain amount of heavy alcohol was adhered to the polystyrene, which was prepared from styrene by heating its solution in heavy alcohol. In order to obtain some knowledge on the mechanism of this attachment of alcohol molecules to the molecules of polystyrene, the average number of alcohol molecules attached to each molecule of polystyrene has been examined in the present research. It was found to be one, the molecule being presumed to attach at the starting point of the chain molecule of polystyrene. At the same time it has been found that this number of alcohol molecules attached to each molecule of polystyrene decreases when benzoyl peroxide is added to the reaction mixture. These results suggest us that the alcohol molecules are expelled out of their place on the polystyrene molecule by benzoyl peroxide molecules, so that the latter can also attach to the chain molecule of polystyrene at its starting point. The experiment showed that this is actually the case. The polystyrene which was made from styrene in the presence of benzoyl peroxide labelled by heavy hydrogen atoms was found to contain a benzoate group which might be formed by the splitting of a molecule of benzoyl peroxide.

It was found further that the polystyrene contained no heavy hydrogen atoms, when it was prepared from styrene by heating its solution in heavy benzene and the resulted polymer was heated in vacuum at 100° for twenty hours. From this experimental result it can be concluded that no hydrogen atoms are exchanged between styrene and benzene when the former is polymerized in the solution of the latter.

Polymerization of Styrene in Heavy Alcohol

The experiment was at first carried out in the following way. A definite amount (1 cc.) of styrene, which was purified directly before the experiment by distillation in vacuum, was sealed together with a definite amount (0.2 cc.) of heavy alcohol and various amount of benzoyl peroxide in an evacuated glass tube. The latter substance was added in order to obtain the polymer of various molecular weight. The heavy alcohol used for this experiment was prepared by mixing one volume of C_2D_5OD of 99.6% purity with five volumes of ordinary alcohol and the mixture was purified by the use of silver oxide until no silver mirror reaction was observed. After the sealed tube was heated for twenty hours at $120° \pm 1°$, the heavy alcohol was distilled off in vacuum and the remained polystyrene was dissolved in 5 cc. of purified benzene, in order to wash out the remaining alcohol. Then the benzene was similarly distilled off in vacuum and the remained polymer was heated in vacuum at 100° for 20 hours in order to expel the last trace of mechanically contained heavy alcohol as well as the other volatile substances such as the nonpolymerized styrene.

The larger part (about 0.6 g.) of the so purified polystyrene was then burnt in a stream of purified air and the excess density of the resulted water, which was carefully purified in a specially devised quartz apparatus, was determined by means of a small glass bouyancy balance. The limit of the error for the density determination was ± 1 p.p.m. The remaining part of the purified polystyrene was used for the determination of the molecular weight, which was carried out by the viscometric method. The specific viscosity η_{sp} of the solution in benzene of known concentration c expressed in mole/l. was measured by means of an Ostwald viscometer and the mean molecular weight $\bar{M}$ was calculated according to the Staudinger's relation:

$$\lim_{c \to 0} \eta_{sp}/c = K_m \bar{M}.$$

The constant K_m used for the calculation was determined by the osmometric method and found 1.2×10^{-4} when no benzoyl peroxide was added and 2.4×10^{-3} when benzoyl peroxide was added without regard to its quantity.

From these data we calculated the average

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[1] Preliminarily reported in *J. Chem. Soc. Japan*, **68**, 31, 45 (1947). The delay of the publication of the detailed report was due to the War.

[2] this Bulletin, **16**, 125 (1941).

number of heavy alcohol molecules attached to each molecule of polystyrene, which is denoted by N in Table 1, as well as the average number of heavy alcohol molecules attached to each gram of polystyrene, which is denoted by N' in the last column of the table. When we compare these two figures it will easily be seen that the average number of the alcohol molecules attached to each molecule of polystyrene N remains satisfactorily constant without regard to the molecular weight of the latter, so long as any quantity of benzoyl peroxide is added to the reaction mixture, while the number of alcohol molecules attached to each gram of polystyrene N' remarkably increases as the molecular weight of the latter decreases. This result indicates that the alcohol molecules are not attached uniformly on the polystyrene molecule but at a certain definite point of it.

Table 1

Polymerization of Styrene in Heavy Alcohol (Resulted polystyrene was heated in vacuum)

Experimental No.	Amount of benzoyl peroxide added, g.	Excess density of water, p.p.m.	Mean molecular weight of polystyrene, $\overline{M}$	N	$N' \times 10^{-6}$
1	0	3.0	54100	0.12	2.2
2	0	3.6	45600	0.12	2.6
3	0.005	7.2	12900	0.069	5.3
4	0.010	7.2	11400	0.059	5.1
5	0.020	9.6	8970	0.062	6.9
6	0.040	14.4	6240	0.064	10.2
7	0.040	15.3	5140	0.056	10.8
8	0·040	18.0	4570	0.059	12.9
9	0.100	21.1	3420	0.051	14.9

It will also be seen from Table 1 that the average number N of the alcohol molecules attached to each molecule of polystyrene definitely increases, when no benzoyl peroxide is added (see exp. No. 1 and 2). This result suggests to us that the point occupied by the alcohol molecule on the molecule of polystyrene can also be attached by the benzoyl peroxide molecule and the former is expelled out of the added place by the latter. The same result can also be seen more clearly from the experiments given in Table 2. In these experiments the polystyrene, which was prepared in heavy alcohol solution in the same way as above, was not heated in vacuum after the experiment. After it was dissolved in purified benzene and the latter was distilled off in vacuum at room temperature, however, the same procedure was repeated once more, because the experiments, which will be described later, showed that the polystyrene, which was prepared in heavy benzene, was found almost completely free from heavy hydrogen, when the polymer was treated in the same way as above, so that the mechanically attached heavy alcohol could also be assumed to be completely removed in this way.

Table 2

Polymerization of Styrene in Heavy Alcohol (Resulted polystyrene was not heated in vacuum but dried in vacuum at room temperature)

Experimental No.	Amount of benzoyl peroxide added, g.	Excess density of water, p.p.m.	Mean molecular weight of polystyrene, $\overline{M}$	N
1	0	25	60000	1.1
2	0	20	87400	1.2
3	0.005	13	22300	0.21
4	0.01	14	16000	0.16
5	0.04	33	6750	0.16
6	0.10	64	4250	0.19

When we compare the average number of alcohol molecules N attached to each molecule of polystyrene given in Table 1 and 2, we see that it is in the whole remarkably increased in the latter. This result can be accounted for by the assumption that some of the alcohol molecules which are chemically attached to the molecule of polystyrene are removed when the latter is heated in vacuum as it was the case in the experiments given in Table 1. But the more interesting fact which can be seen from Table 2 is that the number N becomes almost nearly unity, when no benzoyl peroxide is added to the reaction mixture (see exp. No. 1 and 2). From this result it may be concluded that an alcohol molecule is attached presumably at the starting point of the chain molecule of polystyrene, when the styrene is polymerized in alcoholic solution without adding benzoyl peroxide but the most part of such alcohol molecules is expelled out of its added place by the molecules of the benzoyl peroxide, when the latter substance is added to the reaction mixture.

Polymerization of Styrene in Heavy Benzene

The heavy benzene, benzene-d_1, used in the present experiment was prepared by heating the mixture of calcium benzoate and calcium deuteroxide after the method of Morita⁽³⁾:

$$C_6H_5COO\frac{1}{2}Ca+\frac{1}{2}Ca(OD)_2=C_6H_5D+CaCO_3.$$

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(3) N. Morita and T. Titani, this Bulletin, 10, 557 (1935).

In each experiment one cc. of so prepared heavy benzene was sealed together with one cc. of purified styrene in a glass tube and heated at 120° ± 1° for twenty hours. No benzoyl peroxide was added in some cases, while about 0.02 g. of it was added in other cases. After the heating, the content of the sealed tube was dissolved in five cc. of purified benzene. Then, in the first experiment (No. 1 in Table 3) the benzene was distilled off in vacuum and the remained polymer was heated in vacuum at 100° for five hours. In the second experiment the polymer, which remained after the distillation of benzene, was dissolved once more in benzene and then treated in the same way as in the first experiment. In the third experiment the content of the sealed tube was dissolved in benzene as in the case of the first experiment and the polymer which remained after the distillation of benzene was heated in vacuum at 100° for twenty hours. And in the last forth experiment the polymer was precipitated from its solution in benzene by the addition of purified alcohol and the same process was repeated two times. Then the precipitated polymer was heated in vacuum at 100° for twenty hours as in the case of the third experiment.

In every case the larger part of the purified polymer was burnt to water and its excess density was measured by a glass bouyancy balance. At the same time the remaining part of the polymer was used for the determination of mean molecular weight $\bar{M}$. And from these data the number of heavy benzene molecules, attached to each molecule of polystyrene was calculated. The figure N given in the last column of Table 3 represents this number.

Table 3

Polymerization of Styrene in Heavy Benzene

Experimental No.	Amount of benzoyl peroxide added, g.	Temperaturo and time of drying	Excess density of water, p.p.m.	Mean molecular weight of polymer, $\bar{M}$	N
1	0	100°C, 5hrs	7	55900	0.3
2	0	100°C, 5 〃	7	50100	0.3
3	0.02	100°C, 20 〃	−2	11700	0
4	0.02	100°C, 20 〃	−3	12400	0

From the result given in Table 3 it may be concluded that the last trace of the heavy benzene can be expelled out of the polystyrene when the latter is heated in vacuum at 100° for twenty hours. This result is very interesting when it is compared with that of heavy alcohol shown in Table 1, where it was found that a certain amount of heavy alcohol remained in the polystyrene, even if the polymer was heated in vacuum at 100° for twenty hours, when it was formed in the solution of heavy alcohol. The difference may be accounted for by the polar character of ethyl alcohol and the non-polar character of benzene. From the present result it can also be concluded that no hydrogen atom is exchanged between styrene and benzene when the former is polymerized in the solution of the latter.

Polymerization of Styrene Catalyzed by Heavy Benzoyl Peroxide

The heavy benzoyl peroxide used in the present experiment was prepared in the following way.

At first benzene-d_1 was prepared in the same way as in the preceding research by heating the mixture of calcium bonzoate and calcium deuteroxide. Then, the benzene-d_1 was converted into benzoyl-d_1-chloride by the use of oxalyl chloride:

$$C_6H_5D + (COCl)_2 = C_6H_4DCOCl + CO + HCl.$$

Heavy benzoyl peroxide was obtained by the action of hydrogen peroxide on this benzoyl-d_1-chloride:

$$\begin{aligned} &2C_6H_4DCOCl + H_2O_2 \\ &\quad = C_6H_4D\cdot CO\cdot O\cdot O\cdot CO\cdot C_6H_4D + 2HCl. \end{aligned}$$

Theoretically speaking, the so obtained benzoyl peroxide, therefore, must contain two deuterium atoms in each molecule. But the isotopic analysis showed that this number was little larger than two, namely 2.32. The discrepancy may be accounted for by some side reactions (exchange reaction), which occured in the first step of the reaction, viz. the preparation of heavy benzene, because its isotopic analysis showed a little larger deuterium content than the theoretical one.

In each case of the experiment, one cc. of styrene, which was purified directly before the experiment, was sealed together with 0.01 to 0.04 g. of heavy benzoyl peroxide in a glass tube and heated at 120° ± 1° for twenty hours. After the heating, the content of the glass tube was dissolved in about five cc. of purified benzene and to this solution purified alcohol was carefully added until no more polystyrene was precipitated. Then the precipitated polystyrene was once more dissolved in benzene. In most cases this procedure was repeated from two to three times, in order to make the polystyrene free from the mechanically adhered benzoyl peroxide as completely as possible.

The larger part of the purified polystyrene was then burnt to water and its excess density was determined by the use of a glass bouyancy balance. At the same time the remaining part of the polymer was used for the determination of the mean molecular weight $\overline{M}$, in the same way as described in the preceding research. The result of the experiment is shown in Table 4, where the excess density of water given in brackets is the corrected one, which was calculated from the directly observed one under the assumption that exactly two deuterium atoms were contained in each molecule of benzoyl peroxide and the number N given in the last column represents the average number of deuterium atoms contained in each molecule of the polystyrene, being calculated by the use of the above mentioned corrected value of excess density. But as this number is approximately unity, it may be concluded that just half a molecule of benzoyl peroxide is attached to each molecule of polystyrene, when it is taken into account that each molecule of benzoyl peroxide contains two deuterium atoms.

Table 4

Polymerization of Styrene Catalyzed by Heavy Benzoyl Peroxide

Experimental No.	Amount of benzoyl peroxide added, g.	Number of reprecipitation with alcohol	Excess density of water, p.p.m.	Mean molecular weight of polystyrene, $\overline{M}$	N
1	0.01	1	112(96)	19000	1.3
2	0.01	2	114(98)	17700	1.2
3	0.01	3	113(97)	19000	1.3
4	0.04	2	326(280)	8200	1.6

It follows therefore that the molecule of benzoyl peroxide is split into two equal parts and the so formed free radical $C_6H_5 \cdot CO \cdot O$- is attached to the starting point of the chain molecule of polystyrene.(4)

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(4) According to the literatures, which have recently fallen into the hands of the author, it became known to him that the same conclusion was achieved by many other authors. But as many of these researches were published during the War, they did not come to the author's knowlegde at the time, when the present research was made.