# The Effect of Electrostatic Field on the Polymerization of Styrene(1)

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It has been found previously by Yosida and one of the authors that no exchange reaction of hydrogen atoms occurs during the chain polymerization of styrene in its solution in heavy alcohol or heavy benzene.(2) It has been found further that a half of the molecule of benzoyl peroxide is attached at the starting point of the chain molecule of polystyrene, when it is prepared by the thermal polymerization of styrene in the presence of benzoyl peroxide as a polymerizing catalyst.(2) The same result has also been reported by many other authors.(3) It is also a well known fact that polystyrene can easily be decomposed by heating it at a comparatively low temperature and at this thermal decomposition it gives mainly unaltered monomer molecules of styrene. This fact suggests us that the bond linking the monomer molecules together in the chain is much weaker than the CH-CH$_2$ bond in each monomer molecule, because otherwise the chain polymer may give irregular decomposition products at its thermal decomposition just as in the case of the thermal cracking of long chain hydrocarbons.

From these experimental results we came to the conclusion that the chain molecule of

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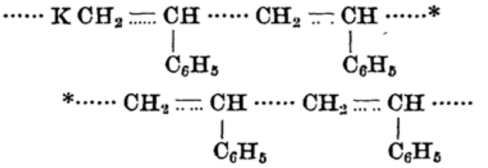
(1) Preliminarily reported in Scientific Papers from the Osaka University, No. 4, 1949.

(2) T. Yosida and T. Titani, this Bulletin **16**, 125 (1941); T. Yosida, *ibid.* **23**, 209 (1950).

(3) B. E. Tate, *J. Am. Chem. Soc.*, **65**, 517 (1943); P. D. Bartlett and J. Cohen, *ibid.*, **65**, 543 (1943); A. T. Blomquist, J. R. Johnson and H. J. Sykes, *ibid.*, **65**, 2446 (1943); H. F. Pfann, F. J. Salley and H. Mark, *ibid.*, **66**, 984 (1944); C. C. Price, R. W. Kell and E. Krebs, *ibid.*, **68**, 1686 (1946).

polystyrene may have a nature of a sort of free radical. The back bone chain of the molecule is linked together by incomplete single bonds $\cdots\cdots$ and incomplete double bonds $\overset{\cdots}{-}$ alternatively and at the starting point of the chain a fraction K of the molecule of the polymerizing catalyst is attached, so that at the end of the chain a weak free valence bond remains, as may be shown by the formula:



$$\cdots\cdots \mathrm{K\,CH_2} \overset{\cdots}{-} \underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}} \cdots\cdots \mathrm{CH_2} \overset{\cdots}{-} \underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}} \cdots\cdots *$$

$$*\cdots\cdots \mathrm{CH_2} \overset{\cdots}{-} \underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}} \cdots\cdots \mathrm{CH_2} \overset{\cdots}{-} \underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}} \cdots\cdots$$

By the incomplete single bond we mean such a bond that is more or less weaker than a normal single bond but is not necessarily a half bond. Similarly the incomplete double bond represents such a bond that is to a certain extent weaker than a normal double bond but is not necessarily a one and a half bond. Moreover, the fraction K of the catalyst molecule may be a free oxygen molecule dissolved in the sample or adsorbed on the wall of the reaction vessel or a fraction of the molecule of some unknown compounds unconsciously contained or formed in the reaction system, when no polymerizing catalysts are intentionally added, as it is the case for the so-called thermal polymerization. The former assumption that the free oxygen molecule plays the role of the polymerizing catalyst is so far plausible as the oxygen molecule having a nature of a free radical and having two non-paired electrons in a molecule. But in any case at the other end of the chain molecule a weak free valence bond always remains, so that the chain polymer must have a nature of a sort of free radical.(4) However, the free radical nature of the so formed chain molecule is largely minimized through the resonance between the free valence bond remaining at the end of the chain and many benzene nuclei attached to the chain, because the back bone of the chain is linked together through the conjugation of many incomplete double bonds. The situation somewhat resembles to the case of the triphenyl-methyl, whose molecule is stabilized through the resonance between the free valence bond which remained at the central carbon atom and three benzene nuclei attached to this carbon atom. In other words, the larger part of the cloud of the non-paired electron remaining at the end of the polymer chain is absorbed by many benzene nuclei attached to the chain, through a sort of conjugated double bond system. And as a result of this polarization of the electron cloud, the end of the chain molecule must be positively while the body of the molecule negatively polarized. Accordingly, when the degree of this polarization reaches a certain extent, the positively polarized end of the molecule must be pulled into the negatively polarized clew-formed body of the molecule and in this way the growth of the chain is stopped.

When this is the case, it may be possible to increase the length of the chain by applying an electrostatic field on the growing chain of the polystyrene, so as to pull out the hiding end of the chain out of the clew-formed molecular body and thus subject to further reaction. The present experiments showed that this is actually the case. The molecular weight of polystyrene, which was prepared by heating liquid styrene at 120° for three to four hours under the influence of the electrostatic field of 8,000 to 9,000 volt per cm. was found about 35 to 36% larger than that of the polystyrene formed under the same conditions but without the electric field.

The experiment was carried out in a small glass cell with a glass stopper, through which two platinum electrodes of the same size 0.9×0.9 cm. were introduced. The distance between the electrodes in the cell was 0.8 cm. Two such cells were constructed with due precautions to make their size and form as equal as possible. In each experiment, both cells were charged with same quantities (2 cc.) of purified styrene, and were placed side by side in an electrically heated air thermostat, the temperature of which was kept constant at 120° ± 2° throughout the experiment. To the electrodes of one cell an electrostatic field generated by a vacuum tube rectifier was applied, while the other cell served as a control test. Thus, two equal portions of the same styrene were separately but simultaneously heated at the same temperature, the one being under the influence of the electric field, while the other not. After three or four hours, the experiment was stopped, and the contents of the cells were separately dissolved in 20 cc. of purified benzene. Ten cc. each of the solutions were then subjected to the distillation in vacuum to make the polystyrene completely free from the non-polymerized monomeric

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(4) The possibility, that the chain starts without the help of any polymerizing catalyst, can not necessarily be excluded and in this case the resulted chain polymer must have a nature of biradical, having a free valence bond not only at the end but also at the head of the molecule. But as the following discussion is little influenced by this situation, we assume here that the chain polymer has a structure of monoradical.

styrene. The portions of the polystyrene were dissolved once more in a weighted amount of purified benzene and the molecular weight of the polymer was determined by measuring the osmotic pressure of this benzene solution using a denitrificated collodion membrane as a semipermeable septum. The results of the experiments are shown in Table 1, from which it can be seen that not only the degree but also the quantities of polymerization somewhat increase under the influence of the electrostatic field.

Table 1

Polymerization of Styrene under the Influence of Electrostatic Field

| No. of experiment | Experimental conditions | | Polymerized quantities, % | Molecular weight of polymer |
|---|---|---|---|---|
| | Voltage applied, per cm. | Duration, hrs. | | |
| 3 | 0 | 4 | 29.4 | 84,000 |
| | 9,000 | 4 | 33.0 | 114,000 |
| 4 | 0 | 3 | 22.0 | 85,000 |
| | 8,000 | 3 | 25.5 | 115,000 |

From the present results the same effect may also be expected for the other sorts of vinyl derivatives of the form R–CH=$CH_2$, so long as the side chain radical R has an unsaturated nature, for examples, –COOH, –$COOCH_3$, –OOC·$CH_3$, –Cl, –Br, –CN etc. Such experiments are now going on in our laboratory.

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