# The Increase of the Mean Molecular Weight of Polystyrene under the Influence of the Electrostatic Field

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In the preceding research(1) it has been found that not only the degree but also the quantities of polymerization increases when an electrostatic field is applied during the thermal polymerization of styrene. And this result has been accounted for by the assumption that the positively polarized end of the chain molecule of polystyrene is pulled out of its negatively polarized clew-formed body under the effect of the electrostatic field and in this way the rate of chain growth viz. the rate of addition of the monomer molecule to the growing end of the polymer molecule increases. But if this is the only effect of the electric field, the degree and the quantities of polymerization must increase at the same rate, so long as the rate of formation of the polymerization nuclei may not be greatly influenced by the electric field. As a matter of fact, however, it has been found in the preceding research that the rate of increase in the degree of polymerization is much larger than that in the quantities of polymerization. This result suggests to us that not only the rate of chain growth viz. the rate of addition of the monomer molecule to the polymer molecule but also the rate of coupling viz. the rate of combination of the polymer molecules with each other must increase under the influence of the electrostatic field. With this presumption we applied in the present research an electrostatic field on the solution of the already polymerized polystyrene and actually found that the mean molecular weight of the latter is remarkably increased by this process.

The apparatus used is generally the same as that was used in the preceding experiment except the form and construction of the electrodes. Instead of the square platinum electrodes, which were introduced vertically into the cell in the preceding experiment, two circular electrodes made of pure nickel were

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(1) T. Titani and G. Mesituka, this Bulletin, 23, 212 (1950).

introduced horizontally into the cell as is shown in Fig. 1. The diameter of the electrodes was made a little smaller than that of the inner diameter of the cell (*ca.* 2 cm.) and the vertical distance of the electrodes in the cell was about 1 cm.

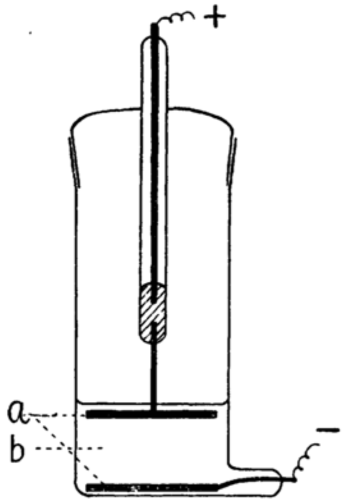

Fig. 1.—Reaction cell.
*a*, electrode; *b*, solution.

In each experiment the cell was charged with a solution of polystyrene in benzene, which was made by dissolving 0.3 g. of polystyrene in 3 cc. of purified benzene. The meniscus of the solution in the cell was adjusted a little higher than the upper surface of the upper electrode. The charged cell was then placed in an electrically heated air-thermostat and the outer ends of the electrodes were connected with the poles of a vacuum tube rectifier. In this way an electrostatic field of various strength was applied to the solution between the electrodes in the cell at a constant temperature. The temperature of the thermostat was kept constant at 60.0° ± 0.5° throughout the whole series of experiments. After 50 hours the experiment was stopped and the solution in the cell was poured out. A part of the so treated solution was then used for the determination of molecular weight, while the residual part was used for the determination of its viscosity. The determination of the molecular weight was carried out by the osmometric method in the same way as in the preceding research while that of the viscosity by means of an Ostwald's viscosimeter. The results of the experiments are summarized in Table 1, where the quantities with suffix 0 are referred to the original polymer, which was used in the whole series of the experiments.

Table 1

Effect of the Electrostatic Field of Various Strength on the Degree of Polymerization of Polystyrene in Benzene Solution

| Expt. | Experimental conditions | | | Mean molecular weight, $M$ | $\frac{\overline{M}}{\overline{M}_0}$ | Viscosity of solution, $\eta$ | $\frac{\eta}{\eta_0}$ |
|---|---|---|---|---|---|---|---|
| No. | Voltage applied, volt/cm. | Temperature, °C | Duration, hrs. | | | | |
| 1 | 0 | Room temp. | 0 | 148,000 | 1.00 | 0.115 | 1.00 |
| 2 | 500 | 60 | 50 | 150,000 | 1.02 | 0.115 | 1.00 |
| 3 | 1,000 | 60 | 50 | 160,000 | 1.08 | 0.114 | 0.99 |
| 4 | 2,000 | 60 | 50 | 164,000 | 1.11 | 0.114 | 0.99 |
| 5 | 4,000 | 60 | 50 | 169,000 | 1.14 | 0.114 | 0.99 |
| 6 | 8,000 | 60 | 50 | 240,000 | 1.62 | 0.116 | 1.01 |

It will be seen from the Table that the mean molecular weight $\overline{M}$ of the polystyrene really increases with the increasing strength of the applied electrostatic field. But quite unexpectedly the viscosity of the solution was found to remain almost constant notwithstanding the increasing molecular weight of the polymer. This interesting result may however be accounted for at least qualitatively in the following way. It has been assumed in the previous communication that a sort of residual valency remains at the end of the chain molecule of the polymer even in its stabilized state. If this is actually the case, the viscosity of the polymer solution will not only be affected by the size of the molecule, as so far being assumed, but also by the strength of the residual valency remaining at the end of each polymer molecule. The viscosity of the solution may increase with the increasing strength of the residual valency just as with the increasing size of the molecule. But as the strength of the residual valency clearly decreases when the size of the molecule increases through the coupling of the molecules under the influence of the electric field, both the effects on the viscosity of the solution may to some extent mutually be cancelled. This may be the reason why the viscosity of the solution does not change so much even when the mean molecular weight of the polymer remarkably increases under the effect of the electrostatic field.

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