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RADIATION-INDUCED IONIC POLYMERIZATION OF α-METHYLSTYRENE: AN APPLICATION OF THE HITTORF METHOD*)

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The radiation-induced ionic polymerization of α-methylstyrene has been studied by means of the Hittorf type conductivity measurement. For extremely dry samples it has been estimated that the chain transfer to monomer is about 10^5. It was concluded that freely moving electrons1) play an important role in the polymerization.

The importance of the anionic species in the radiation-induced polymerization of α-methylstyrene has been emphasized by one of the present authors for some time. Besides some evidences supporting the anionic mechanism,2) the more direct evidences are found to be as follows: anion radicals have been observed by pulse radiolysis with optical absorption measurements.3) Pulse radiolysis with electric conductivity4) has indicated that the reacting anionic species have much larger molecular weight than the monomer and even larger than the cationic species. Although these results support the contribution of anionic species to the radiation-induced polymerization of α-methylstyrene, the importance of that species has not been proved yet since the number of chain transfer during the polymerization has been estimated to be rather large5) in the reaction which is believed to be one of the characteristics of cationic polymerization.

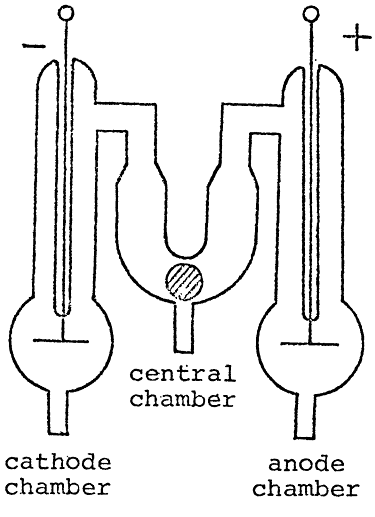

Fig. 1. Hittorf type cell.

Now we have applied the Hittorf Method in order to estimate the number of chain transfer to monomer both for the anionic and cationic polymerization as well as to measure the molecular weight of products of each polymerization independently.

As shown in Fig 1, dry2) α-methylstyrene contained in the cell was irradiated in the central chamber at the shaded part of a diameter of about 1 cm by X-rays for 45 minutes under the applied voltage of 1.7 kV. The electric current during irradiation has been measured by means of an electrometer. Soon after the irradiation reaction mixtures in each chamber were taken out of the cell separately and were poured into a large amount of methanol to precipitate the polymer for further analysis. Some of the results are shown in Table 1. The dose rates were 5.5×10^4 and 4.2×10^4 rad hr^{-1} and observed currents were 6.0×10^{-8} and 1.1×10^{-8} A respectively in experiments A and B.

Table 1. Characteristics of polymers formed in each chamber.

	experiment A		experiment B	
	number of moles	molecular weight	number of moles	molecular weight
anode chamber	2.0×10^{-4}	7.1×10^3	2.9×10^{-5}	7.1×10^3
cathode chamber	1.6×10^{-4}	6.6×10^3	2.9×10^{-5}	7.1×10^3
central chamber	8.8×10^{-4}	4.0×10^3	4.9×10^{-4}	5.4×10^3

The molecular weight has been measured by means of viscosity measurements. The polymerization in a sealed tube under the irradiation of ^{60}Co γ-rays has shown that G(polymer) is 3.5×10^3 for the same sample as used for in experiment A and 1.1×10^2 for the sample in experiment B. The ratio of the number of electronic charge collected at each electrode to the number of polymer molecules collected in anode chamber or cathode chamber during the reaction is about one to 10^5 in experiment A as well as in B. The value 10^5 may give a lower limit of the number of chain transfer to monomer since the contribution from the low molecular weight fractions which do not precipitate upon the addition of methanol is not considered, and the possible effect of impurities is also ignored. The examination of decay curve of the electric current at the end of the X-ray irradiation indicates that the mobility of the main charge carrier is in many orders of magnitude larger than that of ionic species measured by pulse conductivity measurements.4) The low yield of polymer in experiment B indicates that this sample contains large amount of impurities such as water in comparison with sample A. The smaller electric current observed in B during the X-ray irradiation suggests that the main charge carrier with a high mobility is trapped by impurities to suppress the electric current.

Under the present experimental condition, part of the anionic and the cationic species produced in the central chamber by the irradiation tend to drift toward anode and cathode respectively. While each species moves toward the respective electrode, it undergoes polymerization and termination by chain transfer to monomer and to impurities X and Y according to the following sheme:

$$\alpha\text{MS} \rightsquigarrow (\alpha\text{MS})^{\oplus} + e^{\ominus}$$

$$\begin{array}{lcl@{\qquad\qquad}lcl}
\alpha\text{MS} + e^{\ominus} & \longrightarrow & (\alpha\text{MS})^{\ominus} & (\alpha\text{MS})^{\oplus} + \alpha\text{MS} & \longrightarrow & (\alpha\text{MS})_2^{\oplus} \\
(\alpha\text{MS})^{\ominus} + \alpha\text{MS} & \longrightarrow & (\alpha\text{MS})_2^{\ominus} & (\alpha\text{MS})_2^{\oplus} + \alpha\text{MS} & \longrightarrow & (\alpha\text{MS})_3^{\oplus} \\
(\alpha\text{MS})_2^{\ominus} + \alpha\text{MS} & \longrightarrow & (\alpha\text{MS})_3^{\ominus} & & \vdots & \\
 & \vdots & & & & \\
(\alpha\text{MS})_n^{\ominus} + \alpha\text{MS} & \longrightarrow & (\alpha\text{MS})_n + (\alpha\text{MS})^{\ominus} & (\alpha\text{MS})_m^{\oplus} + \alpha\text{MS} & \longrightarrow & (\alpha\text{MS})_m + (\alpha\text{MS})^{\oplus} \\
(\alpha\text{MS})_n^{\ominus} + \text{X} & \longrightarrow & (\alpha\text{MS})_n + \text{X}^{\ominus} & (\alpha\text{MS})_m^{\oplus} + \text{Y} & \longrightarrow & (\alpha\text{MS})_m + \text{Y}^{\oplus}
\end{array}$$

The anionic polymerization starts when a monomer molecule catches a secondary electron which otherwise moves freely in the medium to become $(\alpha\text{MS})^{\ominus}$. It grows to polymer anion, $\sim\!\sim\!\alpha\text{MS}^{\ominus}$, until the electron moves to the other monomer molecule by jumping as $\sim\!\sim\!\alpha\text{MS}^{\ominus}\curvearrowright\alpha\text{MS}$ to form another monomer anion $(\alpha\text{MS})^{\ominus}$. Similarly, cationic polymerization starts when an electron is taken out of a monomer molecule to become $(\alpha\text{MS})^{\oplus}$. It also grows to polymer cation, $\sim\!\sim\!\alpha\text{MS}^{\oplus}$, until an electron from a monomer moves to it as $\sim\!\sim\!\alpha\text{MS}^{\oplus}\curvearrowleft\alpha\text{MS}$ to form another monomer cation $(\alpha\text{MS})^{\oplus}$. These jumping processes, we believe, are the main mechanism of the electric conduction. The jump of electrons may occur at any stage of chain growth. A simple calculation based on a conductivity experiment[4)] indicates that polymer ions would take several hundred seconds to reach anode or cathode chamber from the central chamber under the present experimental condition, having a negligible contribution to the total electric current observed. If we suppose that every ionic species of either charge grows to polymer with degree of polymerization $\overline{\text{DP}}\text{n}$ of about 60 as observed, the distance for an electron to jump would be in an average several thousand angstroms.

It has been suggested[5)] that the cationic mechanism predominates over the anionic one. One of the main pieces of evidence supporting for the cationic mechanism is the high efficiency of chain transfer to monomer which is believed to be unusual for anionic polymerization. We have shown that it is not the case. the chain transfer to monomer is as efficient in the anionic mechanism as in the cationic one.

Now the bulk polymerization can be understood to proceed while electrons move[1]) from anionic species to monomer and from monomer to cationic species. Any substances which can cause to reduce the mobility of the electrons either by scavenging or by any other mechanism will reduce the yield of polymers formed through anionic as well as cationic species. The present experimental results show that the contribution of anionic species to the polymerization is at least equal to that of cationic ones in α-methylstyrene. They suggest that the rate constant of propagation k_p is almost the same for anionic and cationic species if the life times of them are the same. If indeed k_p of cationic polymerization is larger than that of anionic one, the life time of anionic species is longer than that of cationic ones. It should be mentioned here that these arguments are also based on the assumption that every ionic species grows to polymer ions of $\overline{DP}n \simeq 60$.

Similar experiments show that the mechanism stated here for α-methylstyrene also can be applied to the radiation-induced polymerization of styrene.6)

References

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1) R. M. Minday, L. D. Schmidt, and H. T. Davis, J. Chem. Phys., 50, 1473(1969), ibid., 54, 3112(1971).

2) K. Hirota and M. Katayama, Annual Reprt JARRP., 5, 205(1963-1964).

3) M. Katayama, H. Yamazaki, Y. Ozawa, M. Hatada, and K. Hirota, ibid., 6, 269(1964-1965), M. Katayama, M. Hatada, K. Hirota, H. Yamazaki, and Y. Ozawa, Bull. Chem. Soc. Japan, 38, 851(1965), M. Katayama, H. Yamazaki, Y. Ozawa, M. Hatada, and K. Hirota, Nippon Kagaku Zasshi, 87, 37(1966).

4) M. Katayama, H. Yamazaki, and Y. Ozawa, Bull. Chem. Soc. Japan, 42, 2410(1969).

5) P. Ausloos, "Fundamental Processes in Radiation Chemistry," Interscience Publishers, New York, 1968, p. 580.

6) M. Katayama and S. Sawamura, to be published.

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