Radiation-Induced Polymerization of Water-Saturated Styrene in a Wide Range of Dose Rate

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Synopsis

Radiation-induced polymerization of water-saturated styrene (water content 3.5×10^{-2} mole/liter) was carried out in a wide range of dose rate between 1.2×10^3 and 1.8×10^7 rad/sec, and compared with the polymerization of the moderately dried styrene (water content 3.2×10^{-3} mole/liter). Molecular weight distribution curves of the polymerization products showed that they were generally consisted of four parts, namely, oligomers, radical, cationic, and super polymers. Contributions of the four constituents to the polymerization and the number average degrees of polymerization (DP) of the four kinds of polymers were calculated by the graphical analysis of the curves. The rate of radical polymerization and DP of radical polymers are independent of the water content; the dose rate dependences of the polymerization rate and DP agree with the well known square root and inverse square root laws, respectively, of the radical polymerization of styrene. The rate of ionic polymerization is directly proportional to the dose rate, but it decreases, at a given dose rate, inversely proportional to the water content of styrene. DP of ionic polymer is independent of the dose rate but decreases with increasing water content. The super polymer of DP about 10^4 is not formed in the case of the moderately dried styrene. G values for the initiating radical and ion formation are calculated to be, independently of the dose rate and water content, 0.66 and 0.027, respectively. It was suggested that oligomer was formed in the early stage by the interaction of cation with anion and only those cations which had survived underwent polymerization.

INTRODUCTION

A kinetic equation was derived in the previous paper[1] for the radiation-induced polymerization of styrene under the assumption that both radical and cationic polymerizations take place concurrently throughout the whole range of the dose rate of radiation and the water content of the styrene. The equation enables us to calculate rates of the total, radical, and cationic polymerization at a given dose rate and water content. The analysis of the polymerization products by gel permeation chromatography (GPC) showed a satisfactory agreement with the calculated values of the contributions of the radical and cationic mechanisms in the polymerization.

The present paper is concerned with radiation-induced polymerization of water saturated styrene (water content 3.5×10^{-2} mole/l.) because the previous results were obtained chiefly by experiments of the moderately dried styrene (water content 3.2×10^{-3} mole/l.) and styrenes of higher water content are not only interesting from the applicational point of view but also important to get quantitative informations on the chain transfer and termination of the polymerization.

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EXPERIMENTAL

Essentially the same combined technique of kinetic and GPC analyses as in the previous paper was employed. In addition to Co-60 source and a Van de Graaff accelerator which were used in the previous experiments, a new high-dose electron accelerator (HDRA) of rectified transformer type was used for the irradiation.[2] The specification of the accelerator is as follows: the acceleration voltage between 300 and 800 kV, the beam current between 10 μA and 25 mA, and the maximum scanning width 45 cm. The highest dose rate attained is found to be ca. 2×10^7 rad/sec by the cellulose tri-acetate dosimeter.

Time necessary for the polymerization by irradiation at the highest dose rate is only a few seconds, because we are interested for the present, only in the initial stage of polymerization, i.e., a few percent of conversion; even in this case about 10°C temperature rise was observed due to insufficient cooling by an electric fan. In the present paper the rise in temperature was neglected because it is known that the influence of temperature is small for the cationic polymerization of styrene, which plays a dominant role in the polymerization at a very high dose rate.

RESULTS

Polymerization of the Moderately Dried Styrene

Polymerization of the moderately dried styrene was carried out by use of HDRA up to a dose rate I of ca. 2×10^7 rad/sec, that is a dose rate about two orders of magnitude higher than the previous experiments. It is expected that it enables us a direct comparison with polymerization of water saturated styrene in a wide range of the dose rate. The rate of total polymerization R_p at various dose rates are shown in Table I. Figure 1 shows dependence of R_p on the dose rate; it contains not only the results of the present experiments but also the previously reported values, which were obtained by irradiation with electron beams from a Van de Graaff accelerator and gamma rays from a Co-60 source.

TABLE I
Rate, Degree of Polymerization, and Number of Polymer Molecules for Radical and Cationic Polymerization of Moderately Dried Styrene

| Dose rate I (rad/sec)	2.4×10^4	1.1×10^5	4.8×10^5	8.4×10^6
Rate of Polymerization (mole/l./sec)				
Total R_p	1.93×10^{-3}	7.52×10^{-3}	3.59×10^{-2}	3.23×10^{-1}
Radical R_r (expt.)	2.22×10^{-4}	5.65×10^{-4}	—	—
Radical R_r (calc.)	(2.79×10^{-4})	(5.96×10^{-4})	1.24×10^{-3}	5.22×10^{-3}
Ionic R_i (expt.)	1.59×10^{-3}	6.63×10^{-3}	3.35×10^{-2}	3.01×10^{-1}
Oligomeric $R_{\text{olig.}}$	5.60×10^{-5}	2.93×10^{-4}	1.08×10^{-3}	1.68×10^{-2}
Degree of polymerization				
Radical DP_r (expt.)	30	20	—	—
Radical DP_r (calc.)	31	16.5	8.0	1.9
Ionic DP_i (expt.)	500	510	445	355
Number of polymer molecules (mole/l./rad) $\times 10^{10}$				
Radical (expt.)	3.1	2.6	—	—
Radical (calc.)	(3.75)	(3.3)	3.2	3.2
Ionic (expt.)	1.35	1.2	1.55	1.0
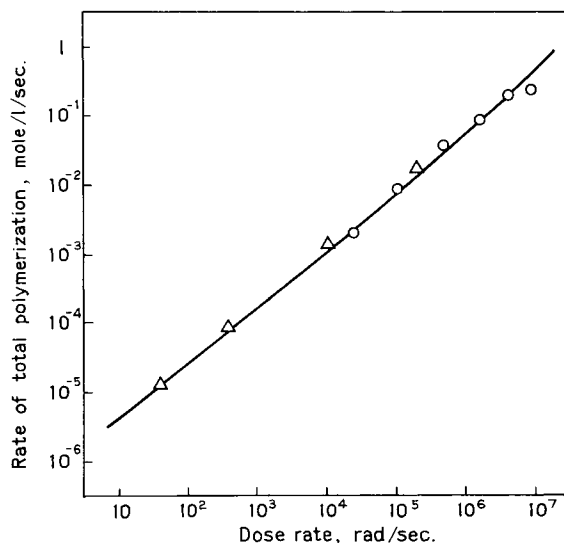
Fig. 1. Dose-rate dependence of the total polymerization rate of moderately dried styrene: (O) present paper; (△) previous paper.

As may be seen from Figure 1, all experimental points lie on a line. It suggests that nothing new occurs at a dose rate two orders of magnitude greater than in the previous report.

GPC curves for the molecular weight distribution of the polymerization products are shown in Figure 2.

The curves for the four different dose rates are similar to one another; they have a prominent peak due to cationic polymerization and additional two peaks of oligomers. To detect the presence of radical polymers from these curves is apparently difficult, however, undistinct peaks which are presumably due to radical polymers are found in curves a and b. Thus in a similar manner as in the previous cases we can divide the curves into three areas corresponding to oligomers, radical polymers, and ionic polymers. The rates of oligomer formation and radical and ionic polymerizations are calculated by multiplication of R_p with the fraction of the contributions of the three different polymers and the values are shown in Table I as R_{olig} (expt.), R_r (expt.), and R_i (expt.), respectively.

In the case of higher dose rate such as 4.8×10^5 and 8.4×10^6 rad/sec, the contribution of the radical polymerization is so small that it cannot give a distinct peak, therefore eq. (1), which had been derived in the previous report was used to find the rates of radical polymerization. The calculated values of R_r are shown in Table I as R_r (calc.). In the case of the polymerization at the lower dose rates both experimental and calculated values are obtained and shown in the table. The agreement is satisfactory:

$$R_r = B_r I^{1/2} = 1.8 \times 10^{-6} I^{1/2} \tag{1}$$

The rate of total polymerization is the sum of the oligomer formation and radical and ionic polymerizations; thus, we may write

$$R_p = R_{olig} + R_r + R_i \tag{2}$$

Throughout the whole dose rate range in the present experiment, ionic polymerization is dominant and we may simply assume that R_p is practically equal
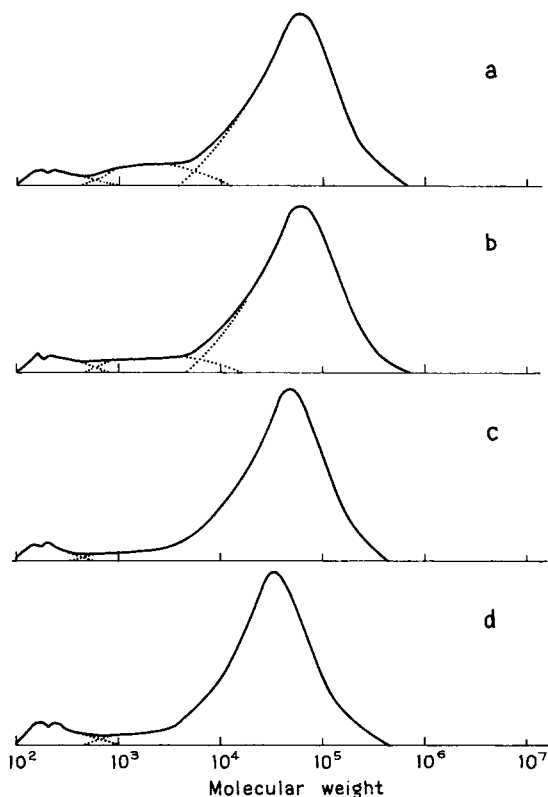
Fig. 2. GPC curves of polymers from the moderately dried styrene at various dose rates (rad/sec): (a) 2.4×10^4; (b) 1.1×10^5; (c) 4.8×10^5; (d) 8.4×10^6.

to R_i; we have, however, calculated for better approximation R_i (expt.) by subtraction of R_r (calc.) and R_{olig} from R_p.

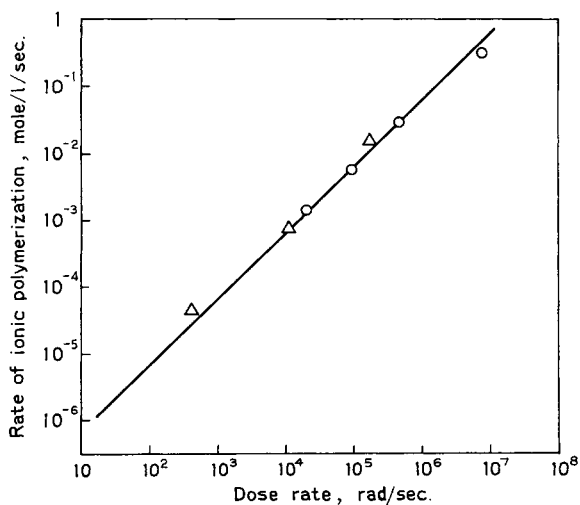Figure 3 shows the dependence of the rate of ionic polymerization on the dose

Fig. 3. Dose-rate dependence of the ionic polymerization rate of the moderately dried styrene: (O) present paper; (△) previous paper.

rate. It may be seen that it is directly proportional to the dose rate. The proportionality is just predicted in the previous paper.[1]

There is no problem to know DP's of ionic polymers, because the prominent peaks of the curves may be regarded to be practically equal to the number average degree of polymerization of the ionic polymers. In the case of the radical polymerization at the lower dose rates [curves 1(a) and 1(b)] where the division of curves into the three parts was possible, peaks of the graphically obtained curves for the radical polymerization were used as number average DP's. The DP's obtained from the GPC curves are designated as DP(expt.) in Table I. At the higher dose rates [curves 1(c) and 1(b)], where the division of the GPC curves was difficult, the number average degree of polymerization was obtained by extrapolation of the curve for the relation between the number average degree of polymerization and the dose rate based upon the results in the previous paper (Fig. 4). The values are shown in Table I as DP_r(calc.)

The rate of polymerization (radical or ionic) divided by the product of the dose rate and the number average degree of polymerization gives the number of polymer molecules produced per liter per rad. The calculated values are also shown in Table I. It is important that neither the number of radical nor the number of ionic polymers changes with dose rate. The average number of radical polymer molecules was 3.4×10^{-10} mole/l./rad in the previous report, while in the present experiment 3.0×10^{-10} mole/l./rad; the agreement is good. On the other hand, the agreement was rather poor between the average number of ionic polymer molecules obtained in the present work (1.3×10^{-10}) and that obtained in the previous one (2.3×10^{-10}), possibly because the latter was the average of three values scattered between 1.6×10^{-10} and 2.8×10^{-10}.

Polymerization of the Water-Saturated Styrene

Polymerization of the water-saturated styrene was carried out under the employment of the same cell and radiation sources as in the case of the moderately dried styrene. The dose rate covers a range between 1.2×10^3 and 1.8×10^7 rad/sec. The experimental rates of total polymerization are given in Table II, and Figure 5 shows a plot of the dependence of the rate of polymerization on the dose rate. The figure contains also values at lower dose rates, which are neither contained in Table I nor reported previously. Although the points are scattered, it is clear that all points lie on a line.
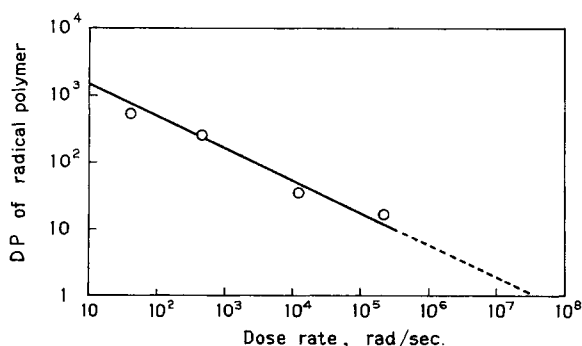

Fig. 4. Dose-rate dependence of degree of polymerization of radical polymers on the basis of the experiments in the previous paper on the moderately dried styrene.

TABLE II

Rates of Polymerization, Contributions of Various Mechanisms, Degrees of Polymerization, and Number of Polymer Molecules for the Polymerization of Water-Saturated Styrene

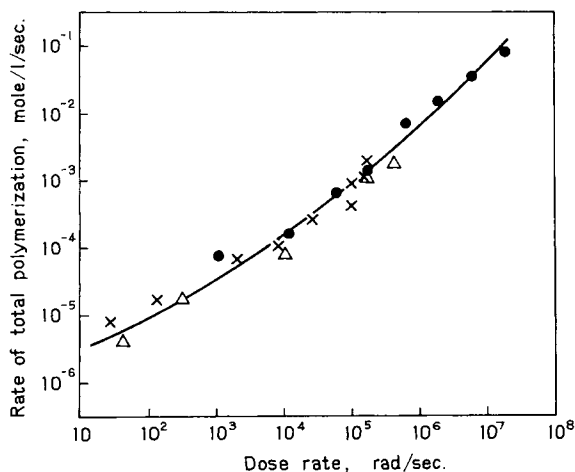| Dose-rate (rad/sec)	1.2×10^3	1.2×10^4	6.0×10^4	1.8×10^5	6.0×10^5	1.8×10^6	6.0×10^6	1.8×10^7
Rate of polymerization (mole/liter/sec)								
Total R_P	7.59×10^{-5}	2.68×10^{-4}	6.10×10^{-4}	1.49×10^{-3}	6.53×10^{-3}	1.42×10^{-2}	3.39×10^{-2}	8.44×10^{-2}
Radical R_r	5.81×10^{-5}	1.71×10^{-4}	3.25×10^{-4}	6.24×10^{-4}	1.80×10^{-3}	4.52×10^{-3}	5.22×10^{-3}	1.29×10^{-2}
Ionic R_i	8.50×10^{-6}	6.11×10^{-5}	1.57×10^{-4}	5.88×10^{-4}	3.43×10^{-3}	6.49×10^{-3}	2.17×10^{-2}	5.29×10^{-2}
Oligomeric R_{olig}	9.4×10^{-6}	2.39×10^{-5}	6.28×10^{-5}	1.68×10^{-4}	8.03×10^{-4}	2.12×10^{-3}	5.12×10^{-3}	1.17×10^{-2}
Super polymer R_{sup}	—	1.17×10^{-5}	6.53×10^{-5}	1.11×10^{-4}	4.96×10^{-4}	1.08×10^{-4}	1.83×10^{-3}	7.26×10^{-3}
Contributions of various mechanisms (%)								
Radical	76.9	63.9	53.3	41.9	27.6	31.8	15.4	15.3
Ionic	11.2	22.8	25.8	39.4	52.5	45.7	64.1	62.2
Oligomeric	12.4	8.9	10.3	11.3	12.3	14.9	15.1	13.8
Super polymer	—	4.4	10.7	7.5	7.6	7.6	5.4	8.6
Degree of polymerization								
Radical DP_r	130	52	14	12	9.5	9.5	9	8
Ionic DP_i	—	155	120	120	155	110	155	155
Super $DP_{sup} \times 10^{-3}$	—	8.0	8.2	7.6	7.6	7.6	7.3	9.6
Number of polymer molecules (mole/liter/rad) $\times 10^{10}$								
Radical	3.74	2.74	3.87	2.89	3.15	2.74	(0.96)	(0.90)
Ionic	—	0.33	0.22	0.27	0.36	0.33	0.23	0.19

Fig. 5. Dose-rate dependence of the total polymerization rate of the water-saturatèd styrene: (●) present paper; (△) unpublished values; (×) former experiment with conventionally purified styrene.

It is of interest to check the rate of polymerization of the conventionally purified styrene. The present authors carried out 15 years ago[3] radiation-induced polymerization of a conventionally purified styrene in a dose rate range between 1 rad/sec and 1×10^5 rad/sec. Styrene was at first washed with an aqueous solution of sodium hydroxide to remove the inhibitor, then dried with anhydrous sodium sulfate, and finally distillation was repeated twice. The distilled styrene was frozen with liquid nitrogen, the freeze-and-thaw on a vacuum line was repeated at least three times, and then transferred into a thin-wall|glass|test|tube for the irradiation either with γ rays from a Co-60 source or electron beams from a Van de Graaff accelerator. The dose rate dependence of the polymerization rate is additionally shown in Figure 5. It is seen clearly that nearly all experimental points fall on the curve. We may, therefore, conclude that the conventionally purified styrene contains water in an amount close to the saturation.

Determination of the molecular weight distribution of the polymerization products was also carried out and four examples of the GPC curves are shown in Figure 6.

When the curves 6(b), 6(c), and 6(d) are compared with curves in Figure 2, it is observed that the curves in Figure 6 are more complicated than those in Figure 1. It is noteworthy that the amount of oligomer is larger and a new peak with a molecular weight of about 10^6 appears apart from other peaks. The new polymer will be called hereafter super polymer. Therefore, we have to assume that the polymerization consists of oligomer formation, radical, ionic, and super polymerization. We use, instead of eq. (2), the following equation:

$$R_p = R_{\mathrm{olig}} + R_r + R_i + R_{\mathrm{sup}} \tag{3}$$

Where it was possible the GPC curves were divided graphically into the four parts, and each contribution for the polymerization was calculated; R_p times the fraction of contribution is equal to the respective polymerization rate. The calculated values also are shown in Table II. There is some difficulty for the graphical division of oligomers and radical polymers in the case of polymerization at higher dose rates, not only because the amount of radical polymer is small but
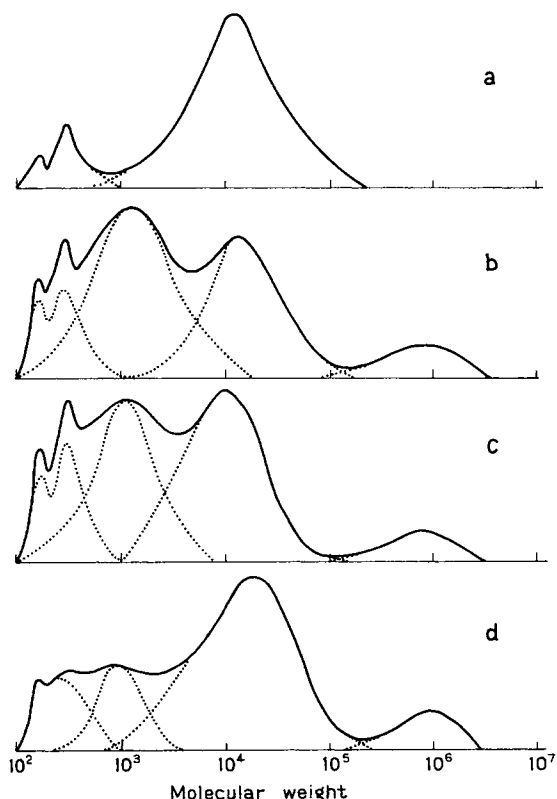
Fig. 6. GPC curves of polymers from the water-saturated styrene at various dose rates (rad/sec): (a) 1.2×10^3; (b) 1.8×10^5; (c) 1.8×10^6; (d) 1.8×10^7.

also because the *DP* of this range is between 1 and 10 and it seems to be unsuitable to draw a smooth continuous curve for the radical polymers; further we can not forget that some amount of radical polymer of very low molecular weight is lost at the determination of polymers by the monomer-evaporation method as reported in the previous paper. For the present we do not want to go into this problem.

At the lowest dose rate the GPC curve [see curve 6(a)] is rather simple; it consists of oligomer and radical polymer of higher molecular weight.

Dependence of the radical polymerization rate of the water saturated styrene on the dose rate is shown in Figure 7 along with the rates of the moderately dried styrene in Table I and the values in the previous report. It is noteworthy that all points lie on a straight line, which shows square root relationship between the polymerization and dose rate. Therefore, it may be regarded that the presence of a large amount of water in the system has practically no influence on the radical polymerization even at higher dose rates. It proceeds quite independently of the oligomer, ionic, and super polymer formation.

Figure 8 shows a plot of ionic polymerization rate vs. dose rate; all experimental points lie on a straight line, which shows direct proportionality of the rate of ionic polymerization on the dose rate. If we compare the straight line with that for the moderately dried styrene (Fig. 3), we see clearly that the ionic polymerization rate of the wet styrene is about one tenth of the value for the moderately dried styrene. This is that, what was predicted in the previous paper, i.e., the rate of ionic polymerization is affected by water as the following equation shows:
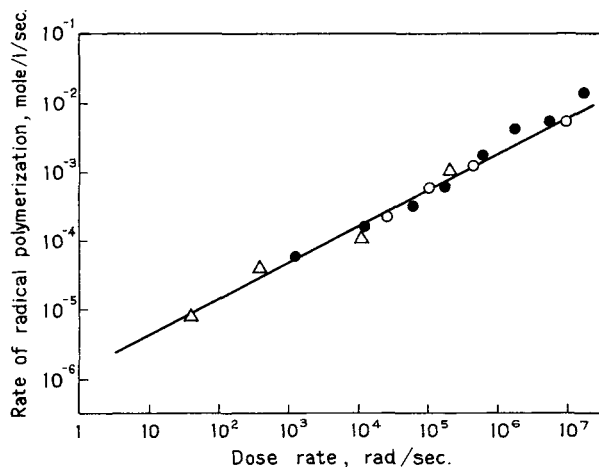
Fig. 7. Dose-rate dependence of the radical polymerization rate of styrenes: (O) moderately dried styrene; (●) water-saturated styrene; (△) moderately dried styrene in the previous paper.
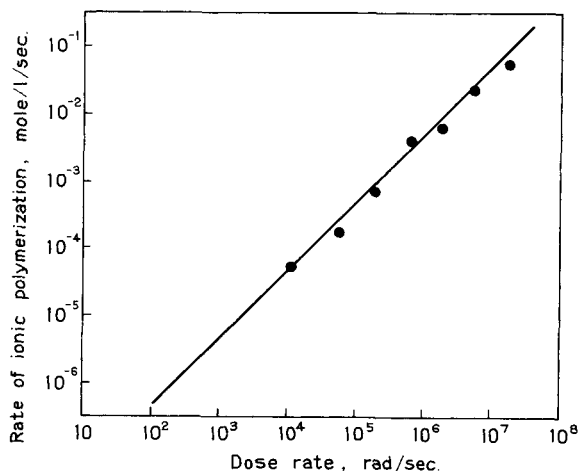

Fig. 8. Dose-rate dependence of the ionic polymerization rate of the water-saturated styrene.

$$R_i = I/[H_2O] \tag{4}$$

According to the equation, the ionic polymerization rate is inversely proportional to the water content. The ratio of the water content of water saturated to moderately dried styrene is $(3.5 \times 10^{-2}$ mole/l.$)/(3.2 \times 10^{-3}$ mole/l.$) = 10.9$. The experimental value of the ratio of polymerization rates of the styrenes of the two different water content agrees satisfactorily with inverse ratio of the water contents of the styrenes. We will come back to this problem later.

From GPC curves we can find number average degrees of polymerization of each polymer species. Peaks of the curves were regarded to be the number average molecular weight, because the calculated number average is practically the same as to the peak according to our calculation. The degrees of polymerization shown in Table II are values corresponding to the peaks. Degree of polymerization of radical polymers is shown in Figure 9 along with the experimental values for the moderately dried styrene. In this case also the points for the styrenes of different water content fall, up to a dose rate of ca. 10^6 rad, on a
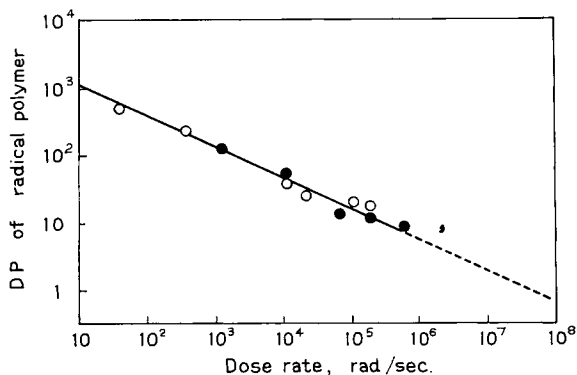
Fig. 9. Dose-rate dependence of degree of polymerization of radical polymers from moderately dried (O) and water-saturated (●) styrene.

straight line, which shows inverse square root proportionality of the degree of polymerization on the dose rate. This is in good accordance with the kinetic study of the rate of radical polymerization. At higher dose rates the drop of the degree of polymerization is much smaller than it is expected from the extrapolation of the straight line. It may be due to the already mentioned difficulty of drawing curves for the oligomer and radical polymer of very low molecular weight. Further studies of oligomers and very low molecular weight polymers are now being carried out.

In the case of ionic polymers, the degree of polymerization is almost constant throughout the whole range of the dose rate and much smaller than ionic polymers obtained from the moderately dried styrene; the quantitative discussion will be done in the following section.

Number of polymer molecules formed in mole/l./rad was further calculated and also given in Table II. In both the radical and ionic polymers the number of polymers was constant throughout the whole range of radiation dose rate as in the case of the moderately dried styrene. This was the most important experimental conclusion obtained in the previous report and is confirmed in the case of the water saturated styrene.

Experimental results of oligomer and super polymer are also listed in Table II. Figure 10 shows dependence of the rates of formation of oligomer and super polymer on the dose rates, and it is seen that the exponents of the dependence are between 0.7 and 0.8

DISCUSSION

The radiation chemical yield is expressed by a G value, which means number of polymer molecules produced or changed per 100 eV absorbed energy. In the radical polymerization of styrene in bulk, it is a well established fact, that the termination mechanism is a coupling of two growing chains and that no chain transfer takes place under ordinary experimental condition. That this is also true in the case of radiation induced polymerization at lower dose rates is known at least since 1962.[4] It was shown in the previous and present papers that the radical polymerization takes place up to a very high dose rate of about 10^7 rad/sec with the same mechanism as in the case of well investigated dose rate range. It is further noteworthy that other reactions such as ionic polymerization, oligomer
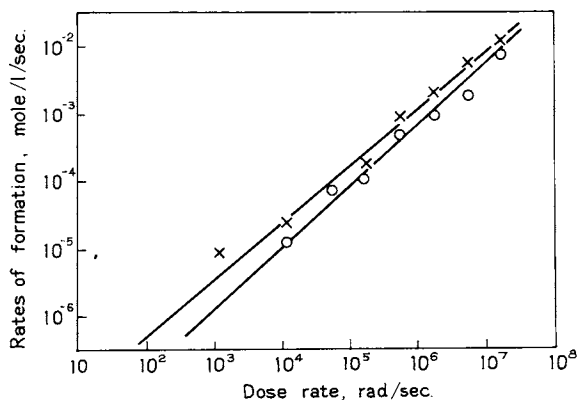
Fig. 10. Dose-rate dependences of the formation of super polymer (O) and oligomer (X) in the water-saturated styrene.

formation, and super polymerization, which become remarkable at higher dose rates and water contents, do not affect the rate and degree of radical polymerization.

According to the mechanism of radical polymerization of styrene in bulk, one stable polymer molecule is formed from two growing radicals. The relation between G value for the initiating radical G_r, the rate of radical polymerization R_r, and the degree of polymerization of radical polymers DP_r, can be written as follows:

$$R_r/DP_r I = 10 \; G_r d\varphi/2N = \text{const.} \tag{5}$$

The left-hand side of the equation is nothing other than the number of radical polymer molecules produced in mole/l./rad. The values have already been shown in Tables I and II. N, d, and φ are Avogadro's number, density of styrene, and a numerical factor for normalizing the radiation energy, respectively.

The average values of number of radical polymers in the previous and present paper for the moderately dried styrene and for the water saturated styrene in the present paper are 3.4×10^{-10}, 3.0×10^{-10}, and 3.2×10^{-10}, respectively; therefore the respective G_r are calculated to be 0.72, 0.64, and 0.68.

The ionic polymerization is a little more complicated than the radical polymerization because the stable polymer molecules are formed not only by the termination but also by transfer. The rate of ionic polymerization is written

$$R_i = k_{pi}[P^+][M] \tag{6}$$

where k_{pi}, $[P^+]$, and $[M]$ are rate constant of ionic polymerization and concentrations of growing chain and monomer, respectively. The rate of initiating ion formation can be expressed as

$$R_{ii} = (10 \; G_i d\varphi/N)I \tag{7}$$

where G_i, d, φ, and N are G value for the initiating ion formation, density of styrene, numerical factor for normalizing radiation energy, and Avogadro's number, respectively.

The termination is assumed to take place as a reaction of the growing chain and water

$$P^+ + H_2O \rightarrow P + \text{fragment}$$
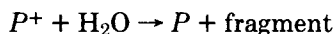
The rate of termination is

$$-\frac{d[P^+]}{dt} = k_{tx}[P^+][H_2O] \tag{8}$$

where k_{tx} is the rate constant of termination.

Assuming a stationary state, the following relation is obtained from eqs. (7) and (8):

$$[P^+] = (10\,G_i d\varphi/k_{tx}[H_2O]N)I \tag{9}$$

Putting the relation of eq. (9) into eq. (6), we get

$$\frac{R_i}{I} = \frac{k_{pi}}{k_{tx}}\frac{10\,G_i d\varphi}{N}\frac{[M]}{[H_2O]} \tag{10}$$

On the right-hand side of the above equation all values are constants except the concentration of water, because we are concerned in this paper only with the initial stage of polymerization. Consequently, R_i/I does not change with the dose rate as long as the water content is kept constant. It has already been shown in Figures 3 and 8 that R_i is directly proportional to the dose rate not only in the moderately dried but also in water saturated styrene, which is in accordance with the above equation. It is expected from eq. (10) that R_i/I is inversely proportional to the water content of styrene. The average values of R_i/I for the water saturated and moderately dried styrene are 3.84×10^{-9} and 5.88×10^{-8}, respectively; therefore, the ratio is calculated to be 1/15.3, whereas the ratio of the water contents is 10.9. The inverse proportionality holds approximately for the experimental results. The small deviation from the theory may be possibly due to the difficulty of precise control and determination of the water content.

The rate of the stable ionic polymer formation is the sum of the chain termination shown as eq. (8) and transfer to monomer:

$$\text{the rate of stable ionic polymer formation} = k_{tx}[P^+][H_2O] + k_{tm}[P^+][M] \tag{11}$$

The second term of the right-hand side of the equation is the rate of transfer to monomer and k_{tm} its rate constant. Equation (6) divided by eq. (11) is the DP of the ionic polymer and we obtain the following relation as the reciprocal of DP_i:

$$\frac{1}{DP_i} = \frac{k_{tm}[M] + k_{tx}[H_2O]}{k_{pi}[M]}$$

$$= \frac{k_{tm}}{k_{pi}} + \frac{k_{tx}[H_2O]}{k_{pi}[M]} \tag{12}$$

Equation (12) shows that DP_i decreases with increasing water content but is independent of the dose rate. The experimental values of DP_i in Tables I and II also decrease with the water content and are practically independent of the dose rate. The average values of DP_i of the moderately dried and water saturated styrenes are 453 and 139, respectively. Under employment of these values and eq. (12), the following values were found for the ratios of various reaction constants: $k_{tm}/k_{pi} = 1.70 \times 10^{-3}$, $k_{tx}/k_{pi} = 1.37$, and $k_{tm}/k_{tx} = 1.24 \times 10^{-3}$.

Number of ionic polymer molecules produced from one initiating ion is ex-

pressed with the following equation:

$$\frac{k_{tm}[M] + k_{tx}[H_2O]}{k_{tx}[H_2O]} = 1 + \frac{k_{tm}}{k_{tx}}\frac{[M]}{[H_2O]}$$

$$= 1 + 1.24 \times 10^{-3}\frac{[M]}{[H_2O]} \qquad (13)$$

The number of ionic polymer molecules from one initiating ion for the moderately dried and water-saturated styrenes are calculated to be 4.37 and 1.31, respectively. Roughly speaking, most of the stable ionic polymers are formed by termination with water in the water-saturated styrene, whereas in moderately dried styrene, stable polymers are formed by chain transfer to monomer.

The average number of ionic polymer molecules is calculated from the individual numbers shown in Tables I and II. The average divided by the number of ionic polymers produced from one initiating ion gives the number of the initiating ions; and hence, by eq. (7), G_i of the initiating ion formation is calculated and shown in Table III.

It may be seen from the table that practically the same number of the initiating ions is produced by a given radiation dose independent of the water content of styrene, and the mean G_i is 0.027. We have proposed the theory of radiation-induced polymerization of styrene under an assumption that the G value for the formation of the initiating ion is independent of the dose rate of irradiation and the water content of styrene. The quantitative experimental proof is provided by the above results.

In conclusion, we discuss the overall mechanism of the radiation-induced polymerization of styrene. The first step is assumed simply to be the formation of cation radical[5]:

$$M \rightarrow {}^+M\cdot + e \qquad (14)$$

The cation radical might grow by radical and cationic mechanism to form dimer cation radical ${}^+M\cdot_2$, then trimer cationic radical, and so on. This type of growing is, however, excluded from the experimental results, that radical and ionic polymers are obtained separately by GPC.

The next important step is the formation of separate radical and cation by the reaction of the monomeric cation radical with the monomer

$$^+M\cdot + M \rightarrow M^+ + M\cdot \qquad (15)$$

If we assume that these primary radicals and cations are initiating radicals and ions, the G values for the formation of initiating radical and cation should be the same. G_r and G_i found in the present study are, however, 0.66 and 0.027, respectively. This means that only about 4% of the primary cations contribute

TABLE III
Average Numbers of Polymer Molecules, Initiating Ions, and G_i Values in the Ionic
Polymerization of the Styrenes

Styrene	Average number of ionic polymers (mole/l./rad) $\times 10^{10}$	Average number of initial ions (mole/l./rad) $\times 10^{11}$	G_i (Number of initial ions per 100 eV) $\times 10^2$
Moderately dry	1.28	2.8	2.98
Water saturated	0.28	2.2	2.34

TABLE IV
Calculation of the G Value for the Formation of the Oligomer

Styrene	Dose rate (rad/sec)	Number of monomer used for the formation of oligomer (mole/liter/rad)	G_{olig} Number of oligomer per 100 eV
Moderately dry	2.4×10^4	2.33×10^{-9}	1.06
	1.1×10^5	2.66×10^{-9}	1.21
	4.8×10^5	2.25×10^{-9}	1.02
	8.4×10^6	2.0×10^{-9}	0.91
			Average 1.05
Water saturated	1.2×10^3	(7.8×10^{-9})	—
	1.2×10^4	1.99×10^{-9}	(0.90)
	6.0×10^4	1.05×10^{-9}	0.48
	1.8×10^5	0.93×10^{-9}	0.42
	6.0×10^5	1.34×10^{-9}	0.61
	1.8×10^6	1.17×10^{-9}	0.53
	6.0×10^6	0.85×10^{-9}	0.39
	1.8×10^7	(0.65×10^{-9})	—
			Average 0.49

to the initiation. The reason for the insufficient initiation of the primary cation is probably that most of the primary cation is consumed in the formation of the oligomer. As pointed out in the previous report, there is no doubt that the formation of the oligomer is closely connected with the cationic polymerization, because the oligomer is formed whenever cationic polymerization is remarkable in the reaction.

Now we wish to calculate the G value of the formation of initiating active species for the oligomer. The rate of oligomer formation R_{olig} is already given in Tables I and II; R_{olig} divided by I is the amount of monomer used for the formation of the oligomer in mole/liter/rad. The calculated values for the moderately dried and water-saturated styrenes at various dose rates are shown in Table IV; it is seen that in both the cases R_{olig}/I is independent of the dose rate. The calculated value divided by the degree of polymerization of the oligomer DP_{olig} gives the number of oligomer molecule produced in mole/liter/rad. As already mentioned there is some difficulty to know the effective value of DP_{olig}; however, we find in all GPC curves two more or less distinct peaks in the oligomer region corresponding to DP 1.5 and 3.1, respectively; tentatively the mean value 2.3 was adopted as DP_{olig} irrespective of the dose rate and water content. The so calculated numbers of oligomer molecules are shown in Table IV, along with G value for the formation of the oligomer G_{olig} calculated as in the case of G_r and G_i.

From Table IV it is clear that there is a difference between G_{olig}'s in moderately dried and water saturated styrenes, which is perhaps due to the fact that the same DP_{olig} was used in the calculation. Important thing is that the average G_{olig}'s of 0.94 for the moderately dried and 0.50 for the water saturated styrene are close to G_r which is independent of the water content, and have a value of 0.66. This is evidence to substantiate the above assumption that in spite of the formation of the same number of primary cations and radicals, the most part of the cations are consumed by the reaction with electrons or anions in the early stage of the reaction and only those cations which have survived contribute to the cationic polymerization. Further experiments are now scheduled to more precisely clarify the consumption of the primary cations.

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