

Radiation-Induced Polymerization of Styrene at High Dose Rates

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Synopsis

A kinetic equation was derived 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 one to calculate rates of the total, radical, and cationic polymerization at a given dose rate and water content and agrees satisfactorily with experimental results, which cover dose rates from 4.2×10 to 2.1×10^5 rad/sec and water contents from 3.2×10^{-3} to 3.5×10^{-2} mol/l. Experimental estimation of the contribution of radical and cationic mechanisms was done by GPC curves of polymers obtained under various conditions. When the contribution of ionic mechanism is expressed in weight percent, it changes from 0% to 100% in the range of the experiment; on the other hand, if it is expressed in mole percent, it is independent of the dose rate and remains constant throughout the whole range of the experiment.

INTRODUCTION

A number of reports on the radiation-induced polymerization of styrene have appeared in the literature, and a full account of the polymerization of styrene under ordinary conditions of purity, dryness, and dose rate can be found in Chapiro.¹ It appeared that the polymerization proceeds mainly by radical mechanism. Since then, however, it has been shown that ionic mechanism plays a predominant part in the polymerization of extremely dry styrene.^{2,3}

Squire et al.⁴ investigated radiation-induced polymerization of not rigorously dried styrene at higher dose rates up to 3 Mrads/sec, and a substantial contribution to the polymerization of concurrent cationic process was observed. We have also carried out similar experiments⁵ in a dose rate range of 4.2×10 to 2.1×10^5 rad/sec. The water content of styrene was varied between 3.2×10^{-3} and 3.5×10^{-2} mole/l.; the latter value corresponds to the saturation water content of styrene at room temperature.

It was shown that the total rate of polymerization, R_p , may be written as the sum of radical R_r and ionic polymerization rate R_i :

$$R_p = R_r + R_i = B_r I^{1/2} + B_i [X]^{-1} I$$

where I and $[X]$ are dose rate and water content, respectively; and B_r and B_i are constants which contain G -values for radical and ion formation and rate constants of radical and ionic polymerization, respectively. Essential applicability of the equation to the experimental results was recognized.

The present paper is also concerned with radiation-induced polymerization of styrene, and it is intended to divide polymerization product into two components, i.e., into radical and ionic polymers, by gel permeation chromatography (GPC). It is expected that by combined kinetic analysis of the polymerization reaction and GPC analysis of the product we will get more detailed and quantitative information about the radiation-induced polymerization than we have at present.

EXPERIMENTAL

Styrene Sample

Styrene monomer was washed with sodium hydroxide and then with water to remove any inhibitor. The washed styrene was dried overnight with CaCl_2 and distilled. The distilled styrene was brought into contact with CaH_2 , kept at least two weeks to dry further, and then distilled for the irradiation. The water content of the finally distilled styrene was about 3×10^{-3} mole/l. This is called, hereafter, moderately dried styrene; most of the experiments were carried out with the moderately dried styrene.

Irradiation Procedure

Irradiation for the polymerization was carried out with electron beams from a 1.5-MeV Van de Graaff accelerator in a dose rate range of 1.1×10^4 to 2.1×10^5 rad/sec, and gamma rays from a 2000-Ci cobalt 60 source was also employed for irradiation at a lower range, 3.7×10^2 to 4.2×10^3 rad/sec. The stainless steel irradiation cell is the same as that used in the previous report.⁵ The inner size of the cell is 50 mm \times 25 mm \times 1 mm, and the thickness of the liquid monomer is 1 mm.

The irradiation was carried out at room temperature, and the cell was cooled by an electric fan during the irradiation. When necessary, the irradiation was performed intermittently (50 sec irradiation and 60 sec interval), so that the temperature rise could be limited to less than 4°C.

Separation of Polymers

As was pointed out in the previous report, separation of polymers from the solution of the reaction products by precipitation with methanol is unsatisfactory because a very large amount, occasionally more than 30%, of low polymers which cannot be precipitated with methanol are formed by the irradiation, especially when the rate is very high. In the present work, all polymers were separated by pumping out the unreacted monomer and solvent at room temperature under vacuum. This precaution is very important.

Sample Analysis

The molecular weights and their distribution were determined by gel permeation chromatography using a high-speed liquid chromatograph HLC-801A of Toyo Soda Kogyo K.K.

TABLE I
Rate of Polymerization of Moderately Dried Styrene as a Function of Dose Rate

Dose rate, rad/sec	Total dose, Mrad	Conver- sion, %	R_p , mole/l.-sec	Wt. fraction of polymers, %		
				Radical	Cationic	Oligomeric
4.2×10	1.8	6.0	1.22×10^{-5}	—	—	1
3.7×10^2	1.9	5.4	9.17×10^{-5}	49	49.5	1.5
1.05×10^4	3.1	3.5	1.02×10^{-3}	10.5	87.0	2.5
2.1×10^5	10.3	11.3	1.97×10^{-2}	6.5	90.5	3

TABLE II
Rate and Molecular Weight for Polymerization of Moderately Dried Styrene
in the Presence of Ammonia (6.0×10^{-1} mole/l.)

Dose rate, rad/sec	Total dose, Mrad	Conversion, %	R_p , mole/l.-sec	Molecular wt. at peak ^a
4.2×10	1.7	3.64	8.00×10^{-6}	56.000
3.7×10^2	23	27.4	4.10×10^{-5}	27.500
1.05×10^4	21	1.00	4.68×10^{-5}	6.000
2.1×10^5	420	5.78	2.70×10^{-4}	3.000

^a The values are virtually the same as the number-average molecular weight calculated from the area of the GPC curve.

RESULTS

Experimental results of dose rate dependence of the rate of polymerization of styrene are shown in Table I. It may be seen that the rate of polymerization increases with increasing dose rate.

Polymerization at various dose rates in the presence of ammonia was also carried out, and the results are shown in Table II. The rate of polymerization in the presence of ammonia (0.60 mole/l.) decreases with increasing dose rate because ammonia is a strong inhibitor for the cationic polymerization which plays a more important part at higher dose rates.

GPC measurements were carried out on polystyrenes formed in the experiments shown in Tables I and II, and typical molecular weight distribution curves are shown in Figures 1(a)–1(d) and 2.

The curve in Figure 1(a) for the polymerization at a dose rate of 4.2×10 rad/sec is, if we neglect small amounts of oligomers, a simple distribution curve with a peak at $M = 5.6 \times 10^4$. Polymerization at the same dose rate in the presence of ammonia gives a similar distribution curve with a peak at the same molecular weight as may be seen in the curve a of Figure 2. Therefore, it is apparently simple to conclude that the polymerization at such a dose rate proceeds by radical mechanism. This is true, roughly speaking; there is some difficulty, however, for the interpretation because polymers produced by ionic mechanism have also a peak at nearly the same position, and there is a possibility that ionic polymer is contained in an amount which cannot be neglected.

The curve in Figure 1(d) for the polymerization without ammonia at 2.1×10^5 rad/sec has a distinct peak at $M = 3.6 \times 10^4$ and a shoulder at $M = 5 \times 10^3$. It is interesting that there are small maxima at molecular weights corresponding

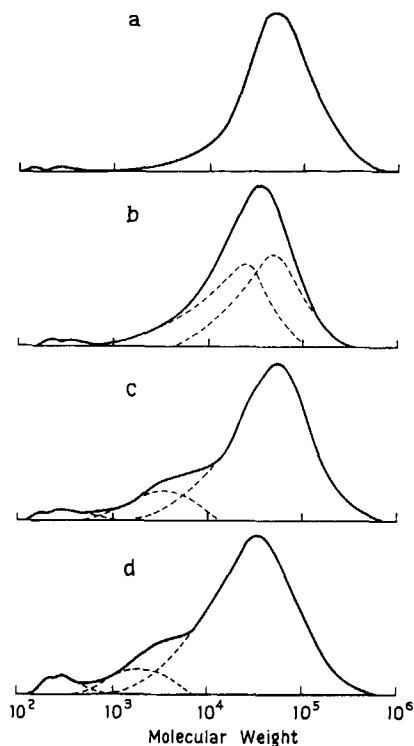


Fig. 1. Molecular weight distribution curves by GPC measurements of polystyrenes obtained by polymerization of moderately dried styrene at various dose rates (rad/sec): (a) 4.2×10^2 ; (b) 3.7×10^3 ; (c) 1.05×10^4 ; (d) 2.1×10^5 .

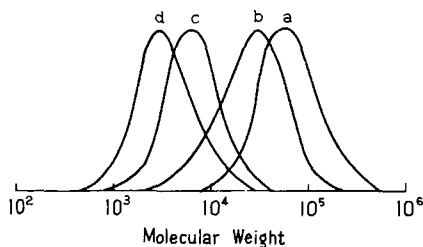


Fig. 2. Molecular weight distribution curves by GPC measurements of polystyrenes obtained by polymerization of moderately dried styrene in the presence of ammonia at various dose rates (rad/sec): (a) 4.2×10^2 ; (b) 3.7×10^3 ; (c) 1.05×10^4 ; (d) 2.1×10^5 .

apparently to oligomers such as dimers, trimers, and tetramers, and the peaks of these maxima become more distinct with increasing dose rate.

Curves of molecular weight distribution of polymers obtained at various dose rates in the presence of ammonia have shapes similar to one another, differing only in the position of peaks. These curves correspond to radical polymerization at various dose rates. Molecular weights at the peaks of curves are also given in Table II. It is seen that the molecular weight decreases with increasing dose rate.

It was intended to divide the distribution curves in Figure 1 into two parts,

but it was necessary to divide them into three parts, i.e., into areas corresponding to radical, ionic, and oligomeric polymers. An important guideline of the graphic division was the curves in Figure 2, which show molecular weight distribution of radical polymers obtained at various dose rates. The procedure is shown with dotted lines for curves b, c, and d in Figure 1; the weight fractions of the three kinds of polymer were calculated, and the results are shown in Table I. It is true that the basis of the division is not sufficiently firm, because master distribution curves for the cationic polymerization are not yet clearly established. It is self-consistent, however, as may be seen in Figures 1(b), 1(c), and 1(d) and will be shown later. Regarding curve a in Figure 1, adoption of the procedure to divide into three components was given up, because of the above-mentioned difficulty that the peaks of radical and ionic polymers were located practically at the same molecular weight, and the ionic polymer content is presumed to be very small.

DISCUSSION

The equation in the introduction was derived under the assumption that both radical and ionic polymerization take place concurrently throughout the whole dose-rate range, and that the number of initiating radicals or ions created by the radiation is dependent only on the radiation dose but independent of the dose rate. The well-known fact that the contribution of ionic mechanism is dominant in the higher dose-rate range is due to our conventional way of calculating the contribution not by the number but by the weight of polymer molecules.

In the present paper, the theoretical derivation of eq. (1) and comparison of the experimental results with theory will be shown in some detail. It is assumed that the overall reaction rate R_p is the sum of the reaction rate by radical mechanism, R_r , and the reaction rate by ionic mechanism, R_i :

$$R_p = R_r + R_i. \quad (1)$$

In the radical polymerization of styrene in bulk, it is known that the termination mechanism is a coupling of two growing chains and that no chain transfer reaction takes place under ordinary experimental conditions. The rate of radical polymerization may be expressed by the following well-known equation:

$$R_r = k_{pr}k_{tr}^{-1/2}(R_{ir})^{1/2}[M] \quad (2)$$

where R_r is the rate of radical polymerization in terms of monomer consumption, in moles/l.-sec; k_{pr} and k_{tr} are rate constants of polymerization and termination, respectively; and $[M]$ means concentration of monomer, in moles/l. R_{ir} is the rate of initiating radical formation, in moles/l.-sec; and can be written as follows:

$$R_{ir} = \frac{10G_r d \varphi}{N} I = \Phi_r I \quad (3)$$

where G_r is the G -value (radiation chemical yield in number of molecules per 100 eV absorbed energy) for the initiating radical formation; I is the dose rate, in rad/sec; N is Avogadro's number; d is the density of styrene; and φ is a factor for normalizing the unit of radiation energy. All the above constants are summarized into one symbol and are denoted by Φ_r .

From eqs. (2) and (3), the following expressions are obtained:

$$R_r = k_{pr}k_{tr}^{-1/2}\Phi_r^{1/2}[M]I^{1/2} \quad (4)$$

$$D.P._r = 2k_{pr}k_{tr}^{-1/2}\Phi_r^{-1/2}[M]I^{-1/2} \quad (5)$$

In the right-hand side of the above equations, all symbols except $[M]$ and I are constants; $[M]$ also may be regarded to be unchanged because we deal with the initial rate and degree of polymerization, and G_r is assumed to be constant throughout the whole range of radiation dose. Therefore, all symbols in eq. (4) except I is summarized in one and denoted by B_r ; so we get

$$R_r = B_r I^{1/2} \quad (6)$$

The degree of polymerization is

$$D.P._r = \text{const. } I^{-1/2} \quad (7)$$

Experimental results in Table II for the polymerization of styrene in the presence of ammonia show fair agreement with eqs. (6) and (7).

For the case of radiation-induced polymerization of highly dried styrene, where cationic polymerization dominates, Williams et al.⁶ have proposed a kinetic scheme in which a monomer cation was an initiator and propagation proceeded in the usual manner by addition of monomer; transfer to monomer and termination both by impurity X (e.g., water) and anions were also taken into account. In the present discussion, termination by anions was neglected because the reaction is carried out in the presence of a moderately large amount of water, so that termination by water may be regarded to be dominant. The rate and degree of polymerization are given by the following equations:

$$R_i = k_{pi}R_{ii} \frac{[M]}{k_{tx}[X]} \quad (8)$$

$$D.P._i = \frac{k_{pi}[M]}{k_{tm}[M] + k_{tx}[X]} \quad (9)$$

where R_{ii} , k_{pi} , k_{tx} , and k_{tm} are rate of formation of initiating cation, rate constants of propagation and termination by impurity (water), and transfer constant to monomer, respectively.

The rate of initiating cation formation is

$$R_{ii} = \frac{10G_i d\varphi}{N} I = \Phi_i I \quad (10)$$

where G_i has a similar meaning as G_r in eq. (3) and is the G -value for the formation of initiating cation. As in the case of radical polymerization, we get the following equation:

$$R_i = k_{pi}k_{tx}^{-1}\Phi_i M \frac{I}{[X]} \quad (11)$$

We may summarize all symbols except I and $[X]$ into one symbol and denote by B_i :

$$R_i = B_i \frac{I}{[X]} \quad (12)$$

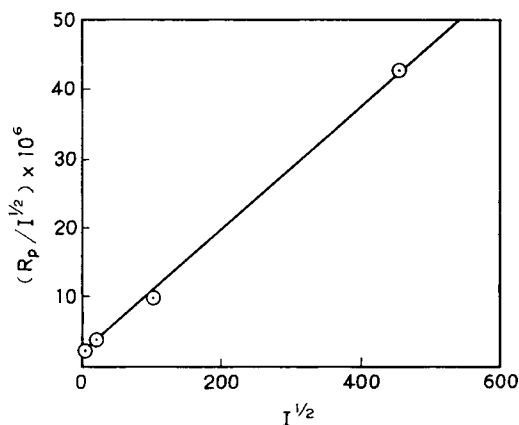


Fig. 3. Effect of dose rate I (rad/sec) on rate of polymerization of moderately dried styrene, R_p (mole/l.-sec).

Equations (1), (6), and (12) lead to the following expression for the overall rate of polymerization:

$$R_p = B_r I^{1/2} + B_i \frac{I}{[X]} \quad (13)$$

This is the equation which has already been shown in the introduction.

To check the applicability of this equation for the polymerization of styrene of constant water content at various dose rates, the equation is transformed to

$$\frac{R_p}{I^{1/2}} = B_r + \frac{B_i}{[X]} I^{1/2} \quad (13')$$

A plot of $R_p/I^{1/2}$ as a function of $I^{1/2}$ is expected to give a straight line. The graphic representation of the experiment in Table I is shown in Figure 3, and a straight line is obtained. This is quantitative evidence that radical and ionic polymerizations take place concurrently throughout the dose rate range of the present experiment. It is found from the intercept and the inclination of the curve that B_r and $B_i/[X]$ are 1.8×10^{-6} and 8.9×10^{-8} , respectively; $B_i = 2.84 \times 10^{-10}$, because the water content of the moderately dried styrene is 3.2×10^{-3} mole/l.

The effect of water content on the rate of polymerization was already reported in a previous paper as time-conversion curves. Table III shows numerically the rate of polymerization of styrene having various water contents at a constant dose rate of 2.1×10^5 rad/sec. According to eq. (13), R_p changes linearly with the reciprocal of the water content. Figure 4 is a graphic representation of the experimental results, and it is seen clearly that R_p shows the expected change with

TABLE III
Rate of Polymerization R_p of Styrenes of Various Water Contents
at a Dose Rate of 2.1×10^5 rad/sec

$[H_2O]$, mole/l.	3.2×10^{-3}	5.7×10^{-3}	2.0×10^{-2}	3.5×10^{-2}
R_p , mole/l.-sec	1.65×10^{-2}	9.1×10^{-3}	1.78×10^{-8}	9.1×10^{-4}

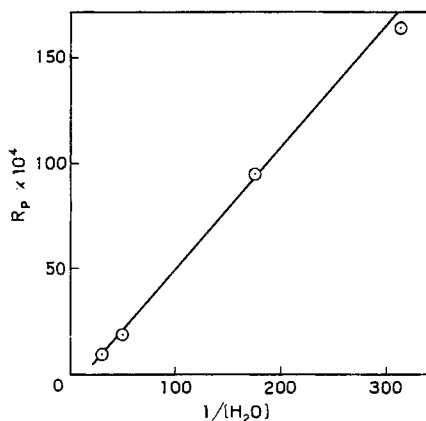


Fig. 4. Influence of water content $1/[H_2O]$ (l/mole) on polymerization rate of styrene.

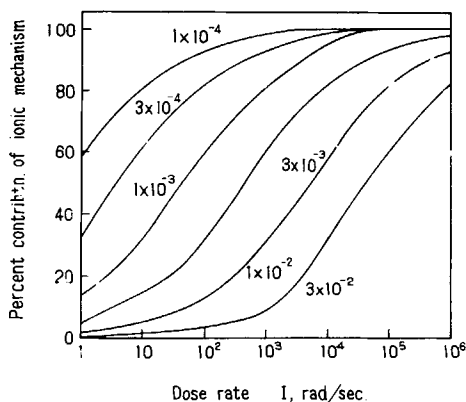


Fig. 5. Influence of water content of styrene and dose rate of irradiation on percent contribution of ionic mechanism in weight percent of polymer. Curves correspond to water contents from 1×10^{-4} to 3×10^{-2} mole/l.

$[H_2O]^{-1}$. The value of B_i found by this method is 2.72×10^{-10} , which agrees satisfactorily with that obtained from Figure 3.

We can now calculate the contributions of the radical and ionic mechanisms for a wide range of dose rate and water content in terms of weight of polymer based upon eq. (13). The calculated values are shown in Figure 5. It covers dose rate and water content ranges from 1 to 1×10^6 rad/sec and from 1×10^{-4} to 3×10^{-2} mole/l., respectively. Water-saturated styrene contains about 3×10^{-2} mole/l. water at room temperature. It may be seen from the figure that the contribution of ionic mechanism at lower water content increases at first very rapidly with increasing dose rate to show a value greater than 80%. On the other hand, in the case of styrene of rather high water content, the curves are S-shaped and the initial increase in ionic mechanism is slow. The figure shows further that at a very high dose rate, such as 10^6 rad/sec, the ionic mechanism is dominant, even in the case of water-saturated styrene.

There are three methods for the estimation of the contribution of radical or cationic mechanism in the polymerization at various dose rates: (1) The polymerization rate in the presence of ammonia is regarded to be due to radical

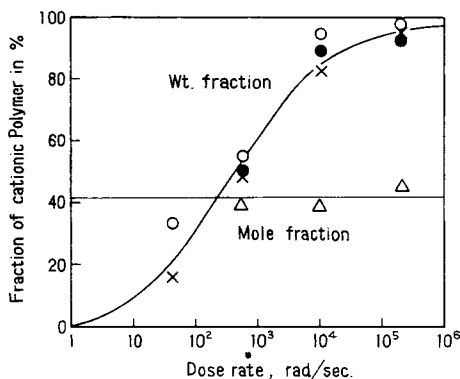


Fig. 6. Fraction of cationic polymer in wt-% and mole-% for polymerization of moderately dried styrene at various dose rates: (O) wt-%, method 1; (●) wt-%, method 2; (X) wt-%, method 3; (Δ) mole-%, GPC method.

mechanism, so the difference of polymerization rates in the absence and presence of ammonia is a result of cationic polymerization. (2) Based on the GPC analysis of polymers, it is possible to know the fractions of radical and cationic polymers. (3) Via employment of the theoretical eq. (13) for the rate of polymerization, the contribution of the two mechanisms in the polymerization at any dose rate and water content can be calculated.

Figure 6 shows the contribution of the cationic mechanism, in weight percent, of the polymer found by the three different methods for moderately dried styrene at various dose rates. The values obtained by different methods show fair agreement to one another.

Though we are not of the opinion that the GPC method gives the most reliable result, this method is employed for further discussion because number-average molecular weights are found from GPC curves. In the following calculation, molecular weights at the peaks of the curves are used, since they are virtually the same as the graphically calculated number-average molecular weight and are less influenced by the graphic division into components than the former.

The rates of radical and cationic polymerizations are calculated from the overall rate of polymerization and contributions of the mechanisms. The rates of radical and cationic polymerizations divided by the number-average degrees of polymerization and dose rate give the number of moles of radical and cationic polymers formed per 1 rad irradiation per liter styrene. The calculated values are shown in Table IV. It may be seen that the numbers of polymer molecules formed by each mechanism are virtually independent of the dose rate, though the numbers at lower dose rates are somewhat larger than the others. In the case of radical polymerization, eqs. (4) and (5) leads to

$$\frac{R_r}{D.P.,I} = \frac{10G_r d\phi}{2N} = \text{const.} \quad (14)$$

and so experiment and theory show essentially good agreement.

From the numbers of radical and cationic polymer molecules formed per rad irradiation per liter styrene, we can calculate the contribution of cationic (or radical) mechanism in mole percent. The calculated values are graphically shown in Figure 6. It is seen that the contribution is independent of the dose

TABLE IV
Rate and Number-Average Degree of Polymerization for Radical and
Cationic Polymerization of Moderately Dried Styrene

Dose rate, I , rad/sec	4.2×10^a	3.7×10^2	1.05×10^4	2.1×10^5
Rate of polymerization, mols/l.·sec				
R_r	(8.1×10^{-6})	4.5×10^{-5}	1.07×10^{-4}	1.28×10^{-3}
R_i	—	4.55×10^{-5}	8.85×10^{-4}	1.78×10^{-2}
Number-average degree of polymerization				
$\frac{D \cdot P \cdot r}{D \cdot P \cdot i}$	(4.9×10^2)	2.7×10^2	3.85×10	2.4×10
	—	4.3×10^2	5×10^2	3.4×10^2
Number of polymer molecules, mols/l. rad				
$R_r/(D \cdot P \cdot r \cdot I)$	(3.9×10^{-10})	4.5×10^{-10}	2.7×10^{-10}	2.7×10^{-10}
$R_i/(D \cdot P \cdot i \cdot I)$	—	2.9×10^{-10}	1.7×10^{-10}	2.4×10^{-10}
G_r	(0.78)	0.90	0.54	0.54
G_i	independent of dose rate			

^a This calculation is based on the polymerization in the presence of ammonia.

rate and has an average value of about of 40% in a wide range of dose rates from 1 to 10^5 rad/sec, in which the contribution of the cationic mechanism in weight per cent changes practically from 0% to 100%.

The G -value for the initiating radical formation, i.e., G_r , is calculated by eq. (14) and shown in Table IV. The average G_r value is 0.68, which agrees with the value of 0.69 calculated by Chapiro¹ from data of different authors for dose rates below 2–3 rad/sec. According to Chapiro, G_r decreases with increasing dose rate to show a value of 0.3–0.46 in a dose rate range of 10–500 rad/sec. In the present paper, the scattering in G_r is regarded to be due to experimental error; the conclusion of Chapiro may be due to the fact that it was not known in 1961 that an appreciable amount of cationic polymers are formed at higher dose rates even with “wet” styrene. According to our experimental results on moderately dried styrene, cationic polymers show higher molecular weights than radical polymers above a dose rate of about 100 rad/sec. Therefore, if the contribution of cationic polymers is not taken into account, we obtain apparently lower G_r values at higher dose rate.

In the case of cationic polymerization, it is somewhat complicated, as eqs. (9) and (14) suggest, to know the number of polymer molecules produced by one initiating cation, because the degree of polymerization is controlled by two factors, namely, chain transfer to monomer and termination by water as eq. (9) shows. The experimental results, however, that the number of cationic polymers produced by a unit dose and their number-average molecular weight are independent of the dose rate show that G_i is also independent of the dose rate of irradiation.

The formation of oligomers in the course of the polymerization was neglected in the discussion. As has already been shown in Table I, the fraction of oligomers increases with dose rate, and it is plausible that they are formed in the initiating stage of cationic polymerization. Further investigation into the field of polymerization of styrene under high dose rates is now in progress. It has already been found that polystyrene of molecular weight about one million is formed not in moderately dried but in water-saturated styrene or in styrenes which contain

a small amount of simple additives. This high molecular weight polystyrene is formed by some other mechanism than the radical and cationic polymers which are discussed in the present paper.

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