Free-Cationic Polymerization of Styrene by Radiation

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ABSTRACT: The cationic polymerization of bulk styrene by radiation has been investigated by dilatometry and electrical conductivity measurements.

In the sample which attained the highest polymerization rate, R_p in this study the dose rate exponent of R_p was still 0.7, however, a 0.6-power dependence was obtained in oxygen containing samples in which R_p in higher dose rate region was considerably lower than that of oxygen-free one. In well-dried, oxygen-free samples, a non-Ohmic current—voltage relationship was observed. These behaviors can be explained by the coexistence of polymeric anions as well as polymeric cations in well-dried, oxygen-free system. Kinetic calculations of the rate constant for propagation, k_p and its activation energy, E_p were made giving $k_p = (2.4 \pm 0.9) \times 10^6 / \text{mol}^{-1} \text{sec}^{-1}$, and $E_p = 2.2 \pm 1.3 \text{ kcal mol}^{-1}$.

From the comparison with the previously reported k_p values with other polymerization mechanisms, it is found that k_p with free-cationic mechanism is the highest probably because of its low E_p values.

KEY WORDS Cationic Polymerization / Radiation / Free Ion / Styrene / Electrical Conductivity / Effect of Oxygen / Termination Reactions / Propagation Rate Constant / Activation Energy / Propagation Mechanism /

It has been recognized that radiation-induced polymerization of vinyl compounds proceeds by a free-ionic mechanism in contrast with the paired-ionic mechanism which is initiated by catalyst. Many studies in this field gave evidences for it on the basis of the following reasons.

1. The polymerization is retarded by a trace of polar impurity especially water.¹⁻⁴ The extreme purification or drying to remove a trace amounts of polar impurities from monomers is also required for a free-anionic polymerization initiated by a catalyst. 2. The half-power dependence of R_p on dose rate can be achieved ultimately.⁵⁻⁸ This is strong confidence for the free-ionic polymerization in the system where an ionic mechanism has already been established. 3. The polymerization takes place with a sufficiently high reaction rate in nonpolar medium,¹⁻⁸ while in such a medium the paired-ionic polymerization proceeds at a very low rate because of slight dissociation of catalyst. 4. The propagation rate constants, k_p evaluated by scavenger^{4,9} and electrical conductivity^{6,10} methods are

in the region between 10^5 and $10^8 / \text{mol}^{-1} \text{sec}^{-1}$.

These values are very large in comparison with those in paired-cation, paired-anion and radical polymerization.¹⁰ 5. In the field of radiation chemistry, the existence of free ion has been confirmatively established experimentally¹¹⁻¹³ as well as theoretically¹⁴ while ion-pair state has not yet been suggested as a stable intermediate. If there were to coexist paired ions with free ions generated by ionizing radiation, the total ion yield should be less than 3—4 ions per 100-eV energy absorbed. Taking account of the free-ion yield, around 0.1 in nonpolar medium, the population of paired ions, if it exists, 30—40 times greater than that of free ion at most. As k_p values in free-ionic polymerization is probably 10^2 — 10^3 times greater than that in paired-ionic one, the contribution from paired-ionic polymerization can be neglected in the total rate of polymerization.

In the preceding papers^{6,10} the estimation method of k_p by combining the determinations of R_p had been proposed through dilatometry

and of the free-ion lifetime through the steady-state electrical conductivity under irradiation. It has been found that the activation energy, E_p , of free-cationic propagation in isobutyl vinyl ether (IBVE)⁶ was strikingly large in comparison with those in the other vinyl monomers such as styrene. However, as it is known that vinyl ethers sometimes show contrasting polymerization behaviours with respect to those of other monomers,¹⁵ the polymerization studies on vinyl monomers other than vinyl ethers by radiation have been required to clarify the general features of free-cationic polymerization.

On the other hand, styrene is one of most popular vinyl monomers and is well known to be capable of polymerization *via* all kinds of mechanisms, free radical, anionic and cationic, wherein the latter two are divided into ion-pair and free-ionic mechanisms, respectively. In the case of styrene, kinetic results such as k_p and E_p values have been reported in all of these polymerization mechanisms except the free-cationic one. A crude evaluation of k_p in radiation-induced cationic polymerization was carried out previously,¹⁰ while evaluation of E_p has not yet been made. In this work the free-cationic polymerization of styrene by radiation was carried out in order to elucidate features of the free-cationic polymerization in contrast to those of other mechanisms. In particular the largest concern of the author rests on the chain propagation step in the free-cationic mechanism.

EXPERIMENTAL

Some improvements were attempted in order to achieve the superdry state as compared with

our former procedure⁶ for isobutyl vinyl ether. Modifications of the vacuum system gave a rise of the vacuum level down to 3×10^{-7} mmHg in a few hours after evacuation of the system. The vacuum-line system was always heated at about 200°C with a wound heater. Styrene was dried by repeated contact with the drying agent dried by baking before use. A sampling ampoule and a dilatometer cell were baked at 400°C and at 200°C, respectively, in the vacuum system for more than 20 hrs and the remaining part was carefully and thoroughly backed out with a flame. The well-dried monomer was sealed in an ampoule or the dilatometer cell after a vacuum level less than 1×10^{-6} mmHg was confirmed.

Silica gel (SG) or molecular sieves (MS) 3A was used as drying agents as well as barium oxide (BaO) after baking out at 400°C for more than two days in high vacuum. These drying agents, except for BaO, initiate the polymerization slowly and their surfaces become covered with polymer when monomer was stored over them for a long period. Accordingly, in order to avoid polymerization, styrene was usually stored over BaO *in vacuo*, and then further dried over SG or MS before use. In the purification of monomers the purity of the sample was little affected by the kind of drying agent used but depended significantly on the drying conditions adopted in the procedures required for vacuum distillation or sampling.

The drying and sampling treatments for each sample studied are summarized in Table I. In the case of sample D, the dried monomer which received an accidental contamination with air was again treated with silica gel after degassing and vacuum distilled into the cell. In sample

Table I. Preparation procedures of polymerization samples

Sample	Drying	Sampling
A	BaO(11 months)→SG(5 days)→SG(5 days)	Degassed
B	BaO(11 months)→SG(17 days)→SG(6 days)→SG(5 days)	Degassed
C	BaO(2.5 months)→MS(9 days)→BaO(5 days)→BaO(3 days)	Equilibrated with oxygen (10 mmHg)
D	BaO(9 days)→SG(88 days) ^a →SG(13 days)	Degassed
E	BaO ^a →MS(3 months)→MS(10 days)	Degassed, insufficiently dried cell ^b
F	SG in the presence of air	Degassed, insufficiently dried cell ^b

^a Contaminated with air and moisture during storage.

^b Cell was evacuated for 2 hrs. without heating.

C, the monomer was kept in equilibrium with dry oxygen (*ca.* 10 mmHg) after transferring into the cell and sealed off. In sample F, insufficiently dried monomer was introduced into the cell which had been evacuated only for two hours without heating the system.

Further details of the experimental procedures concerning dilatometry and electrical conductivity measurements were described in the preceding paper.⁶

Polymers for molecular weight determinations were prepared by ⁶⁰Co γ -ray polymerization in vacuum at 0°, 25°, and 50°C, respectively. Vapor pressure osmometry was carried out using a Hewlett Packard Model 502 osmometer in toluene solutions at 30°C.

RESULTS

Determinations of the rate of polymerization, R_p and specific conductivity, σ as a function of dose rate have been carried out at 25°C for six separate samples, A–F, whose characteristics are given in Table I. The σ values are given as a function of dose rate in Figure 1. In well-dried samples as A and B, there observed a decrease of specific conductance at the high voltage region studied, in spite of relatively large scatter in its value. It is striking that such a non-Ohmic current–voltage relationship was observed in the system of ionic conduction. On the other hand, an Ohmic relation was found to be maintained in samples C, E, and F which supposedly contain relatively large amount of impurities, probably oxygen and/or water. Sample D was an intermediate case in which Ohmic relation was maintained at a higher dose rate.

Figure 1. Specific conductance vs. dose rate in styrene at 25°C; field strength, 100 Vcm⁻¹.

The non-Ohmic relation found in the present study was not observed for the polymerization systems studied previously.^{6,16} It is also striking that σ values considerably vary with the purification grade of samples. From the curves C and F, it is found that mobility of oxygen anion is probably considerably greater than that of impurity cation. However as the σ value is a sum of the concentrations of ionic species multiplied by their mobilities, it is not easy to discuss the differences in the quality and quantity of charged species in each sample from the absolute values of σ . Relatively high dose rate component of σ seems also characteristic to these polymerization systems: 0.53, 0.59, 0.57, 0.62, 0.50, and 0.55 in samples A, B, C, D, E, and F, respectively at the field of 100 V cm⁻¹. It has been kinetically shown that the dose-rate exponent of σ is always 0.5 when there exists a sole charge carrier both for positive and negative species.^{11,12} In other words, a deviation of the dose-rate exponent of σ from 0.5 indicates the coexistence of several kinds of ionic species and interactions between them must be taken into account in the polymerization systems studied.

In Figure 2 the rate of polymerization, R_p at 25°C as a function of the dose rate (I) is shown for three samples which are prepared in vacuum. Sample F did not polymerize with sufficiently high reaction rate for the ionic polymerization of styrene. In sample E, the dose-rate exponent

Figure 2. R_p at 25°C vs. dose rate in vacuum prepared samples.

of R_p is approximately 1, indicating predominance of impurity termination. In sample A and B the R_p — I relationships are given by curved lines; their dose rate exponents become lower at higher dose rate and comparing with sample E at a fixed dose rate, R_p 's are considerably higher while their dose rate exponents are lower. These R_p — I relationships observed well coincide with the kinetic results described previously.⁶ In this study the highest R_p was attained in sample A, in which the rate exponent is still 0.7 at higher dose rate region in spite of rigorous drying and careful sampling procedure. The highest limit of R_p^* in styrene indicated by the power dependence of R_p on dose rate, has been achieved by Metz⁸ and is shown with broken line in Figure 2. The experimental system employed, however, seems to require several attempts and modification of the system to achieve the superdry state. Drying of the dilatometer cell which can not be heated above 250°C is considered to be still incomplete. It seems to be essential to heat the whole vacuum system at high temperature under high vacuum for long time in order to achieve the superdry state. And a slight unnoticed difference in drying or sampling procedures possibly gives a decrease in R_p as shown in sample B as compared with that of sample A.

When air or oxygen is present in the system, polymerization behaviors change as shown in Figure 3. In the case of sample D which was sealed in vacuum, R_p — I relationship is appar-

Figure 3. R_p at 25°C vs. dose rate in oxygen containing samples.

ently similar to that of sample C indicating insufficient removal of air during the degassing process prior to the final drying with silica gel. Comparing with the R_p — I curves in Figure 2, it is clear that R_p 's in oxygen containing samples are higher at low dose-rate region while at high dose-rate region R_p 's become lower. The dose-rate exponent of sample C at higher dose-rate region is 0.6 though R_p is still lower than that of sample A. In other words, R_p — I curves in sample A and C intersect each other and such a behavior cannot be explained with the previously proposed kinetics.^{6,10}

The polymerization was carried out at 25° and 40°C in samples C, D, and E and at 25° and 0°C in sample B, which are also shown in Figures 2 and 3. It is apparent that R_p increases with temperature. R_p — I curves B, C, and D can be regarded to be almost parallel to the curves B', C', and D', respectively. This indicates that the contribution of impurity termination to total termination rate at a fixed dose rate is almost invariant with temperature. In Figure 4, relative values of R_p (40°C) to R_p (25°C) and R_p (0°C) to R_p (25°C) were plotted as a function of the dose rate. It was found that the relative values of R_p are regarded as independent of dose rate at 0 and 40°C in spite of considerable scattering in their values. The relative polymerization rate to 25°C are 0.75 at 0°C and 1.18 at 40°C on the average. The temperature coefficient of R_p in oxygen containing samples (C and D) between 25° and 40°C agreed well with that in oxygen free sample (B) between 0° and 25°C. This suggests that the

Figure 4. Relationship between the the relative R_p value and dose rate.

polymerization mechanism is almost similar in both cases though the absolute rate of each elementary reaction are different. The apparent activation energy of polymerization, E_{app} was evaluated to be 1.6 ± 0.7 kcal mol⁻¹.

Number-average molecular weights of polymers obtained at 0°, 25°, and 40°C were determined to be 5.00, 5.39, and 3.91×10^4 , respectively. From the polymerization rates, impurity levels of these samples were found to be almost the same, corresponding to a little lower level than that of sample B shown in Figure 2. Recently, Huang¹⁷ reported that the molecular weight increases with increasing polymerization temperature from -29° to -10°C with an apparent activation energy of 0.15 kcal mol⁻¹. From our values at 0° and 25°C, we can see that this trend is maintained to a little higher temperature though the absolute values in his determination seems to be a little higher than ours taking account of the temperature difference. If the molecular weight at low temperature polymerization is governed solely by chain-transfer reaction to monomer, a considerable decrease in our molecular weight at 40°C may suggest a slight involvement of another molecular-weight-determining process. However considering the polymerization rates, it is evident that the molecular weights of these polymers were governed predominantly by the chain-transfer reaction to monomer, and the obtained results as to molecular weight and its temperature dependence should give clue to that reaction in styrene.

DISCUSSION

Reaction Mechanism

In the former paper⁶ on vinyl ether, the polymerization behavior such as R_p - I relationship had been well explained in terms of two competitive termination reactions.

where X and Y⁻ represent impurity and anionic species, respectively. Then, as a result of kinetic calculation R_p was shown to be expressed as

$$R_p = k_p[M] \{ (10IG/N) / (pk_{r,(1)}[Y^-] + k_X[X]) \} \quad (3)$$

Here, G and N represent the initiating-ion yield or free-ion yield per 100-eV energy absorbed and the Avogadro number, respectively and $pk_{r,(1)}$ means the contribution of the diffusion of anionic charge carrier (Y⁻) to the recombination rate constant between M_1^+ and Y⁻. In the calculation in the preceding paper⁶, reaction 2 was also assumed to depend on the degree of polymerization of the cation, n , however it is considered better to use a constant value, k_X and final consequence is given by eq 3. In this treatment, each sample of a different batch is characterized only with impurity concentration, $[X]$, and it is easily understood from eq 3 that R_p - I relationships in the samples of different $[X]$ are nearly parallel one another as was schematically illustrated in Figure 1 in ref 10.

Therefore, Figures 2 and 3 indicate that eq 3 is not applicable to both oxygen-free and oxygen-containing examples, without modification of the equation or change of the parameters other than $[X]$. Here, consider a possible influence of oxygen to elementary processes of free-cationic polymerization. If the initiating-ion yield, G or the propagation rate constant, k_p were to decrease by the existence of oxygen, such polymerization behaviors as observed in Figures 2 and 3 would be expected. However, the free-ion yield is known to be governed by the bulk properties of monomer, *i.e.*, electron density, dielectric constant, etc., which are not much influenced by a slight amount of dissolved oxygen. Further, interaction between propagating ion with oxygen which may influence the k_p value seems unlikely in this system. In the field of catalyst-initiated polymerization with cationic mechanism, at least, such a mechanism is still unknown. Concerning the termination process, two possibilities are predominant; one is the scavenging process of oxygen for the cation, and the other is the recombination reaction of cation with O₂⁻ which is formed by electron capture by oxygen.

In anionic polymerization, oxygen is well known as an effective inhibitor.¹⁸ In the pulse radiolysis study of styrene,¹⁹ it has been reported that the transient absorption assigned to be styryl anion was not observed in the presence of oxygen. Therefore, in the absence of oxygen, it may be natural to consider that anionic polymerization

is also taking place as well as cationic polymerization though the latter predominates in the reaction rate considering the effects of additives⁴ and copolymerization studies.^{3,20} In other words, in a superdry and completely oxygen-free system, all the anionic and cationic species are considered to be polymeric ions. In general, there coexists the propagating cation (M_n^+), impurity cation (X^+), propagating anion and probably oxygen anion, O_2^- in the polymerizing system.

Electrical conductivity behaviors are well explained with the above consideration when it is assumed that the non-Ohmic current is due to polymeric ions. The deviation from an Ohmic relation seems to be probable because a greater resistivity to the translational motion of polymeric ion under the influence of electric field can be expected in a good solvent in which the polymer forms a solvent-swollen loose coil. As the mobility of the polymeric ion must be considerably lower than those of the impurity cation or O_2^- , a non-Ohmic relation should be expected only when both polymeric ions are predominant charge carriers in the steady state under irradiation, which corresponds to the cases in samples A and B. On the contrary, an Ohmic relationship was maintained in samples C, E, and F. Deviations of the dose-rate exponent from 0.5 also give a proof for the coexistence of impurity ions and polymeric ions.

Accordingly, it was proposed that in the presence of oxygen, anionic polymerization was retarded yielding O_2^- ion, which would recombine with polymeric cation at considerably higher rate than polymeric anion would. Here, theoretical calculations of R_p — I relationships were made for the cases in which ionic polymerization proceeds in the presence and absence of oxygen. The details of the calculation procedures are described in the APPENDIX. Typical sets of R_p — I curves corresponding to each of the two different cases are given in Figure 5. The $pk_{r,(1)}$ value was determined such that one of the calculated R_p — I curves, each corresponding to different $[X]$ gave the best fit to the actual R_p — I curves in sample A or C, which was chosen as a representative for oxygen-free or oxygen-containing system, respectively. The curves showing the best fit to the results of

Figure 5. Calculated R_p values of as a function of dose rate: ●, sample A in Figure 2; ▲, sample C in Figure 3; a, series 1, 2, 3, 4, $pk_{r,(1)} = 5 \times 10^{10} \text{ l mol}^{-1} \text{ sec}^{-1}$; b, series 1', 2', 3', 4', $pk_{r,(1)} = 3 \times 10^{11} \text{ l mol}^{-1} \text{ sec}^{-1}$; impurity levels ($k_X[X] \text{ sec}^{-1}$), 0.1 (1, 1'), 1(2, 2'), 10(3, 3'), and 10^2 (4, 4').

samples A and C were obtained for $k_X[X]$ values of 1.5 and 5 assuming that $pk_{r,(1)}$ was 5×10^{10} and 3×10^{11} , respectively. From Figure 5, it is apparent that with greater $pk_{r,(1)}$, the maximum R_p level (curve 1 and 1') becomes lower and the dose-rate dependence becomes smaller when compared at a fixed $[X]$. As the diffusion constant of oxygen²¹ was evaluated to be almost the same as that of water in benzene²², it is quite reasonable to assume $pk_{r,(1)} = k'$ (see APPENDIX) in an oxygen-containing system. On the other hand, the smaller $pk_{r,(1)}$ value which fits for oxygen-free system suggests that an anionic species of relatively higher molecular weight is present in the system. However taking into account the square-root relationship between the diffusion constant of polymer and its degree of polymerization (DP),²³ it is likely that the propagating cation recombines preferentially with the propagating anion having lower DP , probably less than 30. Charge recombination between polymer cation and anion of higher DP seems to be more difficult than expected from their diffusion constants because ionic sites are relatively small compared with the whole volume of polymer coils dissolved in monomer, as had been proposed in mutual termination process in radical polymerization.²⁴

The absolute value of R_p at a fixed dose rate

Figure 6. Calculated relationship between the relative amount of propagating ion at steady state and the dose-rate exponent of R_p : curve (a), $pk_{r,(1)} = 5 \times 10^{10} \text{ l/mol}^{-1} \text{ sec}^{-1}$; curve (b), $pk_{r,(1)} = 3 \times 10^{11} \text{ l/mol}^{-1} \text{ sec}^{-1}$.

and the dose-rate exponent of R_p have been used as phenomenal measures to check the purity of monomer. However, the former by itself is an insufficient measure unless R_p — I relationship is well known at the polymerization conditions studied. A relationship between the dose-rate exponent of R_p and the fraction of propagating cation to total ion, $\Sigma[M_i^+]/[Y^-]$, at steady state has been calculated for two cases shown in Figure 5 and is shown in Figure 6. It is always true that when the relative concentration of propagating ion is 1, the dose-rate exponent equals 0.5 and it becomes 1 when all the cation is captured by impurity. However from Figure 6 it is also apparent that the dose-rate exponent depends upon the $pk_{r,(1)}$ value as well as the relative concentration of propagating cation. For instance, when $\Sigma[M_i^+]/[Y^-]$ is 0.87, the dose-rate exponent equals 0.60 in an oxygen-containing system (curve b) while in an oxygen-free system (curve a) it is still 0.70. And this may be one of the reasons why the achievement of the half-power dose-rate dependence of R_p is difficult in styrene especially in an oxygen-free system. The longer lifetime of a propagating ion due to the decrease in the termination rate may be another possible reason.

Some differences have been found in polymerization behavior of styrene between the results described here and Metz's.⁸ He observed a quite complicated temperature dependence of R_p in almost superdry samples. It is easily understood that the variation in polymerization temperature may induce a change in $\Sigma[M_i^+]/$

$[Y^-]$ ratio through $pk_{r,(i)}$ and k_x values and consequently the dose-rate dependence of R_p changes. Therefore unless the dose-rate dependence is invariant with temperature, it seems difficult to draw a meaningful conclusion from the apparent activation energy of R_p . Negative temperature coefficients of R_p in semi-superdry sample was never observed in this experiment. Concerning the effect of oxygen addition, detailed studies of R_p as a function of oxygen concentration seems to be required as a future study.

Estimation of k_p and E_p

In the samples which polymerized with relatively high rates, Ohmic law was maintained only in sample C, which showed the lowest dose-rate exponent of R_p . Accordingly in sample C the lowest impurity concentration was indicated from the comparison with calculated R_p — I curves and it is indicated the predominance of oxygen anion as a negative charge carrier after inhibiting anionic polymerization. Although the half-power dependence of R_p on dose rate was not yet achieved in this sample, a crude evaluation of k_p was attempted using eq 3. The free-ion lifetime was approximated with τ , which is defined as¹⁶

$$\tau = \epsilon / 3.6 \times 10^{12} \pi \sigma \quad (4)$$

where ϵ is the dielectric constant of the medium. In Figure 7, R_p/τ was plotted against the dose rate at 25° and 40°C for sample C. The initiating-ion yield was assumed to be 0.055 at 25°C and 0.063 at 40°C, which had been evaluated for benzene.²⁵ The resulting k_p values are 1.9×10^6 and $2.3 \times 10^6 \text{ l/mol}^{-1} \text{ sec}^{-1}$ at 25° and 40°C, respectively. These values can be regarded as lowest

Figure 7. (R_p/τ) vs. dose rate at 25° and 40°C.

limits of k_p , because of the half-power dose-rate exponent of R_p was not realized. From the calculations shown in Figure 5, R_p in superdry state can be well estimated to be $25 \pm 5\%$ greater than that when R_p is proportional to $I^{0.60}$. This ratio is relatively insensitive to the change of parameters. Therefore the final k_p values are

$$25^{\circ}\text{C} \quad (2.4 \pm 0.9) \times 10^6 \text{ l mol}^{-1} \text{ sec}^{-1}$$

$$40^{\circ}\text{C} \quad (2.9 \pm 1.0) \times 10^6 \text{ l mol}^{-1} \text{ sec}^{-1}$$

where the error limit was evaluated to be within $\pm 35\%$.

Estimation of E_p was carried out by two different ways. From the k_p values given above 2.2 kcal mol⁻¹ was obtained. Secondly, as shown previously,⁶ k_p is expressed as

$$k_p = (N/10IG[M])(R_p/\tau) \quad (5)$$

Then, a following relation is obtained.

$$\begin{aligned} \mathrm{d} \ln k_p / \mathrm{d}(T^{-1}) &= \mathrm{d} \ln R_p / \mathrm{d}(T^{-1}) - \mathrm{d} \ln \tau / \mathrm{d}(T^{-1}) \\ &\quad - \mathrm{d} \ln [M] / \mathrm{d}(T^{-1}) - \mathrm{d} \ln G / \mathrm{d}(T^{-1}) \\ &\quad - \mathrm{d} \ln I / \mathrm{d}(T^{-1}) \\ &= \mathrm{d} \ln R_p / \mathrm{d}(T^{-1}) + \mathrm{d} \ln \sigma / \mathrm{d}(T^{-1}) \\ &\quad - \mathrm{d} \ln G / \mathrm{d}(T^{-1}) - 2 \mathrm{d} \ln \rho / \mathrm{d}(T^{-1}) \\ &\quad - \mathrm{d} \ln \varepsilon / \mathrm{d}(T^{-1}) \\ &= E_{\text{app}} + E_{\sigma} - E_G - 2E_{\rho} - E_{\varepsilon} \quad (6) \end{aligned}$$

E_o is evaluated to be (1.6 ± 0.3) kcal mol⁻¹ in samples C and F. E_G is assumed to be (1.5 ± 0.3) kcal mol⁻¹ from the result for benzene.²⁵ As temperature coefficient of density (ρ) and dielectric constant are -0.17 and -0.19 kcal mol⁻¹, respectively, the result obtained is,

$$E_p = (2.2 \pm 1.3) \text{ kcal mol}^{-1}$$

The agreement of E_p values estimated by the two ways is accidentally good. The κ_p and E_p values thus obtained allowed the evaluation of the frequency factor for propagation, A_p to be $10^{8.0 \pm 1.1}$

Here it must be confirmed that this E_p value can be applied to the whole temperature range studied, 0°—40°C. In the first calculation, E_p was estimated from only two k_p values and in the latter method also a constant temperature coefficient was assumed. However, as discussed previously, in our results on R_p and σ , there was no evidence to suggest a complicated tem-

perature dependences of R_p . These E_p evaluations are crude and rather tentative, nonetheless, the obtained value is believed to be quite significant for the further discussion to elucidate the distinct feature in free-cationic propagation.

The number-average degree of polymerization, $\overline{DP}_n$ of the polymers obtained by free-cationic mechanism is about 400–600, which is considerably higher than those obtained by paired-cationic polymerization.^{26–28} Assuming $\overline{DP}_n$ as k_p/k_{tr} , k_{tr} at 25°C was evaluated as $4.6 \times 10^3 \text{ l mol}^{-1} \text{ sec}^{-1}$. As the temperature coefficient for $\overline{DP}_n$ is supposed to be very small, we can well regard $E_p - E_{tr}$ as $-0.1 \pm 0.3 \text{ kcal mol}^{-1}$.

Comparison of Propagation Processes with Other Polymerization Mechanisms.

Typical values of E_p and $\log A_p$ in the propagation reaction of styrene by several different polymerization mechanisms are cited in Table II. At first sight, it is apparent that the obtained k_p in free-cationic polymerization is the highest among all k_p values reported and that the free-cationic polymerization of bulk styrene is characterized by low E_p values compared with those in other mechanisms and relatively high A_p value. It seems natural that A_p in free-cationic, free-anionic and free-radical polymerizations are relatively large, probably exceeding 10^7 . To show the correlations between them clearly, an illustration as shown in Figure 8 was attempted.

Radical polymerization had been carried out also in bulk state^{29,30} and a great difference between $k_p(\text{radical})$ and $k_p(\text{free cation})$ is found to be due to relatively high E_p in radical polymerization. As E_p in radical polymerization of vinyl monomers are generally in the proximity of 7 ± 1 kcal mol⁻¹,³⁹ the observed difference in E_p can be regarded as a general trend.

It is well known that propagation process in paired ionic polymerization is greatly influenced by the nature of catalyst as well as the polarity of solvent. In the polymerization initiated by weak initiators as iodine, Higashimura¹⁵ gave an indication that the rate-determining process for the propagation is dissociation of contact ion-pair to form a $P^+ \cdots X^-$ complex in a transi-

tion state. The use of stannic chloride³⁶ or boron trifluoride etherate³⁷ increased k_d more

Table II. Characteristic values for the propagation reactions of styrene

	Solvent	Catalyst	$k_p(25^\circ\text{C})$, $\text{l mol}^{-1}\text{sec}^{-1}$	E_p , kcal mol^{-1}	$\log A_p$	Ref
Radical	Bulk	Light	39.5	6.3	6.2	29
	Bulk	BPO	35 (20°C)	7.8	7	30
Paired anion	THF	Cs ⁺	21	5.35	5.7	31
	THP	Na ⁺	14	6.7	6.0	32
	THP	K ⁺	73	5.3	5.8	32
	THP	Rb ⁺	83	4.9	5.5	32
	THP	Cs ⁺	53	4.9	5.3	32
Free anion	THF	Na ⁺ , Cs ⁺	6.5×10^4	5.9	9.05	31
	THP	Li ⁺ , Na ⁺	6×10^4	4.8	8.3	33
	Dimethoxy-ethane	Cs ⁺	4×10^4	5	8.3	34
Pair cation	(CH ₂ Cl) ₂	I ₂	1.8×10^{-3} (20°C)	6–6.5	1.3–2.1	35
	(CH ₂ Cl) ₂	SnCl ₄	0.42 (30°C)	—	—	36
	Benzene	BF ₃ OEt ₂	0.25 (30°C)	—	—	37
	(CH ₂ Cl) ₂	H ₂ SO ₄	7.5	—	—	38
	(CH ₂ Cl) ₂	HClO ₄	7–17 (20°C)	8.3–9.1	7.4–8.0	28
	(CH ₂ Cl) ₂ /CCl ₄ (75/20)	HClO ₄	3.2 (20°C)	11.4	9.0	28
	(CH ₂ Cl) ₂ /CCl ₄ (55/40)	HClO ₄	0.4 (20°C)	13.0	9.3	28
Free cation	Bulk	Radiation	2.4×10^6	2.2 ± 1.3	8.0 ± 1.1	This work

Figure 8. Relationship between $\log A_p$ and E_p in the polymerizations of styrene.

than 100 times. Another extreme case was informed by Pepper.^{28,38} Using a strong protonic acid as sulphuric acid³⁸ or perchloric acid²⁸ in 1,2-dichloroethane, k_p was evaluated to be approximately $10 \text{ l mol}^{-1} \text{ sec}^{-1}$, which is 10^3 times greater than that in the iodine case³⁵ and in this case the propagating end is presumably considered to be rather free-cationic judging from its large A_p value. If so, a comparison of $E_p(\text{HClO}_4)$ with E_p (free cation) should be dis-

cussed in terms of a solvent effect on the free-cationic polymerization and observed tendency in E_p seems reasonable when solvation of propagating cation in polar solvent is taken into account. However this consequence is inconsistent with Pepper's result²⁸ which was carried out in mixed solvent system. Anyhow the effects of solvent polarity on the propagation processes in ionic polymerization, free or paired, are one of the most important problem remained for future study.

On the other hand, in the case of anionic polymerization there has been informed several instances in which free- and paired-ionic polymerizations proceeded simultaneously in the same system.³¹ There, it was found that with the change from paired-ionic to free-ionic mechanism, A_p increased by a factor of 10^2 – 10^3 while E_p was almost invariable, and similar experiments are strongly expected also in the case of cationic polymerization. Although several experimental difficulties still prevent a comparison of k_p (free-cationic) and k_p (free-anionic) in the same system, the author is confident of the predominance of cationic mechanism over anionic one in radiation-induced polymerization of styrene on the

basis of the additive effects^{3,4} and copolymerization studies.^{3,20}

The above-mentioned discussions about styrene are partly inconsistent with the previous findings on IBVE,⁶ in which particularly, a higher E_p compared with paired-cationic mechanism was observed. However it has been pointed out that vinyl ethers sometimes show strange polymerization behaviors in their reactivity from other vinyl monomers¹⁵ and, in the succeeding paper,²⁰ has been attempted the elucidation of the difference in the kinetic behavior between styrene and IBVE.

APPENDIX

Here consider an extreme case where there exists only one kind of anionic species, Y^- , regardless of its species, O_2^- or polymeric anion. Involvement of the coexistence of two anionic species in the kinetics was excluded because it requires too many unknown parameters, *i.e.*, rate constants, concentrations, etc., to comprehend the outline of polymerization. From eq 9 and 12 in ref 6 along with eq 3 in this paper, a following cubic equation as to $[Y^-]$ is obtained,

$$pk_{r,(1)}k_{r,(X)}[Y^-]^3 + k_X k_{r,(X)}[X][Y^-]^2 - k_{r,(X)}R_i[Y^-] - k_X[X]R_i = 0, \quad (A-1)$$

here,

$$R_i = 10IG/N. \quad (A-2)$$

It is clear that⁶

$$\Sigma[M_n^+] + [X^+] = [Y^-] \quad (A-3)$$

$$k_X[X]\Sigma[M_n^+] = k_{r,(X)}[X^+][Y^-] \quad (A-4)$$

When all the parameters except $[Y^-]$ in eq A-1 are known, eq A-1 gives only one positive solution and then, using eq A-3 and A-4, all the ion concentrations $[Y^-]$, $\Sigma[M_n^+]$ and $[X^+]$ can be evaluated at a fixed dose rate. Then R_p-I curves for a fixed impurity concentration, $[X]$ are computed varying I in eq A-2. Therefore when all the rate constants in eq A-1—A-3 are known including k_p , a set of R_p-I curves are obtained changing $[X]$, which is illustrated in Figure 5.

From the definition of $pk_{r,(1)}$ stated previously, it is obvious that

$$pk_{r,(1)} = k_{r,(X)} - k' \quad (A-5)$$

$k_{r,(X)}$ represents the rate constant for the recombination reaction between X^+ and Y^- and therefore k' corresponds to $k_{r,(X)} \times D_{X^+}/(D_{X^+} + D_{Y^-})$, *i.e.*, the contribution of X^+ diffusion to $k_{r,(X)}$. As water is a major impurity in inhibiting the cationic polymerization, k' is presumably evaluated to be $3 \times 10^{11} \text{ l mol}^{-1} \text{ sec}^{-1}$, calculated on the basis of the diffusion constant of water in benzene²² using the equation,⁴⁰ $\mu/D = e/kT$ and Langevin's equation,⁴¹ $k/\mu = 4\pi e/\epsilon$, where μ denotes mobility. G was assumed to be 0.055 (25°C) which was determined for benzene²⁵ and $k_p = 2.4 \times 10^6 \text{ l mol}^{-1} \text{ sec}^{-1}$ was used. Then a set of R_p-I curves can be calculated for a suitable choice of $pk_{r,(1)}$.

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REFERENCES

1. T. H. Bates, J. V. F. Best, and T. F. Williams, *J. Chem. Soc.*, 1531 (1962).
2. J. V. F. Best, T. H. Bates, and T. F. Williams, *Trans. Faraday Soc.*, **58**, 192 (1962).
3. K. Ueno, Ko. Hayashi, and S. Okamura, *Polymer*, **7**, 431 (1966).
4. K. Ueno, F. Williams, Ko. Hayashi, and S. Okamura, *Trans. Faraday Soc.*, **63**, 1478 (1967).
5. D. J. Metz, "Irradiation of Polymer," *Advances Chemistry Series*, No. 66, American Chemical Society, Washington D. C., 1967, p 171.
6. Ka. Hayashi, Ko. Hayashi, and S. Okamura, *J. Polym. Sci., Part A-1*, **9**, 2305 (1971).
7. R. B. Taylor and F. Williams, *J. Amer. Chem. Sci.*, **91**, 3728 (1969).
8. R. C. Potter and D. J. Metz, *J. Polym. Sci. Part A-1*, **9**, 441 (1971).
9. E. Hubman, R. B. Taylor, and F. Williams, *Trans. Faraday Soc.*, **62**, 88 (1966).
10. F. Williams, Ka. Hayashi, K. Ueno, Ko. Hayashi, and S. Okamura, *ibid.*, **63**, 1501 (1967).
11. G. R. Freeman, *J. Chem. Phys.*, **39**, 988 (1963).
12. A. Hummel, A. O. Allen, and F. W. Watson, Jr., *ibid.*, **44**, 3431 (1966).
13. F. Williams, *J. Amer. Chem. Soc.* **86**, 3954 (1964).
14. A. Mozumder and J. L. Magee, *J. Chem. Phys.*, **47**, 939 (1967). A. Mozumder, *ibid.*, **48**, 1659 (1968).

15. T. Higashimura, "Structure and Mechanism in Vinyl Polymerization," T. Tsuruta and K. F. O'driscoll, Ed., Dekker, New York, N.Y., 1969, pp 334-336.
16. Ka. Hayashi, Y. Yamazawa, T. Takagaki, F. Williams, Ko. Hayashi, and S. Okamura, *Trans. Faraday Soc.*, **63**, 1489 (1967).
17. J. F. Westlake and R. Y. Huang, *J. Polym. Sci., Part A-1*, **10**, 1443 (1972).
18. M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N.Y., 1968, p 22.
19. D. J. Metz, R. C. Potter, and J. K. Thomas, *J. Polym. Sci. Part A-1*, **5**, 877 (1967).
20. Ka. Hayashi, Ko. Hayashi, and S. Okamura, *Polymer J.*, in press.
21. I. M. Krieger, G. W. Mulholand, and C. S. Dickey, *J. Phys. Chem.*, **71**, 1123 (1967).
22. R. S. Sitaraman, *A.I. Ch. E.J.*, **8**, 277 (1962).
23. S. I. Klenin, V. L. Migdal, S. V. Bushin, and V. N. Tsvetkov, *Vysokomol. Soedin.*, **8**, 882 (1966).
24. S. W. Benson and A. M. North, *J. Amer. Chem. Soc.*, **81**, 1339 (1959), *ibid.*, **84**, 935 (1962).
25. W. F. Schmidt and A. O. Allen, *J. Chem. Phys.*, **52**, 2345 (1970).
26. S. Okamura, T. Higashimura, and Y. Sakurada, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **61**, 1640 (1958).
27. A. Gandini and P. H. Plesch, *J. Chem. Soc.*, 4846 (1965).
28. D. C. Pepper and P. J. Reilly, *Proc. Roy. Soc. (London)*, **A291**, 41 (1966).
29. G. M. Burnett, *Trans. Faraday Soc.*, **46**, 772 (1950).
30. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Amer. Chem. Soc.*, **73**, 1700 (1951).
31. T. Shimomura, K. J. Tolle, J. Smid, and M. Szwarc, *ibid.*, **89**, 796 (1967).
32. F. S. Dainton, K. J. Ivin, and R. T. Laflair, *Eur. Polym. J.*, **5**, 379 (1969).
33. M. Van Beylen, M. Fisher, J. Smid, and M. Szwarc, *Macromolecules*, **2**, 575 (1969).
34. T. Shimomura, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 5743 (1967).
35. N. Kanoh, T. Higashimura, and S. Okamura, *Makromol. Chem.*, **56**, 65 (1967).
36. N. Kanoh, T. Higashimura, and S. Okamura, *Kobunshi Kagaku (Chem. High Polymers)*, **19**, 181 (1962).
37. T. Higashimura, H. Kusano, T. Masuda, and S. Okamura, *J. Polymer Sci., Part B*, **9**, 463 (1971).
38. M. J. Hayes and D. C. Pepper, *Proc. Roy. Soc. (London)*, **A263**, 58, 63 (1961).
39. P. J. Flory, "Principles of polymer chemistry," Cornell Univ. Press, Ithaca, N.Y., 1952, p 158.
40. H. A. Kramers, *Physica*, **18**, 665 (1952).
41. P. Langevin, *Ann. Chim. Phys.*, **VII**, **28**, 433 (1903).